Supporting Information for

Synthesis and Crystallization-Driven Solution Self-Assembly of Polyferrocenylsilane Diblock Copolymers with Polymethacrylate Corona-Forming Blocks

Nina McGrath,[a] Felix H. Schacher,[a,⊥] Huibin Qiu,[a] Stephen Mann,[b] Mitchell A. Winnik*[c] and Ian Manners*[a]

[a] School of Chemistry, University of Bristol, Bristol, United Kingdom, BS8 1TS; E-mail: ian.manners@bristol.ac.uk

[b] Centre for Organized Matter Chemistry, School of Chemistry, University of Bristol, Bristol, United Kingdom, BS8 1TS

[c] Department of Chemistry, University of Toronto, Toronto, Ontario, Canada, M5S 3H6; E-mail: mwinnik@chem.utoronto.ca

[⊥] Present address: Institute of Organic and Macromolecular Chemistry and Jena Center for Soft Matter (JCSM), Friedrich-Schiller-University, Jena, Lessingstraße 8, D-07743 Jena, Germany

General Comments

THF was pre-dried with Na before being distilled from Na/benzophenone under nitrogen. Dimethylsilaferrocenophane was prepared by a previously reported method.[1] *tert*-Butyl methacrylate, *n*-butyl methacrylate and *N*,*N*-dimethylaminoethyl methacrylate were purchased from Aldrich and dried over CaH_2 before distillation under reduced pressure. They were distilled again from trioctyl aluminium immediately before use. *n*-Butyllithium (*n*BuLi) was purchased from Acros (1.6 M in hexanes) and used as received. All of the self-assembly experiments were performed in HPLC grade solvents purchased from

Fisher. Gel Permeation Chromatography (GPC) was carried out on a Viscotek GPCmax chromatograph equipped with a triple detector array. A flow rate of 1.0 ml/min was used with THF as the eluent. GPC of PFS-*b*-PDMAEMA was carried out on a Viscotex GPCmax chromatograph using a flow rate of 1.0 ml/min and THF (1% *n*-butyl ammonium bromide) as an eluent. Transmission electron microscopy samples were prepared by drop-casting one drop (approx. 10 uL) of the sample onto carbon-coated copper grid before imaging using a JEOL TEM 1200. The average lengths and dispersities (L_n, L_w, L_w/L_n) of cylindrical micelles were determined by tracing 100 objects on TEM images using the software package ImageJ. WAXS data was collected on a Bruker D8 advance diffractometer. ^{1}H NMR spectra were obtained on a Varian 400 spectrometer.

Synthesis of PFS_{57}-*b*-P*t*BMA_{798}

Dimethylsila[1]ferrocenophane (200 mg, 0.83 mmol) in THF (2 mL) was placed in a vial. *n*-BuLi (10.5µL, 1.6 M) was added to the rapidly stirring solution which was then stirred for 1 h (a colour change from red to amber was observed). An aliquot (0.5 mL) was removed for GPC analysis. DPE (11.5 µL, 0.065 mmol) was added followed by DMSB (3 µL, 0.023 mmol). The reaction was stirred at room temperature before cooling to -55 °C. LiCl (7 mg, 0.17 mmol) was dissolved in THF (~ 6 mL) and to this was added *t*BMA (0.71 mL, 4.37 mmol). This solution was cooled to -55 °C before being added to the rapidly stirred living PFS solution. The reaction was allowed to proceed for 1 h before it was quenched by addition of a few grains of NH_4Cl. This mixture was allowed to stir for 1 h at -55 °C before removal from the glovebox, and precipitation into methanol. The polymer was purified by dissolution of the sample in THF, followed by dropwise addition of methanol until a precipitate was seen. This precipitate was found to be PFS homopolymer and was removed by centrifugation. The diblock copolymer was precipitated in methanol and dried to give an orange solid (622 mg, 76%). GPC: M_n = 127,000 g/mol, PDI = 1.02. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.46 (s, 6H, Si(CH_3)$_2$), 1.2-0.9 (br, 3H, C-CH_3), 1.44 (m, 9H, -C(CH_3)$_3$) 2.0-2.3 (br, 2H, C(CH_3)-CH_2) 4.01 (m, 4H, Cp) 4.22 (m, 4H, Cp).

