

Supporting Information

Toward Uniform Nanofibers with a π -Conjugated Core: Optimizing the “Living” Crystallization-Driven Self-Assembly of Diblock Copolymers with a Poly(3-octylthiophene) Core-Forming Block

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I. Experimental

Equipment and Materials. Unless stated otherwise all experiments were performed on a glass vacuum line under nitrogen or in a MBraun glove box under argon atmosphere. 2,5-Dibromo-3-octylthiophene, [1,3-Bis(diphenylphosphino)propane]dichloronickel(II) [Ni(dppp)Cl₂], tert-butylmagnesium chloride solution (1 M in THF), ethynylmagnesium bromide solution (0.5 M in THF), tetrabutylammonium bromide (TBAB), sodium azide, *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA), copper bromide, *n*Butyllithium (*n*BuLi, 1.6 M in hexanes), and *s*Butyllithium (*s*BuLi, 1.4 M in hexanes) were purchased from Aldrich and used as received. For general synthesis, THF purified using Anhydrous Engineering double alumina and alumina/copper catalyst drying columns was used. For anionic polymerisation, THF and cyclohexane were distilled from Na/benzophenone and CaH₂, respectively. 1,1-diphenylethylene (DPE) purchased from Aldrich was titrated with *n*Butyllithium (*n*BuLi) and then distilled under reduced pressure. 1,3-Dibromopropane (DBP) purchased from Aldrich, was dried over CaH₂ and purified by distillation under reduced pressure. Lithium chloride (99.99%) purchased from Aldrich was vacuum dried at 120°C overnight. Styrene purchased from Adrich was dried over CaH₂ and distilled under reduced pressure. Hexamethylcyclotrisiloxane (D3) purchased from Aldrich was dissolved in pentane and dried over CaH₂ overnight. After distillation, the solution was concentrated and stored at -60°C for at least 12 h. The precipitate formed was collected and sublimed at room temperature under static vacuum.

¹H NMR spectra were obtained using an Eclipse (ECP) 400 spectrometer or a Varian 500 (¹H: 499.9 MHz) at ambient temperatures with all resonances referenced to residual NMR solvent resonances.

Gel Permeation Chromatography (GPC) was carried out on a Viscotek GPCmax chromatograph equipped with a UV detector operating at 440 nm and a refractometer. A flow rate of 1.0 ml min⁻¹ was used with *n*Bu₄NBr/THF (0.1 wt% *n*Bu₄NBr) as the eluent at 35°C. Calibration was performed using polystyrene standards (Viscotek).

Matrix assisted laser desorption/ionization – time of flight (MALDI-TOF) mass spectrometry measurements of P3OT homopolymers were performed using a Bruker Ultraflextreme running in

linear mode. Samples were prepared using a *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile matrix (20 mg/mL, THF) and the polymer solution (2 mg/mL, THF), mixed in a volume ratio of 10:1. 1.5 μ L of the mixed solution was deposited onto the sample plate and allowed to dry in air. The molecular weight of the diblock copolymers was then determined by combining the molecular weight M_n of the first P3OT block obtained from MALDI-TOF mass spectrometry with the block ratio of the diblock copolymer which was obtained from the integration of the ^1H NMR signal intensities of the respective blocks.

Transmission Electron Microscopy (TEM) images were obtained using a JEOL JEM 1200 EX microscope operating at 120 kV and equipped with a SIS MegaViewIII digital camera or a JEOL 1400 microscope operating at 120 kV and fitted with a Gatan digital camera. No staining was necessary. TEM samples were prepared by drop casting an aliquot of the micelle solutions (ca. 20 μ L) onto carbon-coated copper grids placed on filter paper to remove excess solvent. Images were analyzed using ImageJ software developed at the US National Institute of Health. For the statistical length analysis, 200 micelles (or 100 micelles in the case of seed control experiments) were carefully traced by hand to determine the contour length. From this data, number average contour length (L_n) and length average contour length (L_w) of each micelle sample was calculated as shown below (equations (1), L = length of object, N = number).

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

The standard deviations (σ) of the measured lengths are related to length dispersity (L_w/L_n) through the following expression (2).

$$\frac{L_w}{L_n} - 1 = \left(\frac{\sigma}{L_n} \right)^2 \quad (2)$$

Wide angle X-Ray scattering (WAXS) experiments were carried out on a Bruker D8 Advance diffractometer fitted with a 0.6 mm fixed divergence slit, knife-edge collimator and a LynxEye area

detector using Cu-K α ($\lambda = 1.54 \text{ \AA}$). WAXS samples were prepared by drop casting the solutions onto silicon wafers and drying the samples at room temperature.

Differential Scanning Calorimetry (DSC) measurements were conducted on a TA Instruments DSC Q100 coupled to a refrigerated cooling system (RCS90) at a scan rate of $10^\circ\text{C}/\text{min}$ under N_2 atmosphere using aluminium pans.

UV/vis data were obtained on a Lambda 35 Spectrometer employing standard quartz cells (1 cm) from 200 to 900 nm.

Fluorescence data were obtained on a Jasco FP-6500 Spectrofluorometer using an excitation wavelength of $\lambda_{\text{ext}} = 440 \text{ nm}$.

Polymer synthesis

Synthesis of alkyne terminated P3OT homopolymer.

Regioregular P3OT was synthesized via Grignard metathesis.¹⁻³ 2,5-Dibromo-3-octylthiophene (4.9 g, 13.9 mmol) was dissolved in 50 mL THF and stirred under N_2 . After addition of tert-butyilmagnesium chloride solution (13.9 mL, 13.9 mmol, 1 M in THF), the mixture was stirred for 2 h at room temperature. The reaction mixture was diluted with 100 mL THF and Ni(dppp)Cl_2 (0.31 mmol, 167 mg) was added in one portion. The mixture was stirred for 10 min before adding ethynylmagnesium bromide solution (9.1 mL, 4.56 mmol, 0.5 M in THF) to quench the polymerization and introduce the alkyne end-functionalization of the polymer chains. After stirring for 2 min, the reaction mixture was poured into methanol in order to precipitate the polymer. The polymer collected in an extraction thimble was washed by Soxhlet extraction with methanol, hexane, and chloroform. Finally, the polymer was precipitated into MeOH and dried under vacuum overnight. Yield: 1.45 g, 54 %. ^1H NMR (499.9 MHz, CDCl_3): $\delta = 6.98$ (s, thiophene), 3.52 (s, alkynyl), 2.80 (t, $J = 7.5 \text{ Hz}$, -octyl), 1.71 (m, -octyl), 1.43 (m, -octyl), 1.29 (m, -octyl), 0.89 (t, $J = 6.5 \text{ Hz}$, -octyl) (Figure S1). $M_n = 5200 \text{ g mol}^{-1}$ ($\text{DP}_n = 26$; determined by MALDI ToF mass spectrometry) and $\text{PDI} = 1.07$ (determined by GPC relative to polystyrene standard). Degree of mono-capped and di-capped alkyne end-functionalization: 76 % and 10% (determined by MALDI ToF mass spectrometry).

For the synthesis of P3OT-*b*-PS, alkyne terminated P3OT homopolymer with $M_n = 4000 \text{ g mol}^{-1}$ ($DP_n = 20$; determined by MALDI ToF mass spectrometry), $PDI = 1.30$ (determined by GPC relative to polystyrene standard) and a degree of mono-capped and di-capped alkyne end-functionalization of 77 % and 8% (determined by MALDI ToF mass spectrometry) was used.

Synthesis of azide terminated PDMS.

Hexamethylcyclotrisiloxane (1.50 g, 6.7 mmol) was dissolved in 8 mL THF before adding *n*-butyllithium (169 μl , 0.27 mmol, 1.6 M in hexanes) to initiate the polymerization. After stirring for 2h at room temperature, the reaction was quenched by adding (bromomethyl)chlorodimethylsilane (5-fold molar excess with respect to initiator). The reaction solution was poured into a mixture of 100 mL of methanol/triethylamine (10:1 v/v). The precipitated polymer was isolated and the precipitation repeated twice by pouring a solution of the polymer in THF into 100 mL methanol. After drying in vacuum at 40°C overnight, the bromo-terminated PDMS was obtained as a colourless viscous liquid. Yield: 1.21 g, 81 %.

Azide-terminated PDMS was obtained by dissolving the bromo-terminated PDMS (0.9 g) in 10 mL THF, adding sodium azide (105 mg, 1.61 mmol) and tetrabutylammonium bromide (0.52 g, 1.61 mmol), and stirring the mixture at 50°C for 2 days. The polymer was precipitated into methanol and isolated by centrifugation. The precipitation was repeated twice and the isolated polymer was dried at 40°C in vacuum overnight. Azide-terminated PDMS was obtained as a colourless viscous liquid. Yield: 0.79 g, 88 %. GPC: $M_n = 6700 \text{ g mol}^{-1}$ and $PDI = 1.10$ (determined by GPC relative to polystyrene standard)

Azide terminated PDMS with different molecular weights were prepared analogously: $M_n = 11\,500 \text{ g mol}^{-1}$, $PDI = 1.09$ (Yield: 0.27 g, 68 %, started with 0.40 g D3) and $M_n = 2\,500 \text{ g mol}^{-1}$, $PDI = 1.09$ (Yield: 0.22 g, 29 %, started with 0.75 g D3).

Synthesis of P3OT-*b*-PDMS.

The synthesis of the representative P3OT₂₆-*b*-PDMS₅₀ diblock copolymer is described. In a Schlenk tube alkyne-terminated P3OT (193 mg, 37 μ mol), azide-terminated PDMS (138 mg, 37 μ mol) and PMDETA (15 μ L, 0.07 mmol) were dissolved in ca. 15 mL THF. After applying three freeze-pump-thaw cycles to remove oxygen, a small spatula of CuBr was added to the solution and subsequently, the mixture was stirred for 2 days at 50°C. Cu/PMDETA was removed by passing the reaction mixture through an alumina column. The P3OT-*b*-PDMS diblock copolymer was purified from unreacted homopolymer by repeated size exclusion chromatography, as previously reported for the preparation of P3HT-*b*-PDMS.⁴ The diblock copolymer (see Scheme S1) was finally isolated by precipitation into methanol. Yield: 109 mg, 33 %. ¹H NMR (499.9 MHz, CDCl₃): δ = 6.98 (s, thiophene), 2.80 (t, J = 7.5 Hz, -octyl), 1.71 (m, -octyl), 1.43 (m, -octyl), 1.29 (m, -octyl), 0.88 (t, J = 6.5 Hz, -octyl), 0.08 (s, -Si(CH₃)₂).

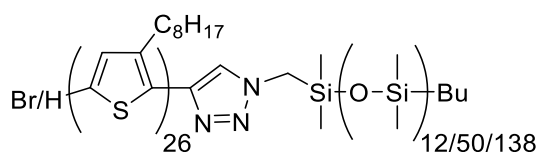
P3OT-*b*-PDMS diblock copolymers with three different block ratios were synthesized and the block ratio was determined by ¹H NMR spectroscopy (see Figures S2, S3 and S4). M_n of the diblock copolymers was determined by combining the molecular weight M_n of the P3OT block obtained from MALDI-TOF mass spectrometry with the block ratio of the diblock copolymer obtained from the integration of the ¹H NMR signal intensities of the respective PDMS blocks. The PDI of the diblock copolymers was determined by GPC relative to polystyrene standards

P3OT₂₆-*b*-PDMS₁₂: Yield: 16 mg (7 %), M_n = 6100 g mol⁻¹, PDI = 1.19;

P3OT₂₆-*b*-PDMS₅₀: Yield: 109 mg (33 %), M_n = 8800 g mol⁻¹, PDI = 1.15;

P3OT₂₆-*b*-PDMS₁₃₈: Yield: 6 mg (3 %), M_n = 15500 g mol⁻¹, PDI = 1.11.

Scheme S1. Chemical structure of P3OT-*b*-PDMS diblock copolymers.



Synthesis of azide-terminated PS.

Styrene (1.56 g, 15.0 mmol) was dissolved in 6 mL cyclohexane at room temperature and the anionic polymerization was initiated by adding sec-butyl lithium (107 μ L, 0.15 mmol, 1.4 M in hexanes). After stirring at room temperature for 1 h, the reaction mixture was diluted with 6 mL THF and, after stirring for another 5 min, DPE (27 μ L, 0.15 mmol) was added to the mixture. The reaction solution was cooled to -78°C and stirred for 10 min before adding it dropwise to a solution of excess DBP (234 μ L, 2.31 mmol) in THF at -78°C in order to quench the polymerization. The polymer was precipitated into MeOH and isolated by centrifugation. After drying at 40°C in vacuum overnight, bromo-terminated PS was obtained as a white solid. Yield = 1.40 g, 90 %.

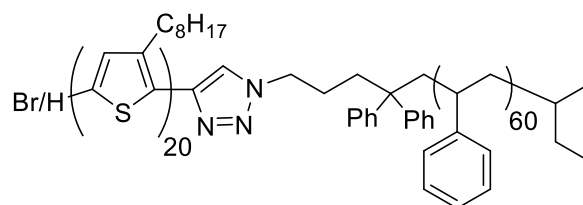
The bromo-terminated PS (1.40 g) and sodium azide (55 mg, 0.85 mmol) were dissolved in 15 mL DMF. After stirring the reaction mixture at room temperature overnight, the polymer was precipitated into MeOH and isolated by centrifugation and dried at 40°C in vacuum overnight. Yield: 1.17 g, 84 %. GPC: M_n = 8100 g mol⁻¹, PDI = 1.11 (determined relative to polystyrene standards). ¹H NMR (499.9 MHz, CDCl₃): δ = 6.90-7.25 (br, phenyl-H in ortho and para position), 6.30-6.75 (br, phenyl-H in meta position), 1.70-2.30 (br, CH₂CH(Ph)), 1.25-1.70 (br, CH₂CH(Ph)).

Synthesis of P3OT₂₀-*b*-PS₆₀.

P3OT₂₀-*b*-PS₆₀ (see Scheme S2) was prepared analogously to P3OT-*b*-PDMS described above and analogously to P3HT-*b*-PS,⁴ via Cu-catalyzed azide-alkyne cycloaddition using alkynyl-end functionalized P3OT (81 mg, 20 μ mol) and azide-terminated PS (243 mg, 30 μ mol), PMDETA (11 μ L, 0.05 mmol) and CuBr (one small spatula). The P3OT-*b*-PS diblock copolymer was purified by repeated size exclusion chromatography as described for P3OT-*b*-PDMS. PS homopolymer impurities were removed by precipitating the polymer in acetone. The collected diblock copolymer P3OT-*b*-PS was dried at 40°C in vacuum overnight. Yield: 41 mg (17 %), M_n = 10100 g mol⁻¹, PDI = 1.13.

¹H NMR (499.9 MHz, CDCl₃): δ = 6.90-7.25 (br, thiophene-H and phenyl-H in ortho and para position), 6.30-6.75 (br, phenyl in meta position), 2.80 (t, J = 7.5 Hz, -octyl), 1.86 (br, CH₂CH(Ph)), 1.71 (br, -octyl), 1.25-1.55 (br, CH₂CH(Ph) and -octyl), 0.89 (t, J = 6.5 Hz, -octyl); see Figure S30.

Scheme S2. Chemical structure of P3OT₂₀-*b*-PS₆₀ diblock copolymers.



Self-assembly of diblock copolymers

Preparation of fiber-like micelles from P3OT-*b*-PDMS and P3OT-*b*-PS diblock copolymers. A mixture of P3OT-*b*-PDMS in decane or P3OT-*b*-PS in butyl acetate was heated to 100°C for 2 h in a sealed glass vial (0.3 mg mL⁻¹) and then allowed to slowly cool to 22°C, followed by aging the solution at 22°C for several days. TEM analysis was performed by drop casting an aliquot of the respective solution (ca. 20 μL) onto a carbon coated copper TEM grid.

Preparation of small P3OT-*b*-PDMS and P3OT-*b*-PS seed micelles. Polydisperse, fiber-like micelles, prepared by heating a mixture of P3OT-*b*-PDMS in decane, followed by slowly cooling the solution to 22°C, were sonicated in a water bath of a 160 W ultrasonic cleaning apparatus (Bandelin, Germany) at 22°C for 30 min (0.3 mg mL⁻¹ in decane), which gave fragmented micelles with number-average contour length L_n of ca. 80 nm. Alternatively, micelles were diluted to 0.05 mg mL⁻¹ or 0.025 mg mL⁻¹ and sonicated with a 100W ultrasonic processor equipped with a titanium sonotrode at -10°C - 0°C for 4 h, which gave small stub-like seed micelles with L_n of ca. 30-40 nm (depending on the P3OT/PDMS block length ratio).

P3OT-*b*-PS seed micelles with $L_n = 40$ nm were prepared by diluting a solution of polydisperse, multi-micron-long fiber-like micelles to 0.025 mg mL⁻¹ in butyl acetate and sonicating the solution for 4h at 0°C using a 100W ultrasonic processor equipped with a titanium sonotrode.

The seed fragments were analysed via TEM by drop casting an aliquot of the micelle solution (ca. 20 μL) onto a carbon coated copper TEM grid. Due to the aggregation of P3OT-*b*-PS micelles on carbon coated copper TEM grids, TEM samples for these micelle solutions were prepared according a previously established protocol,⁴ mixing a drop of the micelle solution with another drop of a PS₆₀

homopolymer solution in butyl acetate (1 mg mL^{-1}) before drop-casting the mixture onto a carbon coated copper TEM grid. This procedure allowed to reduce the aggregation of P3OT-*b*-PS micelles and thus to measure the contour lengths of these micelles.

Preparation of small P3OT-*b*-PDMS seed micelles without sonication using promoted self-nucleation. 498 μL decane was cooled to 0°C in a glass vial. 2.5 μL P3OT₂₆-*b*-PDMS₅₀ unimer as a 10 mg mL^{-1} solution in THF was added under rapid stirring (1000 rpm) and stirring was continued for another 30 min at 0°C before the solution was slowly warmed up to room temperature (within ca. 1.5 h) under rapid stirring. Then, stirring was stopped and the solution was aged at room temperature overnight. The small micelles formed were analyzed via TEM by drop-casting an aliquot of the solution (ca. 20 μL) onto a carbon coated copper TEM grid. Further growth of the micelles was excluded based on the analysis of another aliquot of the solution (20 μL) taken after another two days.

Seeded growth experiments with P3OT-*b*-PDMS and P3OT-*b*-PS. P3OT-*b*-PDMS seed micelle solutions in decane were diluted to 0.014 mg mL^{-1} , using decane or a decane/THF solvent mixture (the THF fraction of the decane/THF solvent mixture was set so that the final THF fraction after addition of unimer solution in THF was 3, 6 or 9 vol%). P3OT-*b*-PDMS unimer as a 10 mg mL^{-1} THF solution was added during vigorous stirring (300 rpm), corresponding to a unimer-to-seed mass ratio of 2.5, 5, 7.5, 10, 12.5, 15, 20, or 25, after equilibrating the micelle solutions at 22°C , 35°C , or 40°C for ca. 45 min. Subsequently, the solutions were aged at the respective temperature in sealed glass vials for 2 days. TEM analysis was then carried out by drop casting an aliquot of the solutions (ca. 20 μL) onto a carbon coated copper TEM grid.

Growth from the P3OT-*b*-PS seed micelles in butyl acetate was demonstrated analogously by diluting the micelle solution with butyl acetate or butyl acetate/THF to 0.014 mg mL^{-1} and adding P3OT-*b*-PS unimer (10 mg mL^{-1} THF solution) during vigorous stirring (300 rpm) after equilibrating the solution at 22°C or 35°C . The solutions were then aged at the respective temperature in a sealed glass vial for 2 days. Before drop-casting an aliquot of the solutions (ca. 20 μL) onto a carbon coated copper TEM

grid, a drop of the micelle solution was mixed with another drop of a PS₆₀ homopolymer solution in butyl acetate (1 mg mL⁻¹).

Control experiments with micelle seeds in the presence of different amounts of THF. Control experiments with P3OT₂₆-*b*-PDMS₅₀ micelle seeds (see Table S3) were performed by diluting seed solutions (0.023 mg mL⁻¹ in decane) with THF which is a common solvent for both blocks and aging the solutions (total volume of 150 µL) in sealed glass vials at 22°C, 40°C or 45°C for 2 days. For TEM analysis an aliquot of the solutions (ca. 20 µL) was drop cast onto a carbon coated copper TEM grid.

Self-assembly control experiments in the absence of seed micelles. In these experiments, P3OT₂₆-*b*-PDMS₅₀ unimer solution (6 µl or 12 µl of a 10 mg mL⁻¹ unimer solution in THF) was injected into decane or a decane/THF solvent mixture consisting of a final THF fraction of 9 vol% (with the same solvent volume as used for the seeded growth experiments) and aged at room temperature for two days, the same length of time as for the seeded growth experiments. Subsequently, an aliquot of the solutions (ca. 20 µL) was drop cast onto a carbon coated copper TEM grid and, after drying, analysed by TEM.