Synthesis of PFS_{36}-*b*-P*n*BMA_{756}

Dimethylsila[1]ferrocenophane (200 mg, 0.83 mmol) in THF (3 mL) was placed in a vial. *n*-BuLi (10 µL, 1.6 M) was added to the rapidly stirring solution which was then stirred for 80 minutes at 0 °C (a colour change from red to amber was observed). An aliquot (0.2mL) was removed for GPC analysis. DPE (12 µL, 0.064 mmol) was added followed by DMSB (4 µL, 0.032 mmol). The reaction was stirred for 30 minutes at room temperature before cooling to -70 °C. LiCl (8 mg, 0.16 mmol) was dissolved in THF (~ 7 mL) and to this was added *n*BMA (1.2 mL, 7.5 mmol). This solution was cooled to -70 °C before being added to the rapidly stirring living PFS solution. The reaction was allowed to proceed for 45 minutes before quenching by addition of a Me_3SiCl (0.5 mL, 3.9 mmol) and isolation by precipitation into methanol and drying. The polymer was purified by dissolution of the sample in THF, followed by dropwise addition of methanol until a precipitate was seen. The diblock copolymer was afterwards precipitated in methanol and dried to give an orange solid (950 mg, 75 % yield). GPC: M_n = 116,000 g/mol, PDI = 1.27. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.46 (s, 6H, Si(CH_3)$_2$), 0.8-1.1 (br, 3H, C-CH_3), 1.41 (br, 2H, -CH_2-CH_3, 1.62 (br, 4H, -CH_2CH_2-CH_3), 1.8-2.0 (br, 2H, C(CH_3)-CH_2), 3.94 (br, 2H, O-CH_2), 4.01 (m, 4H, Cp), 4.22 (m, 4H, Cp).

Synthesis of PFS_{67}-*b*-PDMAEMA$_{1139}$

The same procedure as described for the synthesis of PFS_{57}-*b*-P*t*BMA_{798} but using 1.96 g DMAMEA monomer and the polymerization of the DMAEMA monomer was performed at -40 °C. The diblock copolymer was precipitated into hexanes before isolation and drying to give an orange solid. The polymer was purified by dissolution of the sample in THF, followed by dropwise addition of hexanes until a precipitate was seen. This precipitate was found to be the pure PFS-*b*-PDMAEMA diblock copolymer and was isolated by centrifugation and dried to give an orange solid (1.456 g, 72%). GPC: M_n = 195,000 g/mol, PDI = 1.10. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.46 (s, 6H, Si(CH_3)$_2$), 0.8-1.1 (br, 3H, C-CH_3), 1.8-2.0 (br, 2H, C(CH_3)-CH_2), 2.29 (s, 6H, -N(CH_3)$_2$,) 2.56 (br, 2H, CH_2-N), 4.01 (m, 4H, Cp), 4.06 (br, 2H, O-CH_2), 4.22 (m, 4H, Cp).

Solution self-assembly of PFS_{57}-*b*-P*t*BMA_{798}, PFS_{36}-*b*-P*n*BMA_{756} and PFS_{67}-*b*-$PDMAEMA_{1139}$

Micelle solutions were prepared by mixing the diblock copolymers in acetone at a concentration of 1 mg/mL before heated to 55°C for 1 h followed by cooling to room temperature and aging for 2 months. Fragmentation of the micelles by sonication was performed in an ultrasonic cleaning bath (Bandelin Sonorex Digitec DT 225H, 35 kHz, 160 W output).

Living crystallization-driven self-assembly

In a typical experiment, 1 mL aliquot of a freshly sonicated solution of short seed micelles of PFS_{57}-*b*-P*t*BMA_{798} (0.01 mg/mL in acetone) was stirred at 600 rpm and 10 μL of PFS_{57}-*b*-P*t*BMA_{798} in THF (10 mg/mL) was injected rapidly. The solution was allowed to stir for 10 seconds and allowed to age for 4 days.

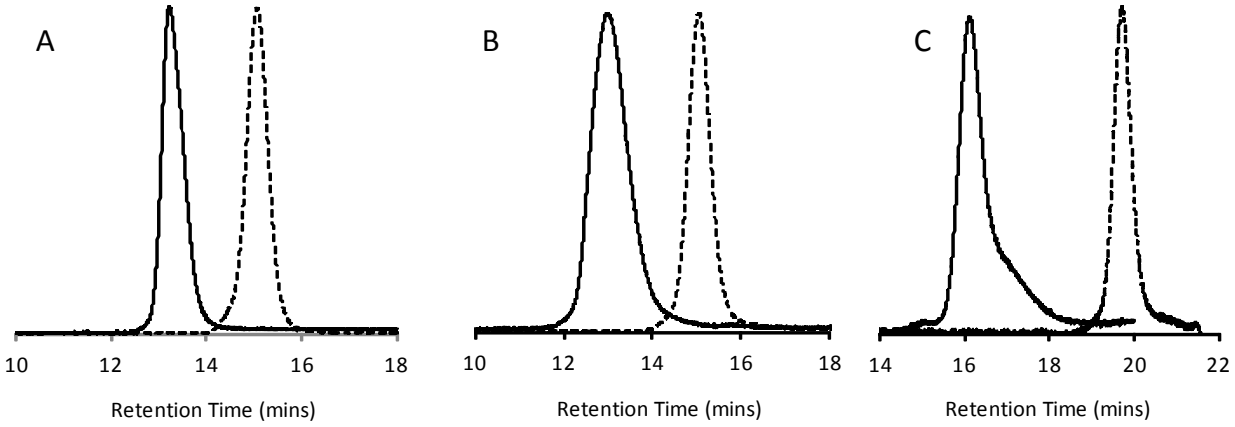

Figure S1. GPC traces of (A) PFS_{57}-*b*-P*t*BMA_{798} (black line) and its PFS_{57} precursor (dashed line), (B) PFS_{36}-*b*-P*n*BMA_{756} (black line) and its PFS_{36} precursor (dashed line) and (C) PFS_{67}-*b*-$PDMAEMA_{1139}$ (black line) and its PFS_{67} precursor (dashed line). Some tailing is observed in the GPC trace of PFS-*b*-PDMAEMA. This is likely due to interactions between the lone pairs on the nitrogen of PDMAEMA with the GPC column, which means that the elution is hindered.