Discussion: Seeded growth experiments with P3OT₂₆-*b*-PDMS₅₀ at 40°C

Performing seeded growth experiments with P3OT₂₆-*b*-PDMS₅₀ at 40°C and THF fractions < 1.5% leads to an average micelle length of 235 nm (PDI = 1.21), 368 nm (PDI = 1.27) and 434 nm (PDI = 1.24) for unimer-to-seed ratios of 5, 7.5 and 10 (see Figure 8a and Figure S27). These lengths are higher than the micelle lengths obtained at 35°C in analogous experiments, which are close to the theoretically expected micelle lengths. Thus the theoretical lengths were exceeded by ca. 10-20% when conducting seeded growth at 40°C. This indicates that micelle growth is promoted at a higher temperature, allowing for efficient CDSA without significant amounts of unimer left in solution in case the unimer-to-mass ratio is ≤ 10 (see UV/vis spectra in Figure S28). The theoretically predicated micelle length is lower at this stage which is probably due to partial dissolution of seed crystals as a result of an increased solvent quality of the diBCP at 40°C. Using higher unimer-to-mass ratios or

performing seeded growth experiments in the presence of common solvent, however, did not lead to further micelle growth, and micelles with broad length polydispersities were observed under these conditions (e.g. at $m_{\text{unimer}}/m_{\text{seed}} = 10$ and a THF fraction of 3%: $L_n = 509$ nm and PDI = 1.38). In the presence of increased fractions of common solvent substantial amounts of unimer were observed in the form of a film by TEM and in solution by UV/vis spectroscopy (see Figure S29). In addition, large amounts of unimer were also found to be disadvantageous for imaging micelles by TEM since the contour of some micelles incorporated in higher amounts of unimer film became blurred. Combining an elevated temperature of 40°C and a THF fraction of ca. $\geq 2\%$ increases the solvent quality of the polymer above a beneficial level and dominates the advantageous temperature effect on micelle growth and thus does not allow for controlled growth of well-defined micelles. This suggests that seed crystals may partially dissolve and dissolved diBCP may partially crystallize at existing seed micelles, thus leading to high fractions of small seed crystals but also to considerable amounts of longer micelles after aging a solution of seed micelles at 40°C in the presence of increased amounts of THF (see control experiments in Table S3). Most obviously, aging seed micelles in decane at a further increased temperature of 45°C in the presence of 1.5% THF, the length L_n and the length polydispersity of seeds increases from initially 32 nm and 1.06 to 60 nm and 2.40 and the fraction of surviving seed micelles decreases to below 90%, indicating that self-seeding occurs at 45°C to a higher extent, even in the presence of low amounts of THF, thus rendering these conditions unattractive for seeded growth experiments.

It should be noted that the increased lengths detected above room temperature might also be explained by a decrease in the linear aggregation number (the number of BCP molecules per unit length) which would lead to a smaller core width. However, this possible explanation was dismissed as the core-forming P3OT block does not chain-fold at the relatively low degree of polymerization ($DP = 26$) used in this work. Consistent with the rejection of this possible explanation, no decrease in micelle width was detected by TEM at elevated temperatures (core widths = 12.4 nm (22°C), 12.1 nm (35°C), 12.5 nm (40°C) were identical within experimental error).

II. Supporting Tables

Table S1. Data for seeded growth experiments with P3OT₂₆-*b*-PDMS₅₀ diblock copolymers. For these experiments the respective amount of P3OT₂₆-*b*-PDMS₅₀ unimer in THF was added to 6 μ g of P3OT₂₆-*b*-PDMS₅₀ seed micelles in decane or a decane/THF solvent mixture with varying THF contents at 22°C, 35°C, or 40°C, followed by aging the solutions for 2 days at the respective temperature. The seed micelles used exhibited an average micelle length L_n of 36 nm and a dispersity L_w/L_n of 1.14.

Entry	Temperature (°C)	THF vol%	$m_{\text{unimer}}/m_{\text{seed}}$	L_n (nm)	PDI (L_w/L_n)	σ/L_n	Theoretical L_n (nm)
1-1	22	0.3	2.5	120	1.22	0.47	126
1-2	22	0.7	5	203	1.17	0.41	216
1-3	22	1.0	7.5	239	1.17	0.41	306
1-4	22	1.4	10	262	1.11	0.33	396
1-5	22	1.7	12.5	274	1.13	0.35	486
1-6	22	2.1	15	329	1.15	0.38	576
1-7	22	2.7	20	368	1.14	0.38	756
1-8	22	3.0	10	299	1.16	0.40	396
1-9	22	6.0	10	334	1.19	0.44	396
1-10	22	9.0	10	393	1.23	0.39	396
1-11	22	9.0	25	503	1.25	0.50	936
1-12	35	0.7	5	215	1.24	0.49	216
1-13	35	1.0	7.5	271	1.23	0.48	306
1-14	35	1.4	10	330	1.21	0.46	396
1-15	35	1.7	12.5	416	1.22	0.47	486
1-16	35	2.1	15	443	1.25	0.50	576
1-17	35	2.7	20	545	1.26	0.51	756
1-18	35	3.4	25	572	1.22	0.47	936
1-19	35	3.0	10	360	1.31	0.56	396
1-20	35	6.0	10	412	1.21	0.46	396
1-21	35	9.0	10	449	1.35	0.59	396
1-22	40	0.7	5	235	1.21	0.46	216
1-23	40	1.0	7.5	368	1.27	0.52	306
1-24	40	1.4	10	434	1.24	0.49	396
1-25	40	3.4	25	514	1.24	0.49	936
1-26	40	3.0	10	509	1.38	0.62	396

Table S2. Data for seeded growth experiments with P3OT₂₆-*b*-PDMS₁₃₈ diblock copolymers. For these experiments the respective amount of P3OT₂₆-*b*-PDMS₁₃₈ unimer in THF was added to 6 µg of P3OT₂₆-*b*-PDMS₁₃₈ seed micelles in decane at 22°C, followed by aging the solutions for 2 days at 22°C. The seed micelles used exhibited an average micelle length L_n of 29 nm and a dispersity L_w/L_n of 1.19.

Entry	Temperature (°C)	THF vol%	$m_{\text{unimer}}/m_{\text{seed}}$	L_n (nm)	PDI (L_w/L_n)	σ/L_n	Theoretical L_n (nm)
2-1	22	0.3	2.5	110	1.39	0.62	102
2-2	22	0.7	5	149	1.30	0.54	174
2-3	22	1.0	7.5	166	1.30	0.55	247
2-4	22	1.4	10	197	1.31	0.56	319
2-5	22	1.7	12.5	231	1.21	0.46	392
2-6	22	2.1	15	304	1.18	0.43	464
2-7	22	2.7	20	358	1.20	0.45	609

Table S3. Control experiments with P3OT₂₆-*b*-PDMS₅₀ seed micelles with an average micelle lengths L_n of 35 nm and a dispersity L_w/L_n of 1.21. Seed micelles were aged in decane/THF solvent mixtures with varying THF contents at 22°C or 40°C for 2 days. Independent of the temperature, micelles remained colloidally stable and the average contour length L_n of the micelles did not significantly change compared to the length of the initial seed micelles for THF fractions < 10%, indicating that self-seeding does not take place under these conditions.

Entry	Temperature (°C)	THF vol%	L_n (nm)	PDI (L_w/L_n)	σ/L_n
3-1	22	1.5	38	1.24	0.49
3-2	22	3	40	1.26	0.51
3-3	22	6	43	1.38	0.61
3-4	22	9	39	1.36	0.60
3-5	22	12	67	1.74	0.86
3-6	22	15	87	1.97	0.98
3-7	40	1.5	27	1.18	0.41
3-8	40	3	35	1.23	0.47
3-9	40	6	33	1.48	0.69
3-10	40	9	34	1.30	0.54
3-11	40	12	52	1.26	0.51

Table S4. Data for seeded growth experiments with P3OT₂₀-*b*-PS₆₀ diblock copolymers. For these experiments the respective amount of P3OT₂₀-*b*-PS₆₀ unimer in THF was added to 6 µg of P3OT₂₀-*b*-PS₆₀ seed micelles in butyl acetate or a butyl acetate/THF solvent mixture with a final THF fraction of 9% at 22°C or 35°C, followed by aging the solutions for 2 days at the respective temperature. The seed micelles used exhibited an average micelle length L_n of 40 nm and a dispersity L_w/L_n of 1.09.

Entry	Temperature (°C)	THF vol%	$m_{\text{unimer}}/m_{\text{seed}}$	L_n (nm)	PDI (L_w/L_n)	σ/L_n	Theoretical L_n (nm)
1	22	1.4	10	120	1.20	0.45	440
2	22	9	10	198	1.16	0.40	440
3	35	1.4	10	358	1.16	0.39	440
4	35	9	10	537	1.25	0.50	440

III. Supporting Figures

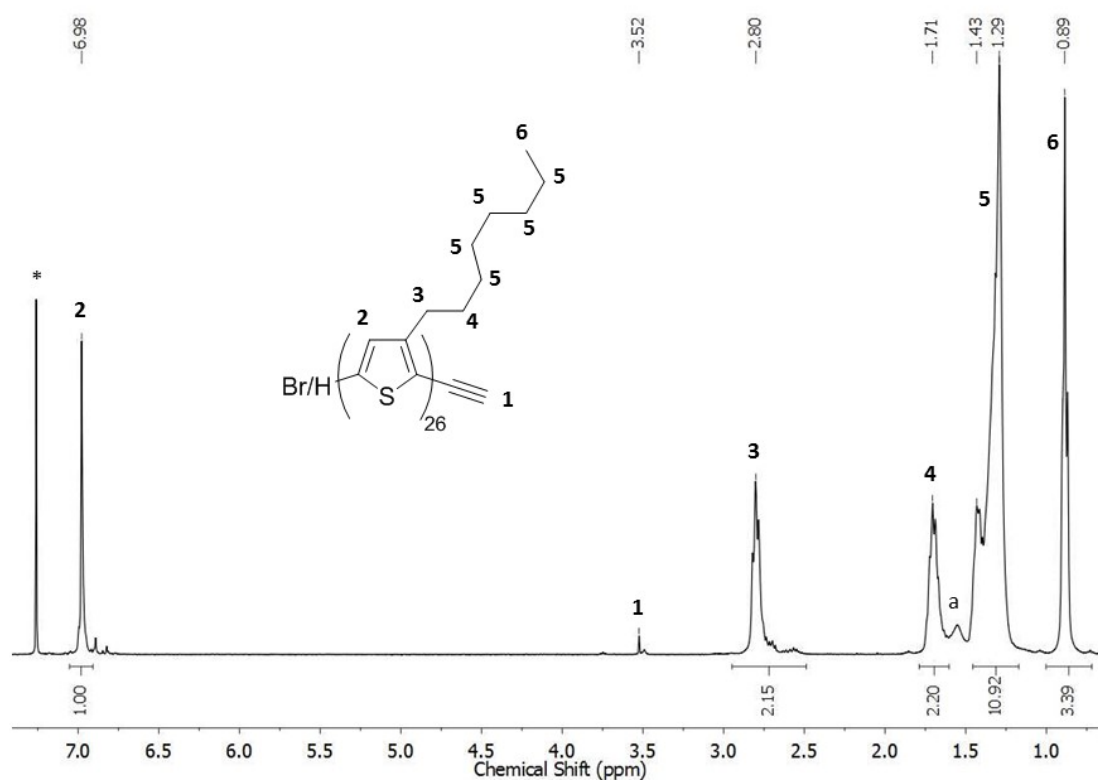


Figure S1. ¹H NMR spectrum of alkyne-P3OT₂₆ in CDCl₃. The asterisk denotes residual protonated solvent signal and 'a' denotes residual H₂O.