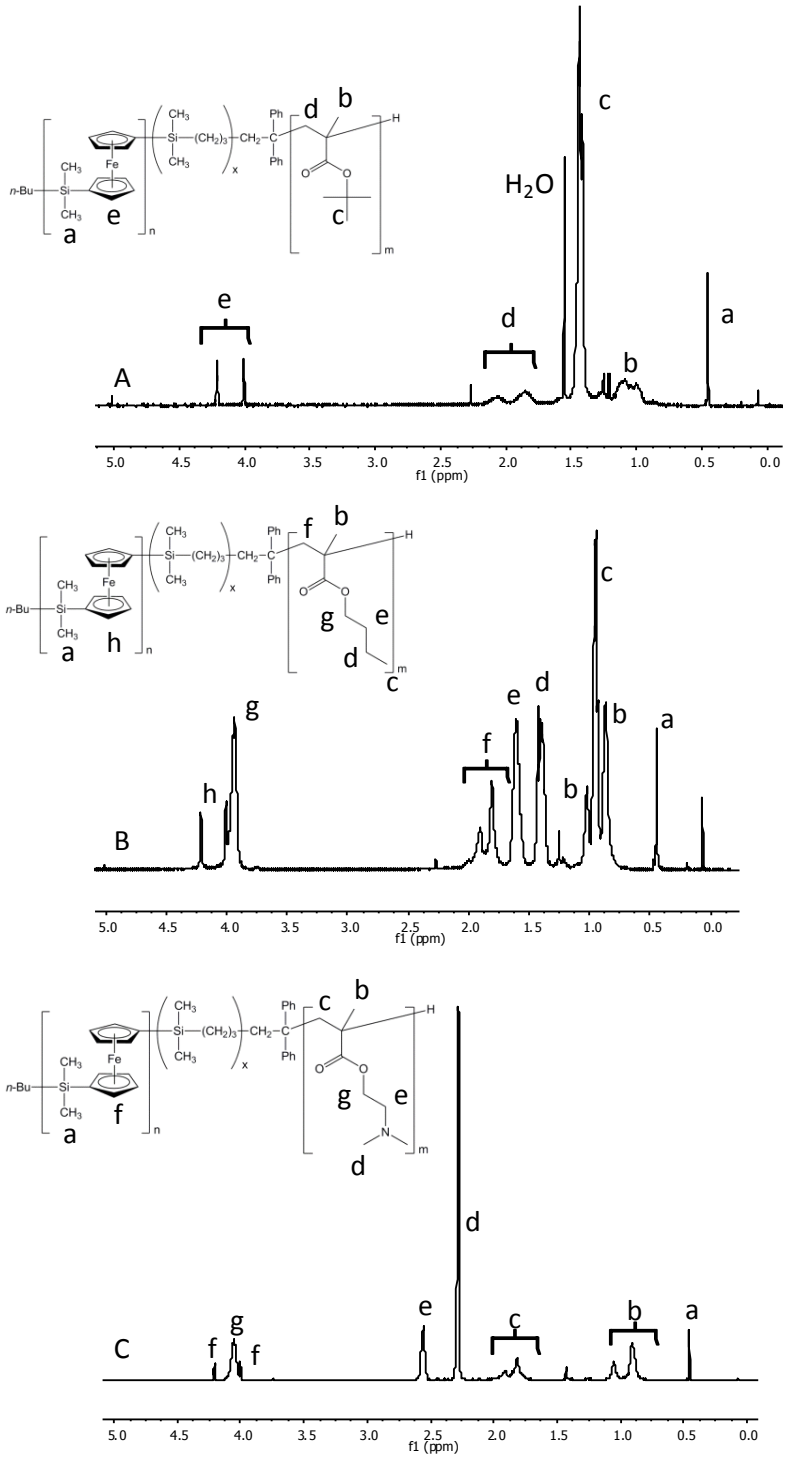

Figure S2 ^{1}H NMR spectra of (A) PFS_{57}-*b*-P*t*BMA_{798} (B) PFS_{57}-*b*-P*n*BMA_{756} and (C) PFS_{67}-*b*-$PDMAEMA_{1139}$. ($CDCl_3$, 400 MHz). Signals around 0.1 ppm can be assigned to silicone grease.

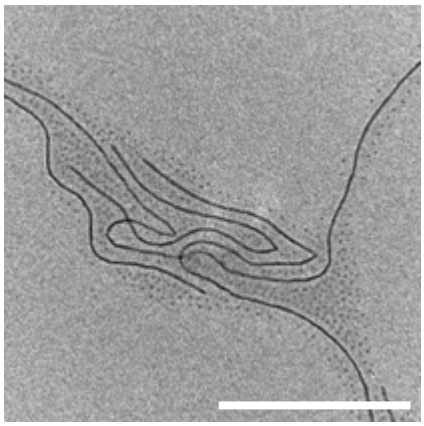

Figure S3 TEM image of a drop-cast aliquot of the solution of PFS-*b*-PtBMA micelles in acetone, which was allowed to age for 7 days. The solution comprised of both cylindrical and spherical micelles. Scale bar = 500 nm.

Table S1 WAXS data for PFS_{57}-*b*-P*t*BMA_{798}, PFS_{36}-*b*-P*n*BMA_{756} and PFS_{67}-*b*-$PDMAEMA_{1139}$.

Diblock Copolymer	*2theta*	*d spacing(Å)*
PFS_{57}-*b*-P*t*BMA_{798}	13.7°	6.46
PFS_{36}-*b*-$PnBMA_{756}$	13.7°	6.45
PFS_{67}-*b*-$PDMAEMA_{1139}$	13.7°	6.45