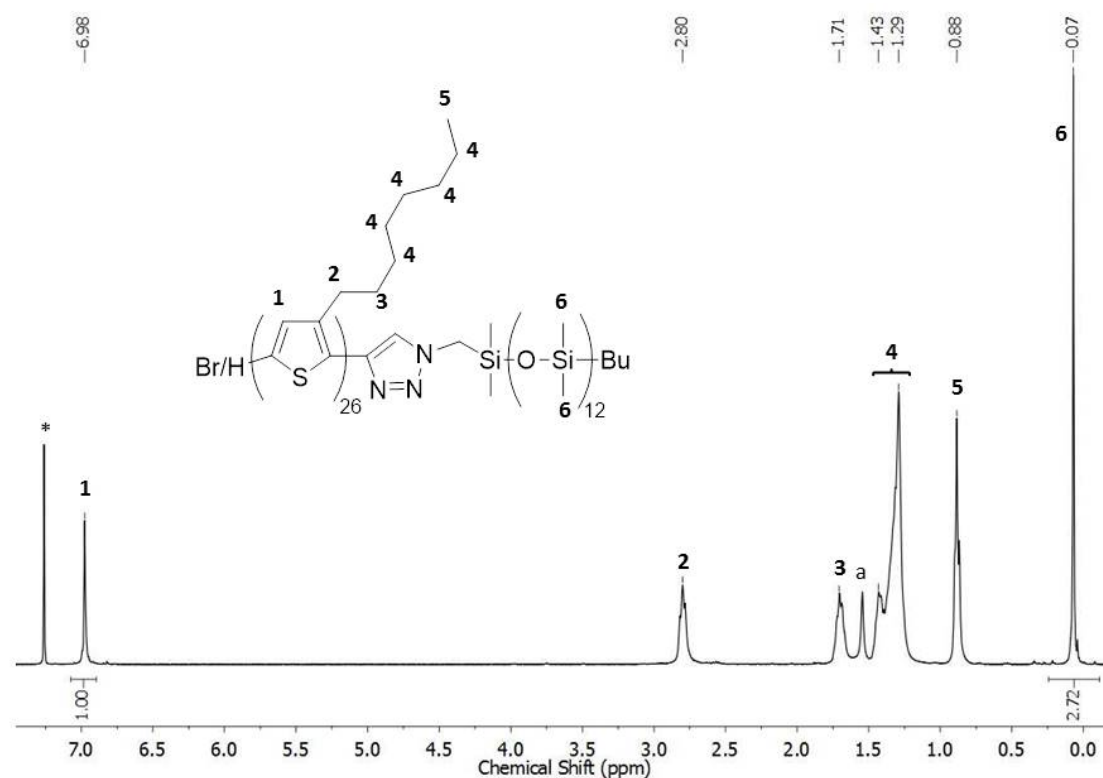


Figure S2. ¹H NMR spectrum of P3OT₂₆-b-PDMS₁₂ in CDCl₃. The asterisk denotes residual protonated solvent signal and 'a' denotes residual H₂O.

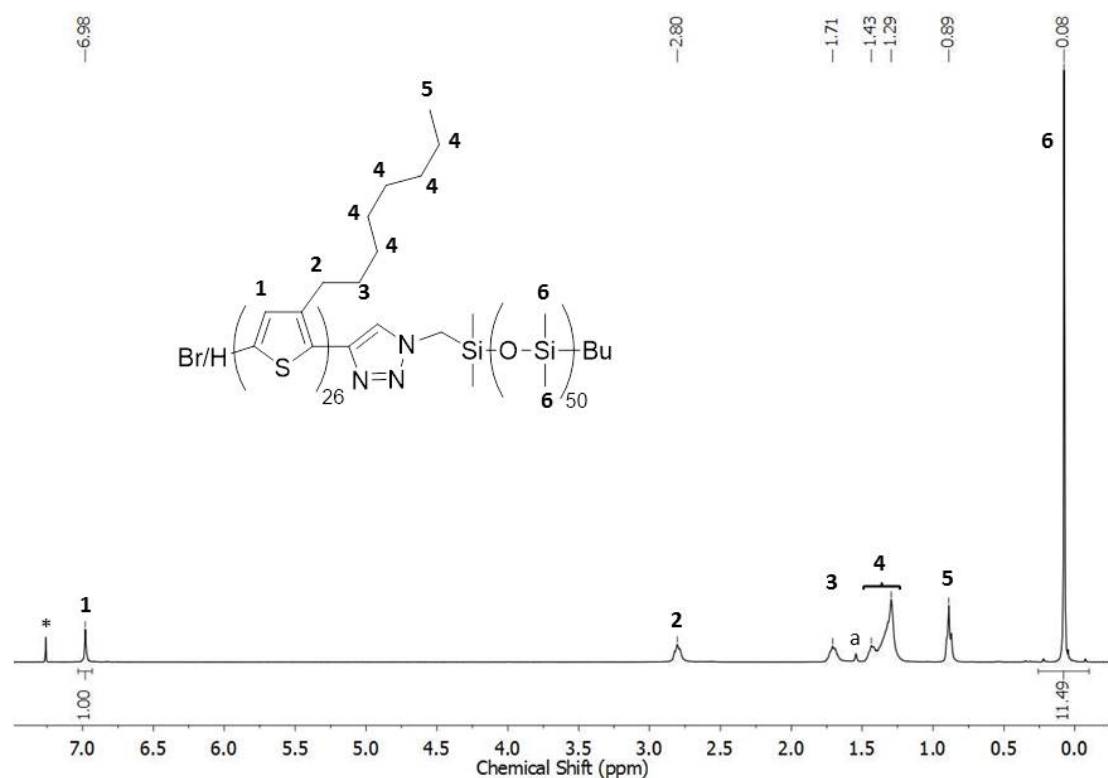


Figure S3. ¹H NMR spectrum of P3OT₂₆-b-PDMS₅₀ in CDCl₃. The asterisk denotes residual protonated solvent signal and 'a' denotes residual H₂O.

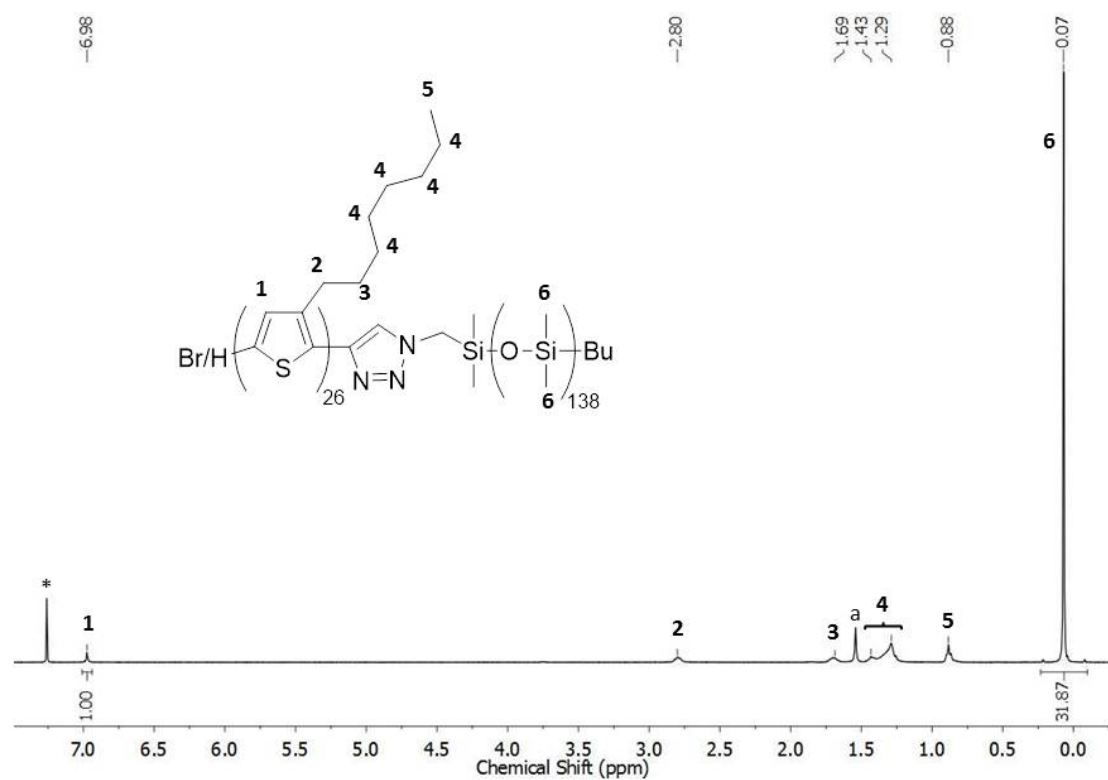


Figure S4. ¹H NMR spectrum of P3OT₂₆-b-PDMS₁₃₈ in CDCl₃. The asterisk denotes residual protonated solvent signal and 'a' denotes residual H₂O.

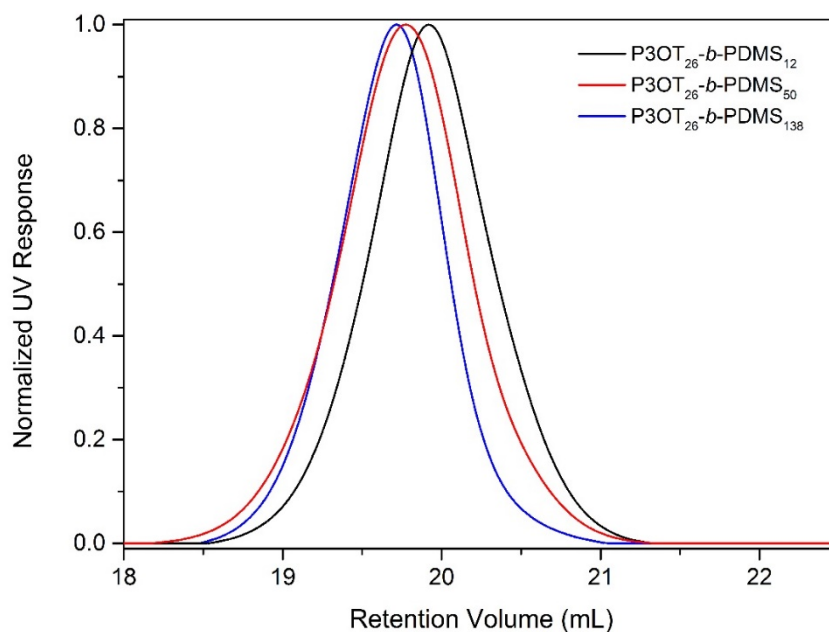


Figure S5. GPC traces (UV response, $\lambda = 440$ nm) of P3OT-*b*-PDMS diblock copolymers dissolved in THF (P3OT₂₆-*b*-PDMS₁₂, P3OT₂₆-*b*-PDMS₅₀ and P3OT₂₆-*b*-PDMS₁₃₈) relative to polystyrene standards.