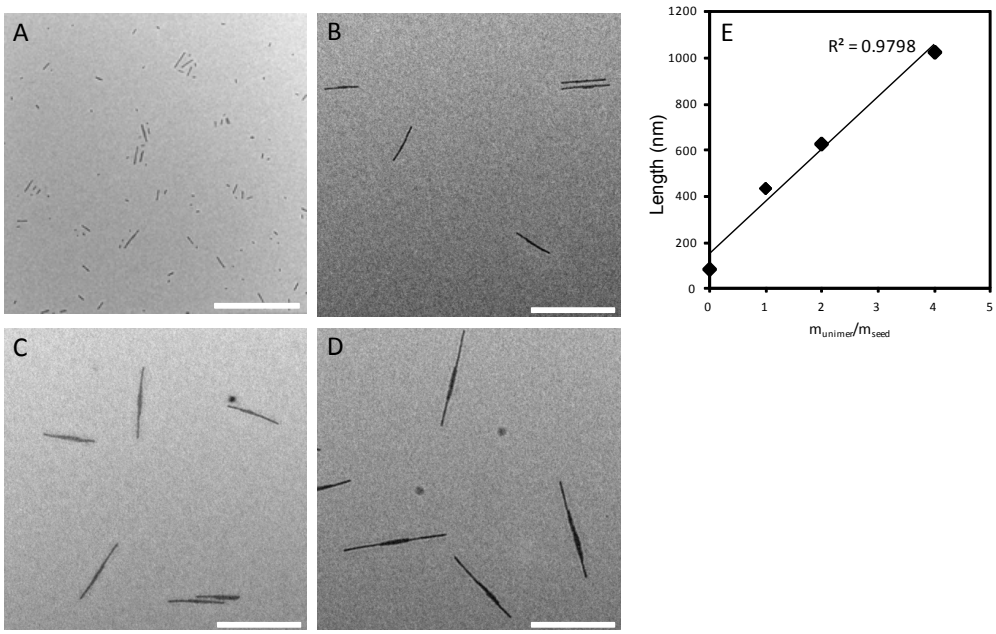

Figure S4 (A) TEM image of PFS_{36}-*b*-P*n*BMA_{756} short micelles in acetone obtained by sonicating PFS_{36}-*b*-P*n*BMA_{756} long micelles in acetone for 10 min (L_n = 85 nm, L_w/L_n = 1.32). (B-D) TEM images of longer cylindrical micelles of PFS_{36}-*b*-P*n*BMA_{756} obtained by adding 0.1, 0.2 and 0.4 mg of PFS_{36}-*b*-P*n*BMA_{756} unimer to micelle seeds of PFS_{36}-*b*-P*n*BMA_{756} shown in (A) (L_n = 435 (L_w/L_n = 1.04), 625 (L_w/L_n = 1.03) and 1025 (L_w/L_n = 1.02) nm respectively). (E) Linear relationship between micelle contour length and unimer-to-seed ratio. Scale bar = 1000 nm.

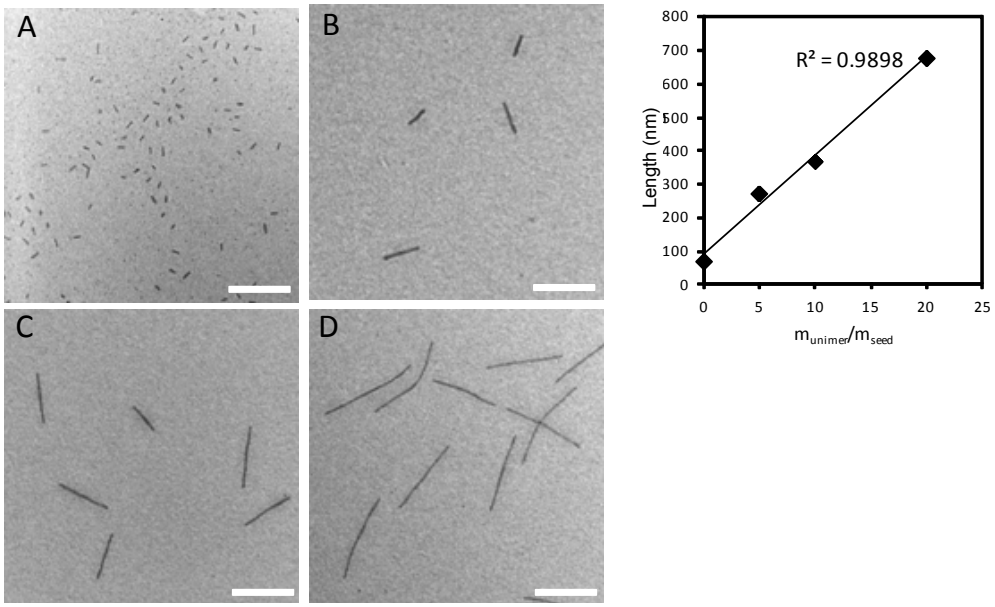

Figure S5 (A) TEM image of PFS_{67}-*b*-$PDMAEMA_{1139}$ short micelles in acetone obtained by sonicating PFS_{67}-*b*-$PDMAEMA_{1139}$ long micelles in acetone for 10 min (L_n = 70 nm, L_w/L_n – 1.03). (B-D) TEM images of long micelles of PFS_{67}-*b*-$PDMAEMA_{1139}$ obtained by adding 0.1, 0.2 and 0.4 mg of PFS_{67}-*b*-$PDMAEMA_{1139}$ unimer to micelle seeds of PFS_{67}-*b*-$PDMAEMA_{1139}$ shown in (A) (L_n = 270 (L_w/L_n = 1.06), 365 (L_w/L_n = 1.05) and 675 (L_w/L_n = 1.04) nm respectively). (E) Linear relationship between micelle contour length and unimer-to-seed ratio. Scale bar = 500 nm.