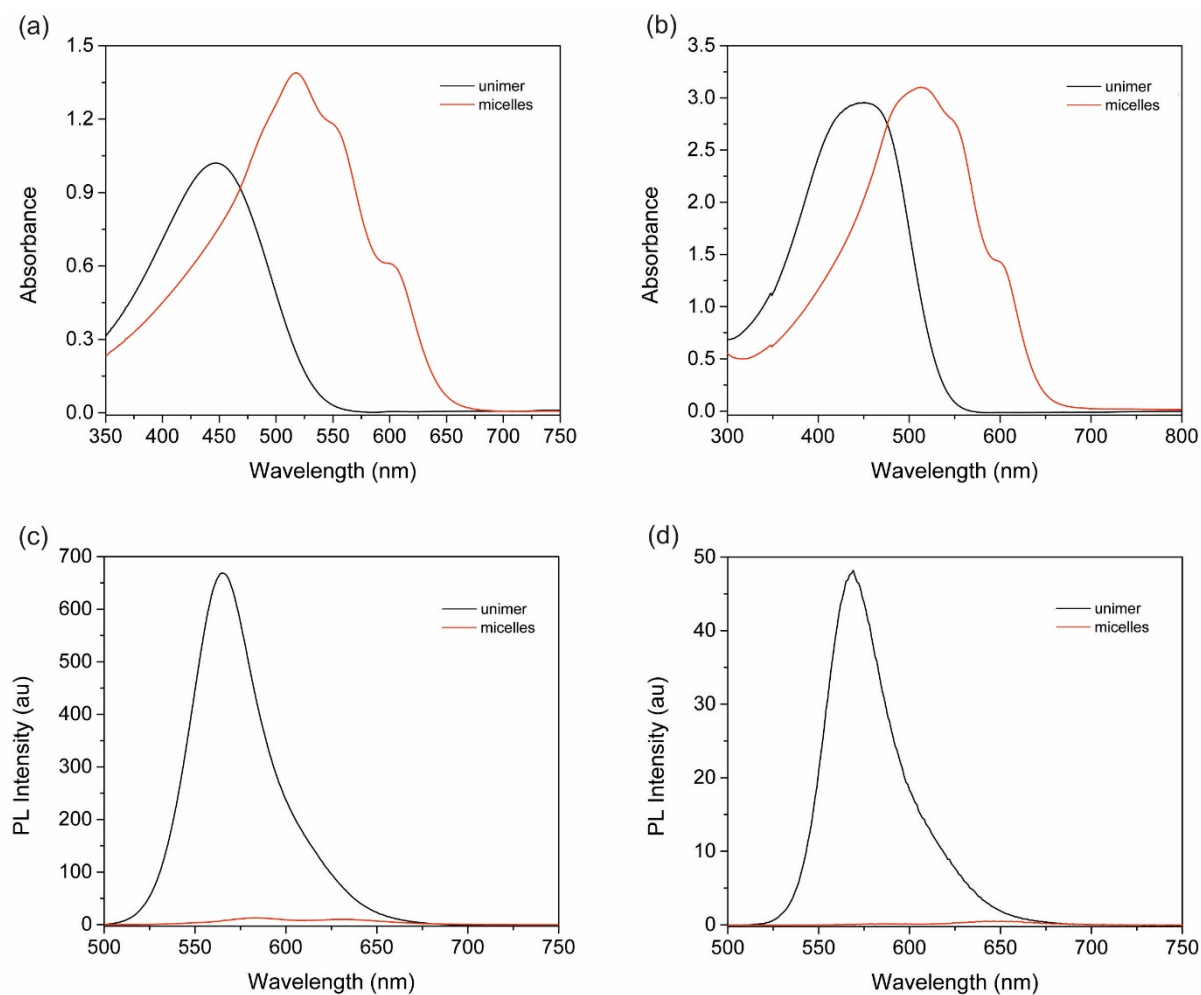


Figure S6. Solution-state UV/vis spectra of (a) P3OT₂₆-*b*-PDMS₁₃₈ unimers (0.1 mg mL⁻¹ in THF, black) and micelles (0.1 mg mL⁻¹ in decane, red) and (b) P3OT₂₆-*b*-PDMS₁₂ unimers (0.1 mg mL⁻¹ in

THF, black) and micelles (0.1 mg mL⁻¹ in decane, red). Solution PL spectra of (c) P3OT₂₆-*b*-PDMS₁₃₈ unimers (0.3 mg mL⁻¹ in THF, black) and micelles (0.3 mg mL⁻¹ in decane, red) and (d) P3OT₂₆-*b*-PDMS₁₂ unimers (0.3 mg mL⁻¹ in THF, black) and micelles (0.3 mg mL⁻¹ in decane, red).

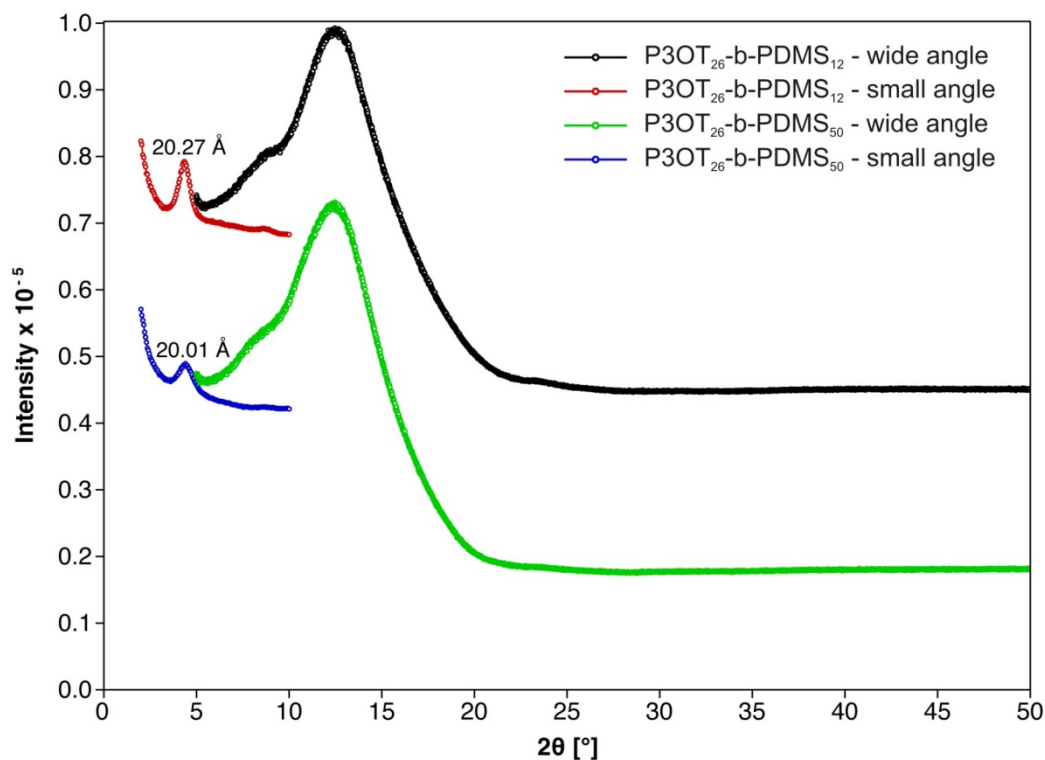


Figure S7. WAXS pattern for P3OT₂₆-*b*-PDMS₁₂ and P3OT₂₆-*b*-PDMS₅₀ diblock copolymer films cast from THF solutions (concentration 20 mg mL⁻¹ and 10 mg mL⁻¹, respectively). WAXS was not attempted for the diBCP with the longest PDMS block length, P3OT₂₆-*b*-PDMS₁₃₈, as the percentage of crystallisable material in the sample was very low.

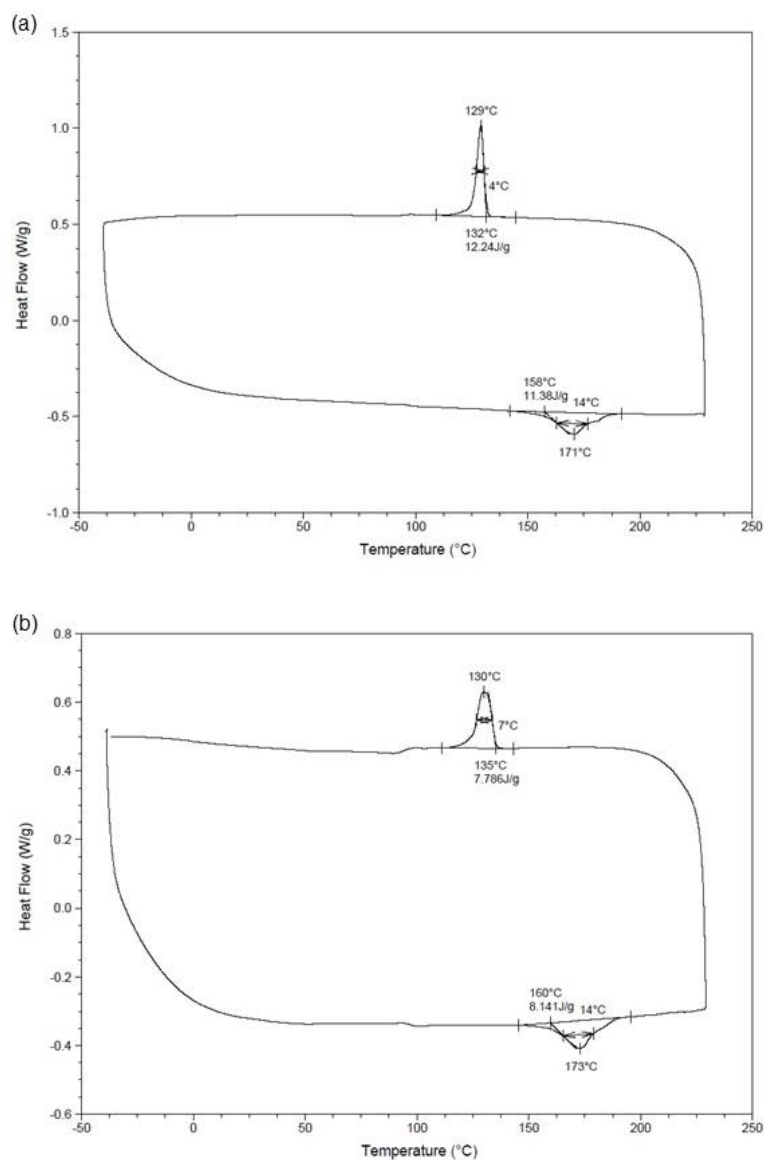


Figure S8. DSC traces of P3OT₂₆-b-PDMS₁₂ (a) and P3OT₂₆-b-PDMS₅₀ (b). Scan rate = 10°C/min. A similar melt transition (T_m) was observed at 171°C and 173°C for P3OT₂₆-b-PDMS₁₂ and P3OT₂₆-b-PDMS₅₀, respectively. The enthalpy of fusion was found to be higher for P3OT₂₆-b-PDMS₁₂ (11.38 J g⁻¹) than for P3OT₂₆-b-PDMS₅₀ with the longer polysiloxane block (8.14 J g⁻¹), and this corresponded to ca. 15% and 11% of the enthalpy of fusion of an ideal P3OT crystal (73.6 J g⁻¹).⁵ In addition to a similar T_m , both diBCPs exhibit a similar crystallization exotherm of T_c = 129-130°C, which is expected due to the same DP_n of the polythiophene blocks.⁶ DSC was not attempted for P3OT₂₆-b-PDMS₁₃₈, as the percentage of crystallisable material in this sample was very low.

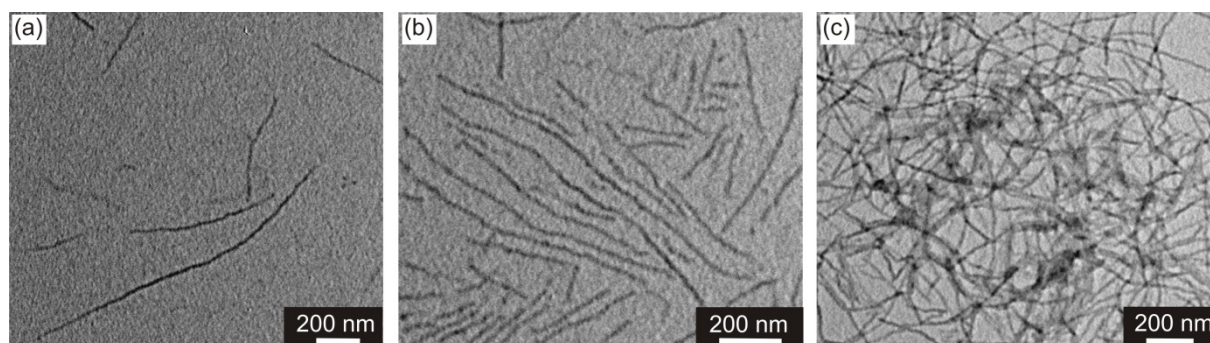


Figure S9. TEM micrographs of P3OT₂₆-*b*-PDMS₁₃₈ (a), P3OT₂₆-*b*-PDMS₅₀ (b) and P3OT₂₆-*b*-PDMS₁₂ (c) micelles obtained from heating a solution of the respective polymer in decane (0.3 mg mL⁻¹) to 100°C for 2 h and slowly cooling to room temperature.

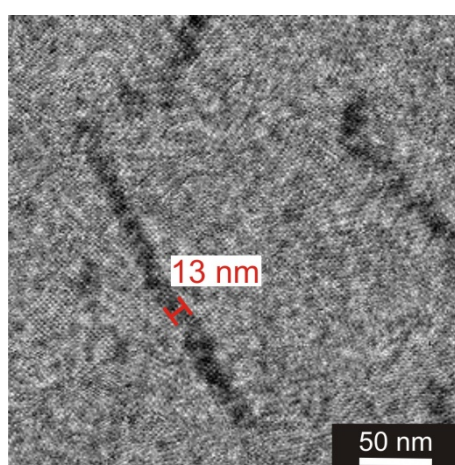


Figure S10. TEM micrograph of P3OT₂₆-*b*-PDMS₅₀ micelles obtained from heating a solution of the polymer in decane (0.3 mg mL⁻¹) to 100°C for 2 h and slowly cooling to room temperature.

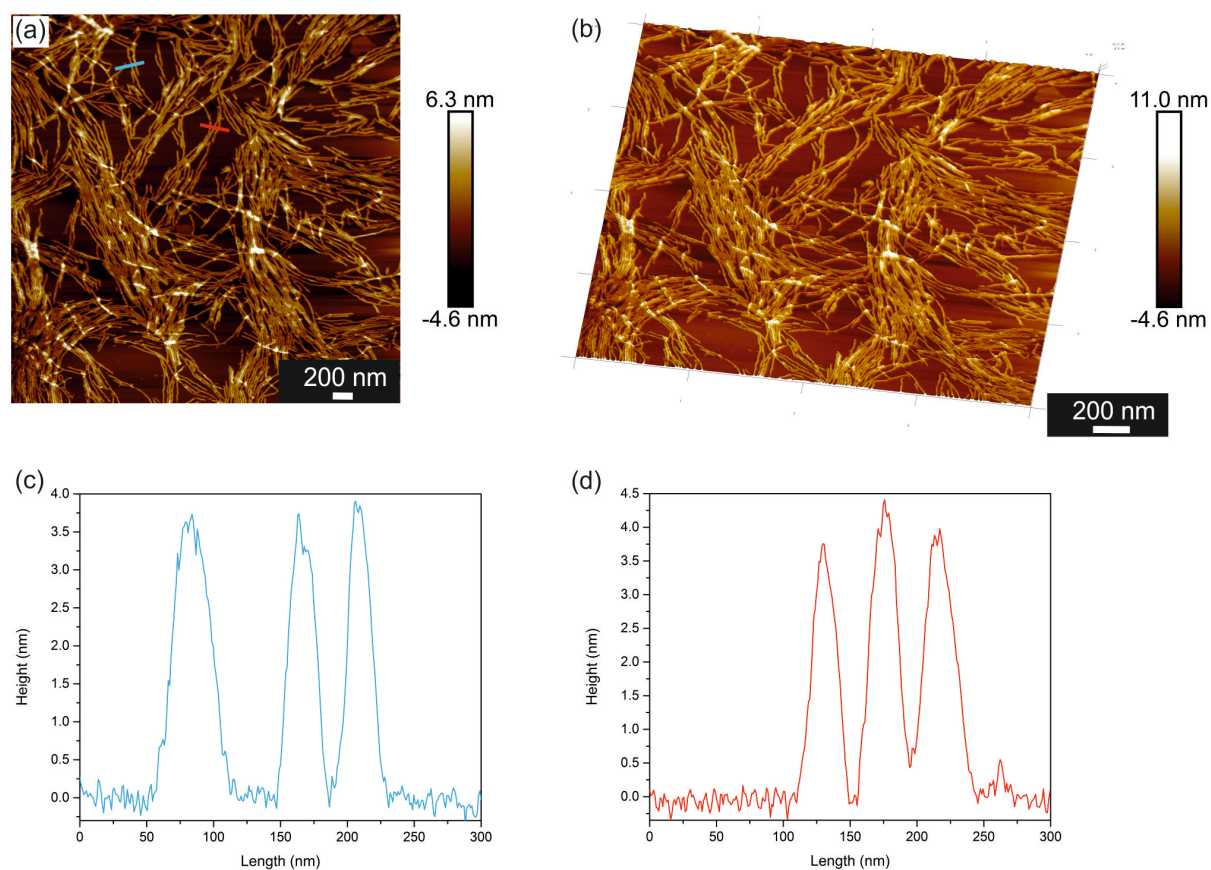


Figure S11. (a,b) AFM height image and 3D height image of polydisperse, multi-micrometer sized fiber-like P3OT₂₆-*b*-PDMS₅₀ micelles drop-cast from decane and dried for 1 day. The Z profile of the 3D height image was multiplied by 5 for clarity. (c,d) Representative height profiles of P3OT₂₆-*b*-PDMS₅₀ micelles taken from blue (c) and red (d) line in AFM height image in Figure 1a. Height variations of ca. ± 0.5 nm are likely due to the soft PDMS micelle corona, which may bunch up during drying.

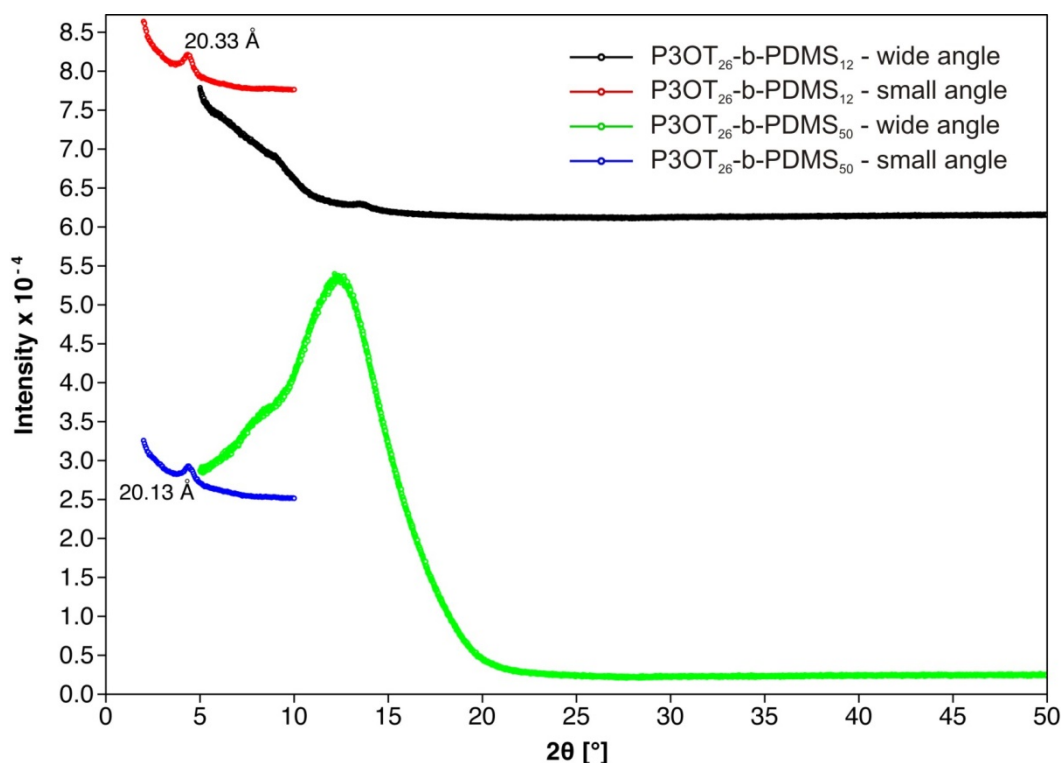


Figure S12. WAXS patterns of films cast from P3OT₂₆-*b*-PDMS₁₂ and P3OT₂₆-*b*-PDMS₅₀ micelle solutions in decane (0.3 mg mL⁻¹). Micelles were prepared by heating a solution of the respective diblock copolymer to 100°C for 2h, followed by slowly cooling down and aging the solution at room temperature.

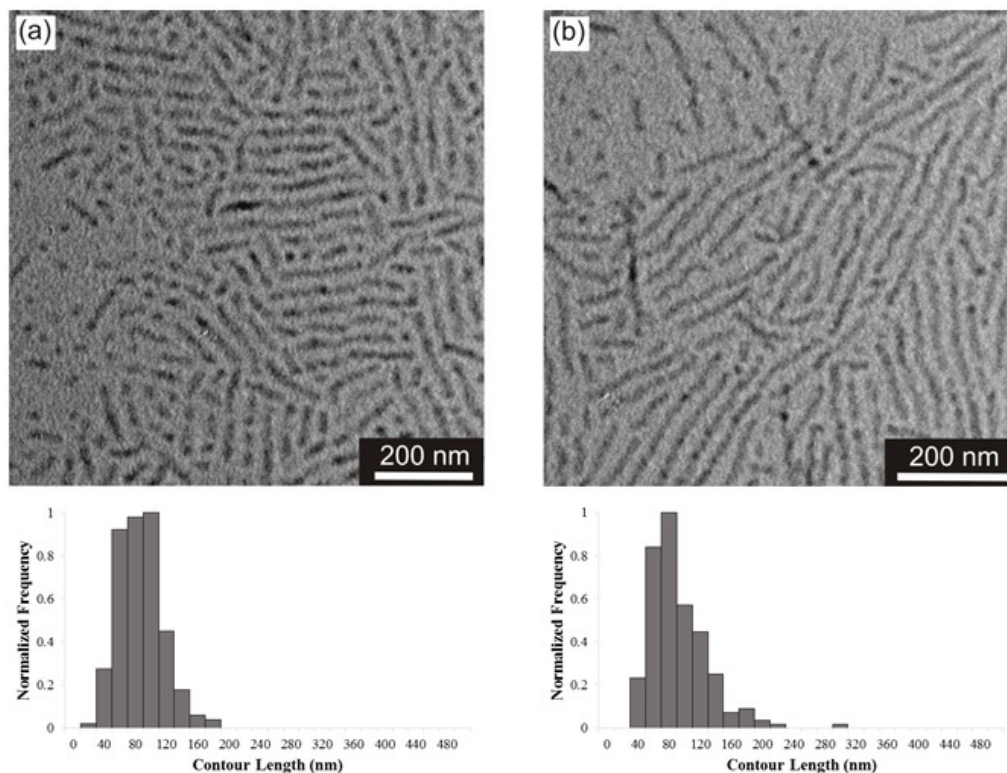


Figure S13. TEM micrographs and corresponding histograms of P3OT₂₆-*b*-PDMS₁₃₈ (a, $L_n = 77$ nm, PDI = 1.13, $\sigma/L_n = 0.36$) and P3OT₂₆-*b*-PDMS₅₀ (b, $L_n = 82$ nm, PDI = 1.20, $\sigma/L_n = 0.45$) seed micelles obtained by sonication of multi-micron-long micelles at 22°C for 30 min in a water bath.