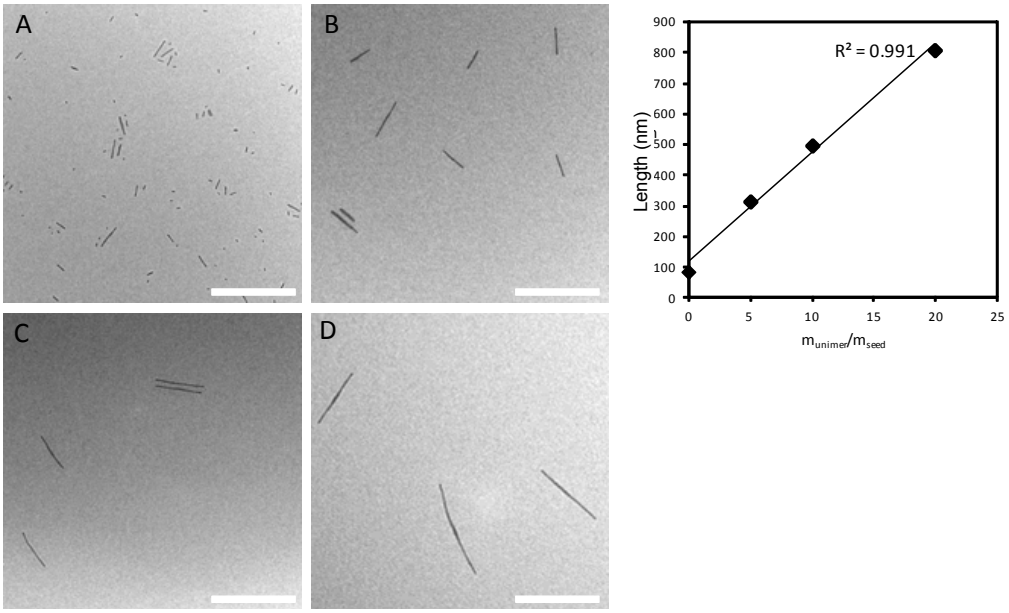

Figure S6 (A) TEM image of PFS_{36}-*b*-P*n*BMA_{756} short micelles in acetone obtained by sonicating PFS_{36}-*b*-P*n*BMA_{756} long micelles in acetone for 10 min (L_n =85 nm, L_w/L_n = 1.32). (B-D) TEM images of the triblock co-micelles obtained by adding 0.1, 0.2 and 0.4 mg of PFS_{57}-*b*-P*t*BMA_{798} unimer to micelle seeds of PFS_{36}-*b*-P*n*BMA_{756} shown in (A) (L_n = 315 (L_w/L_n = 1.03), 495 (L_w/L_n = 1.04) and 805 (L_w/L_n = 1.06) nm respectively). (E) Linear relationship between micelle contour length and unimer-to-seed ratio. Scale bar = 1000 nm.

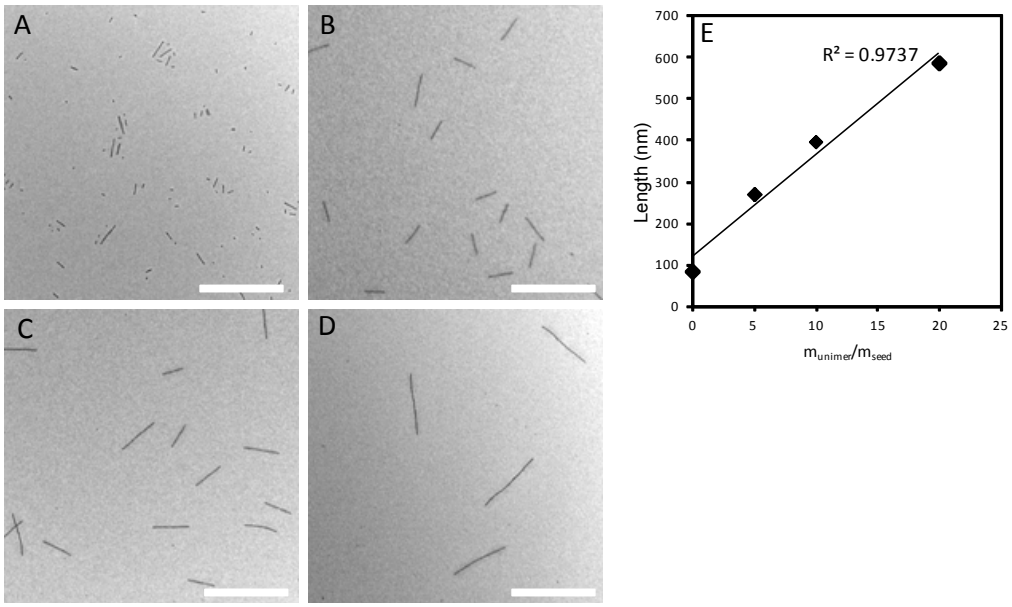

Figure S7 (A) TEM image of PFS_{36}-*b*-P*n*BMA_{756} short micelles in acetone obtained by sonicating PFS_{36}-*b*-P*n*BMA_{756} long micelles in acetone for 10 minutes (L_n = 85 nm, L_w/L_n = 1.32). (B-D) TEM images of the triblock co-micelles obtained by adding 0.05, 0.1 and 0.2 mg of PFS_{67}-*b*-$PDMAEMA_{1139}$ unimer to micelle seeds of PFS_{36}-*b*-P*n*BMA_{756} shown in (A) (L_n = 270 (L_w/L_n = 1.08), 395 (L_w/L_n = 1.05) and 585 (L_w/L_n = 1.04) nm respectively). (E) Linear relationship between micelle contour length and unimer-to-seed ratio. Scale bar = 1000 nm.