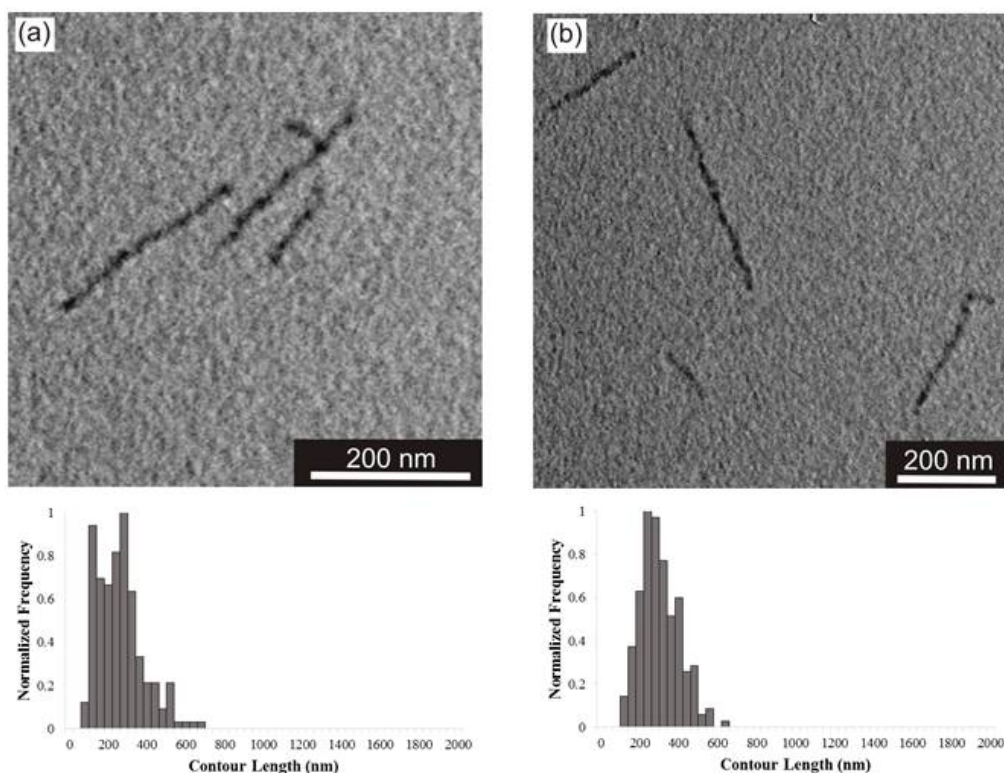


Figure S14. TEM micrographs and corresponding histograms for the fiber-like micelles which were obtained from adding 75 μg P3OT₂₆-*b*-PDMS₁₃₈ unimer (a) and 75 μg P3OT₂₆-*b*-PDMS₅₀ unimer (b) to 30 μg of P3OT₂₆-*b*-PDMS₁₃₈ and P3OT₂₆-*b*-PDMS₅₀ seed micelles in decane, respectively.

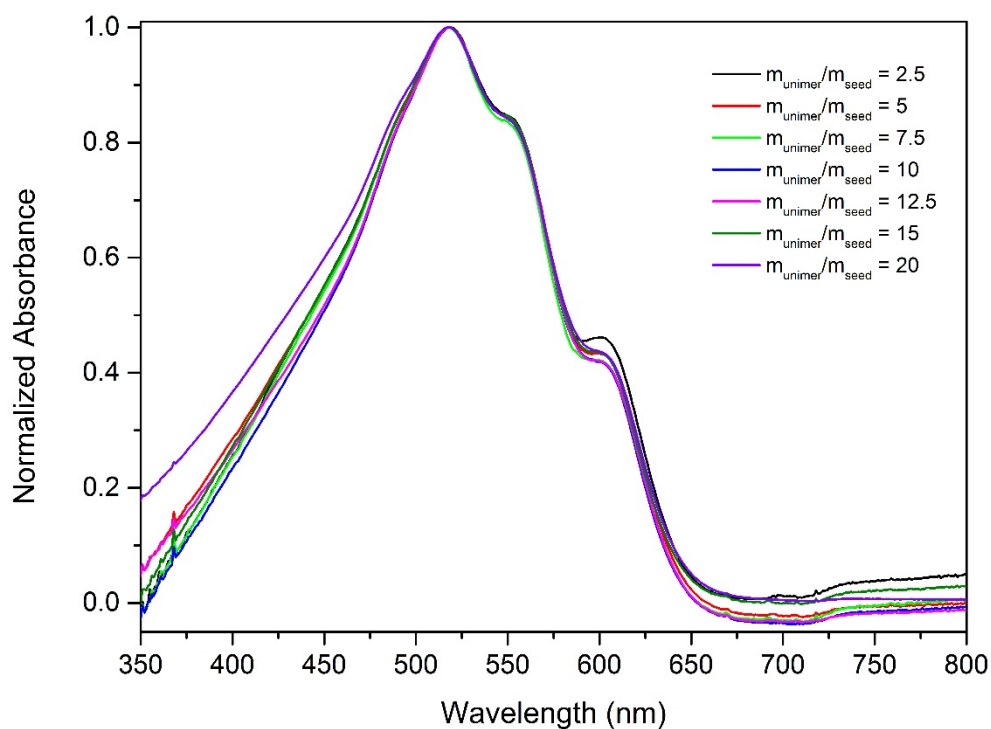


Figure S15. UV/vis spectra of P3OT₂₆-*b*-PDMS₅₀ micelle solutions obtained from adding the respective amount of unimer to 6 μg of seed micelles in decane at 22°C, micelles aged at 22°C for at least two days.

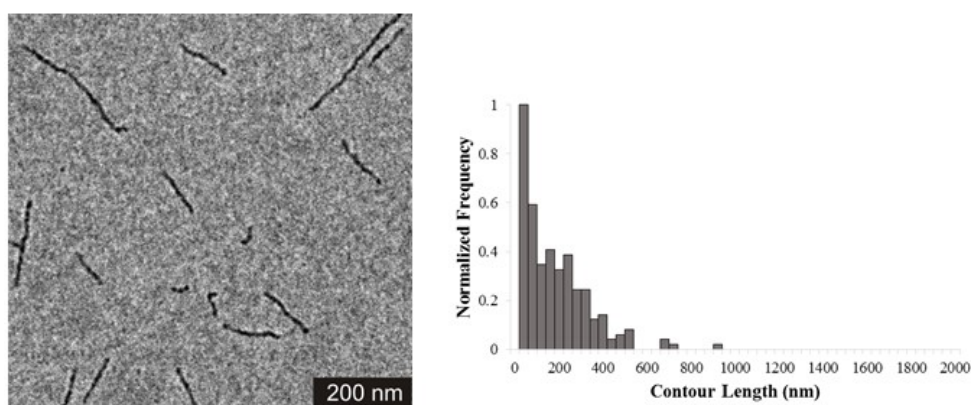


Figure S16. TEM micrograph and corresponding histogram of micelles obtained from injecting 120 μg P3OT₂₆-*b*-PDMS₅₀ unimer solution in THF (10 mg mL⁻¹) into decane (same amount of decane as used for seeded growth experiments illustrated in Figure 4) in the absence of seed micelles. The solution was aged for 2 days at 22°C.

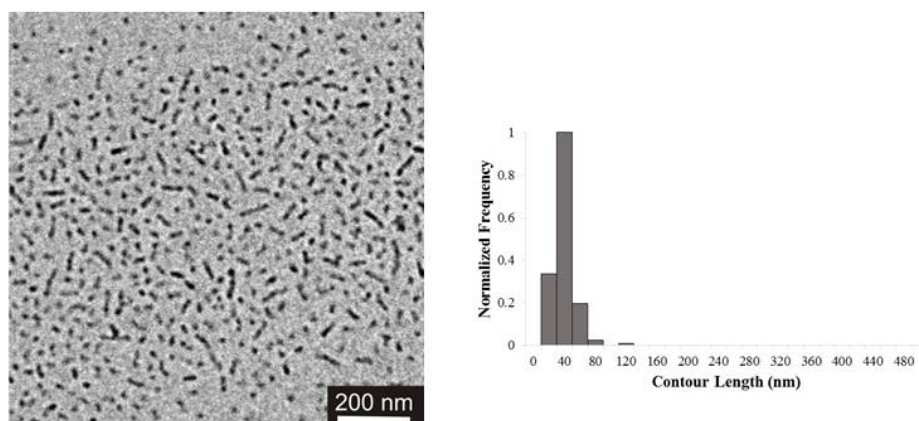


Figure S17. TEM micrograph and corresponding histogram of P3OT₂₆-*b*-PDMS₁₃₈ seed micelles ($L_n = 29$ nm, PDI = 1.19) obtained by sonication of multi-micron-long micelles at 0°C for 4 h.

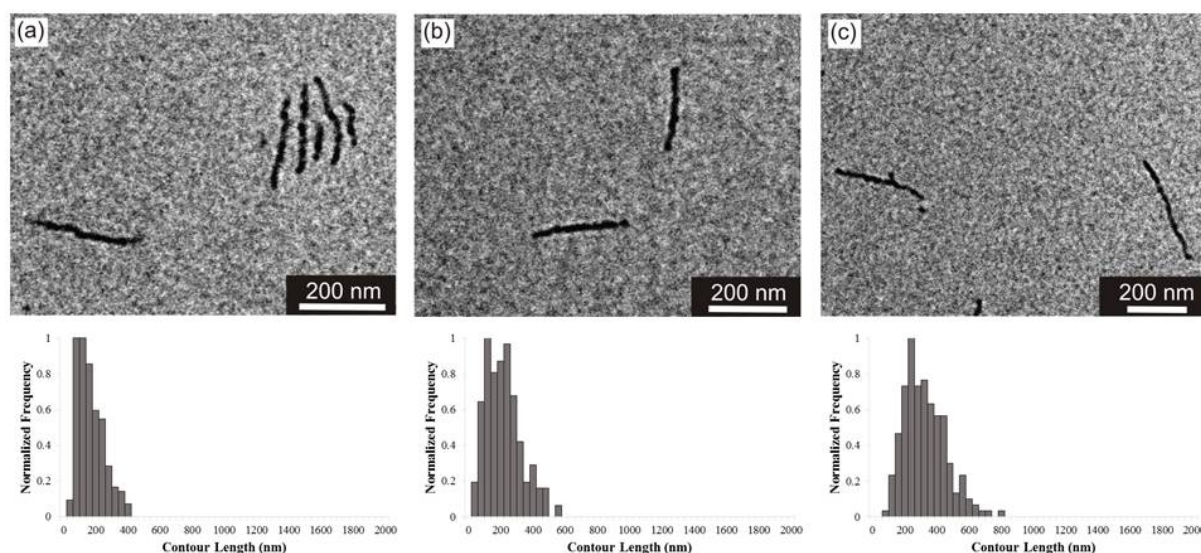


Figure S18. TEM micrographs and corresponding histograms for the fiber-like micelles which were obtained from adding 30 μg (a), 60 μg (b), and 90 μg (c) P3OT₂₆-*b*-PDMS₁₃₈ unimer to 6 μg of P3OT₂₆-*b*-PDMS₁₃₈ seed micelles ($L_n = 29$ nm, PDI = 1.19) in decane.