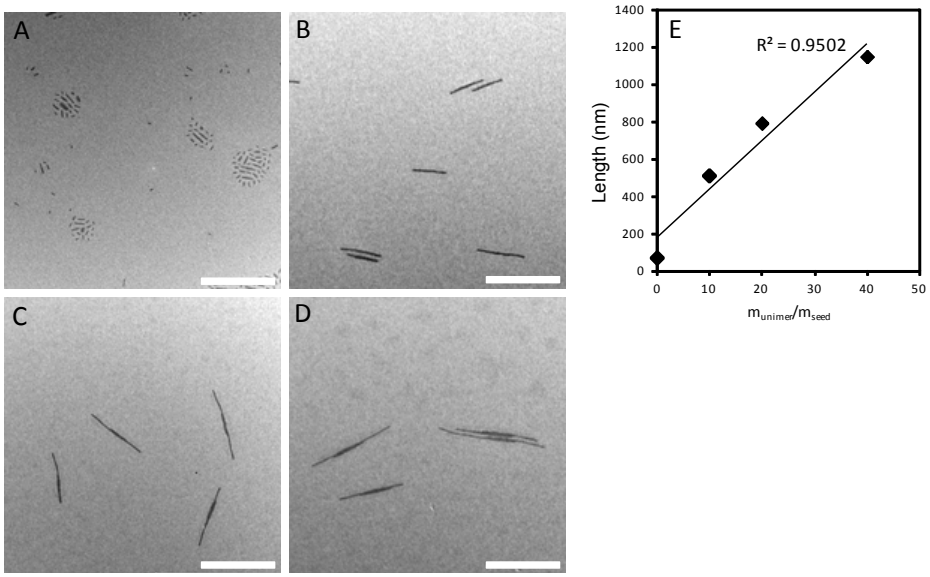

Figure S8 (A) TEM image of PFS_{57}-*b*-P*t*BMA_{798} short micelles in acetone obtained by sonicating PFS_{67}-*b*-$PDMAEMA_{1139}$ long micelles in acetone for 10 minutes (L_n = 70 nm, L_w/L_n = 1.22). (B-D) TEM images of the triblock co-micelles obtained by adding 0.1, 0.2 and 0.4 mg of PFS_{36}-*b*-P*n*BMA_{756} unimer to micelle seeds of PFS_{57}-*b*-P*t*BMA_{798} shown in (A) (L_n = 510 (L_w/L_n = 1.03), 795 (L_w/L_n = 1.02) and 1150 (L_w/L_n = 1.03) nm respectively). (E) Linear relationship between micelle contour length and unimer-to-seed ratio. Scale bar = 1000 nm.

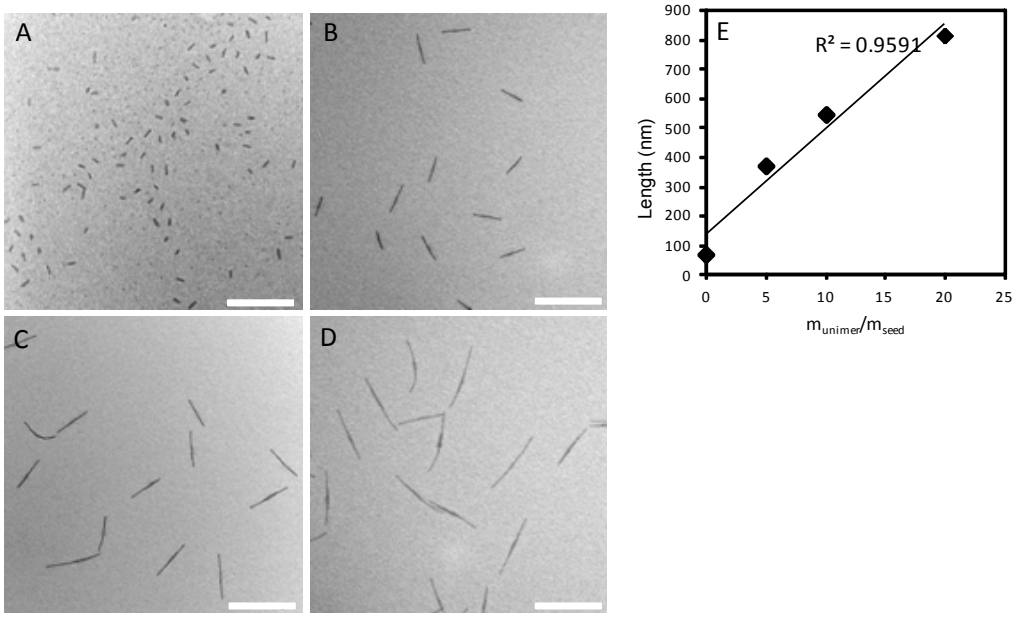

Figure S9 (A) TEM image of PFS_{67}-*b*-$PDMAEMA_{1139}$ short micelles in acetone obtained by sonicating PFS_{67}-*b*-$PDMAEMA_{1139}$ long micelles in acetone for 10 minutes (L_n = 70 nm, L_w/L_n = 1.03). (B-D) TEM images of the triblock co-micelles obtained by adding 0.1, 0.2 and 0.4 mg of PFS_{36}-*b*-P*n*BMA_{756} unimer to micelle seeds of PFS_{67}-*b*-$PDMAEMA_{1139}$ shown in (A) (L_n = 380 (L_w/L_n = 1.03), 540 (L_w/L_n = 1.05) and 815 (L_w/L_n = 1.04) nm respectively). (E) Linear relationship between micelle contour length and unimer-to-seed ratio. Scale bar = 500 nm.

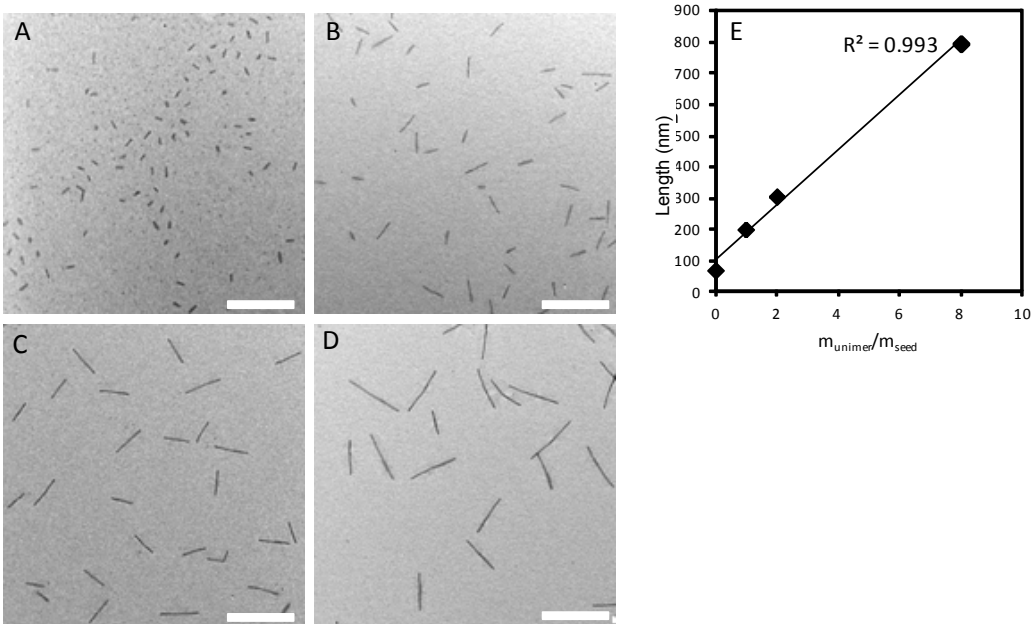

Figure S10 (A) TEM image of PFS_{67}-*b*-$PDMAEMA_{1139}$ short micelles in acetone obtained by sonicating PFS_{67}-*b*-$PDMAEMA_{1139}$ long micelles in acetone for 10 minutes (L_n = 70 nm, L_w/L_n = 1.03). (B-D) TEM images of the triblock co-micelles obtained by adding 0.1, 0.2 and 0.4 mg of PFS_{57}-*b*-P*t*BMA_{798} unimer to micelle seeds of PFS_{67}-*b*-$PDMAEMA_{1139}$ shown in (A) (L_n = 200, 305 and 795 nm respectively). (E) Linear relationship between micelle contour length and unimer-to-seed ratio. Scale bar = 500 nm.

Reference

[1] J. Massey, K. N. Power, I. Manners and M. A. Winnik, *J. Am. Chem. Soc.*, 1998, **120**, 9533-9540.