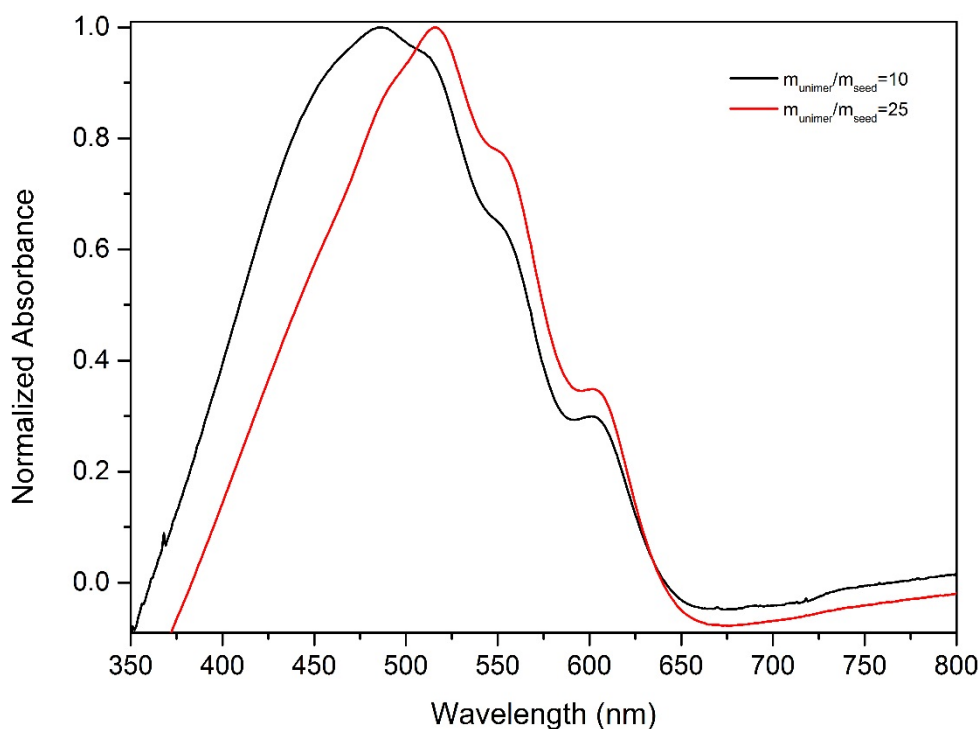


Figure S19. UV/vis spectra of P3OT₂₆-*b*-PDMS₅₀ micelle solutions obtained from adding the respective amount of unimer to 6 μg of seed micelles ($L_n = 36$ nm, PDI = 1.14) in a decane/THF solvent mixture with a final THF fraction of 9 vol% at 22 $^{\circ}\text{C}$, micelles aged at 22 $^{\circ}\text{C}$ for two days. When increasing the amount of unimer added to a seed solution from a unimer-to-mass ratio of 10 to 25 and adjusting the final THF volume fraction to 9%, micelles with an increased contour length and a larger dispersity ($L_n = 503$ nm, PDI = 1.25) were obtained. The larger dispersity is probably caused by homogeneous nucleation taking place simultaneously to epitaxial crystallization at micelle seeds since the amount of unimer in solution was found to be significantly decreased according to UV/vis spectroscopy compared to analogous experiment for which a unimer-to-seed ratio of 10 was used.

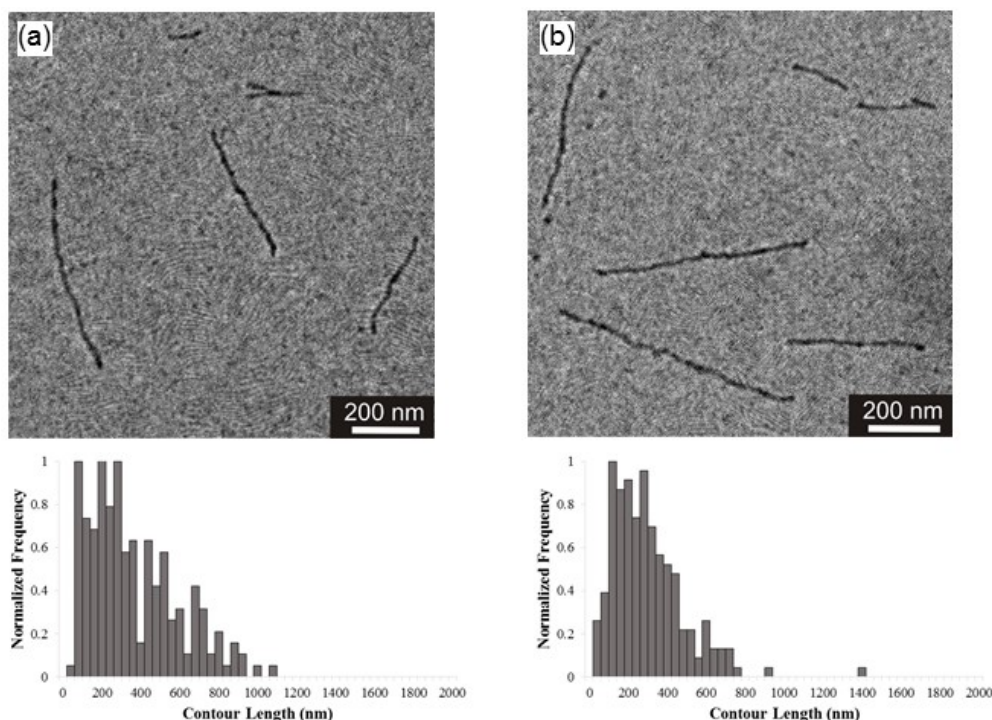


Figure S20. TEM micrographs and corresponding histograms of micelles obtained from injecting 60 μg (a) and 120 μg (b) P3OT₂₆-*b*-PDMS₅₀ unimer solution in THF (10 mg mL⁻¹) into a decane/THF solvent mixture with a final THF fraction of 9% (same solvent volume as used for seeded growth experiments illustrated in Figure 4) in the absence of seed micelles. The solutions were aged for 2 days at 22°C before TEM analysis.

The experiment, in which 6 μL of a 10 mg mL⁻¹ P3OT₂₆-*b*-PDMS₅₀ unimer solution in THF were injected into a decane/THF solvent mixture consisting of a total THF fraction of 9 vol%, reveals that unimer self-assembled in the decane/THF solvent mixture in the absence of seed micelles. This gave rise to polydisperse fibers with an average contour length of 339 nm (PDI = 1.44, see Figure S20a) and suggests that micelles obtained in the analogous seeded growth experiment with a lower dispersity of 1.23 indicate epitaxial crystallization at the end of the seed micelles. When increasing the amount of P3OT₂₆-*b*-PDMS₅₀ unimer solution (12 μL of a 10 mg mL⁻¹ unimer solution in THF) injected into a decane/THF solvent mixture with of a total THF fraction of 9 vol%, fibers with an average contour length of 277 nm (PDI 1.45, see Figure S20b) formed. This control experiment suggests that it is possible for homogenous nucleation to take place in a decane/THF solvent mixture with THF fractions < 10 vol%, particularly when working with high amounts of unimer, which correspond to $m_{\text{unimer}}/m_{\text{seed}} = 20$ in seeded growth experiments. However, compared to the analogous control experiment in which the same amount of unimer solution was injected into pure decane (see Figure S16: $L_n = 165$ nm, PDI = 1.80), this control experiment in which fibers with a longer average contour length ($L_n = 277$ nm) and a lower dispersity (PDI = 1.45) formed indicates that micelle growth is favoured and homogenous nucleation disfavoured in the presence of increased THF fractions.

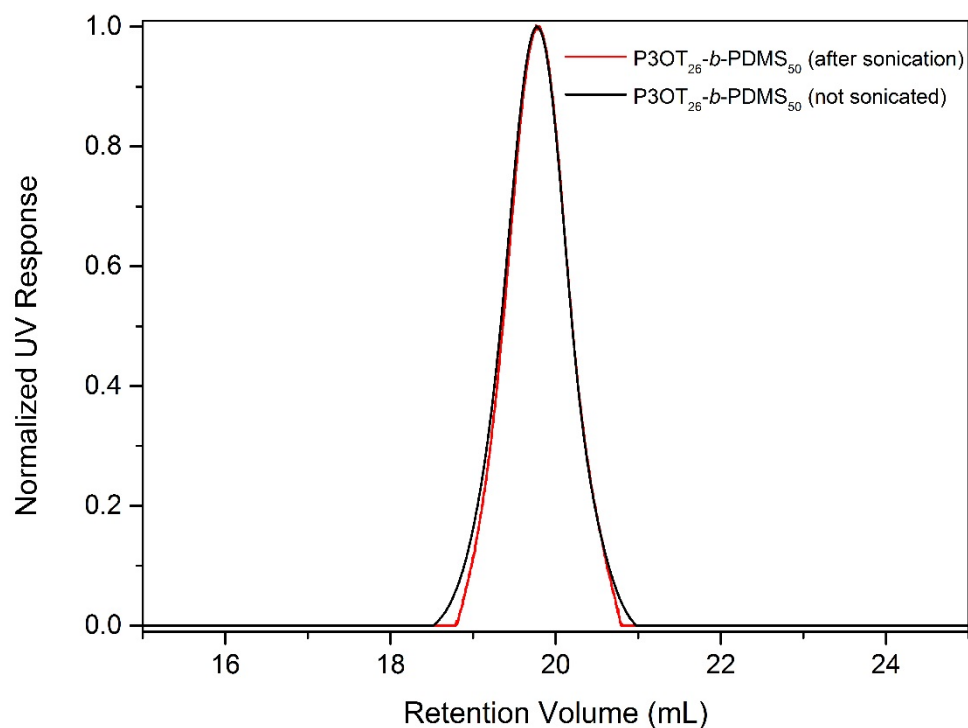


Figure S21. GPC traces (UV response, $\lambda = 440$ nm) of P3OT₂₆-*b*-PDMS₅₀ dissolved in THF relative to polystyrene standards. Red: P3OT₂₆-*b*-PDMS₅₀ seed micelles were re-dissolved in THF after vigorous sonication at 0°C for 4 h. Black: Reference GPC trace of the same diblock copolymer which was not used for crystallization and sonication experiments.

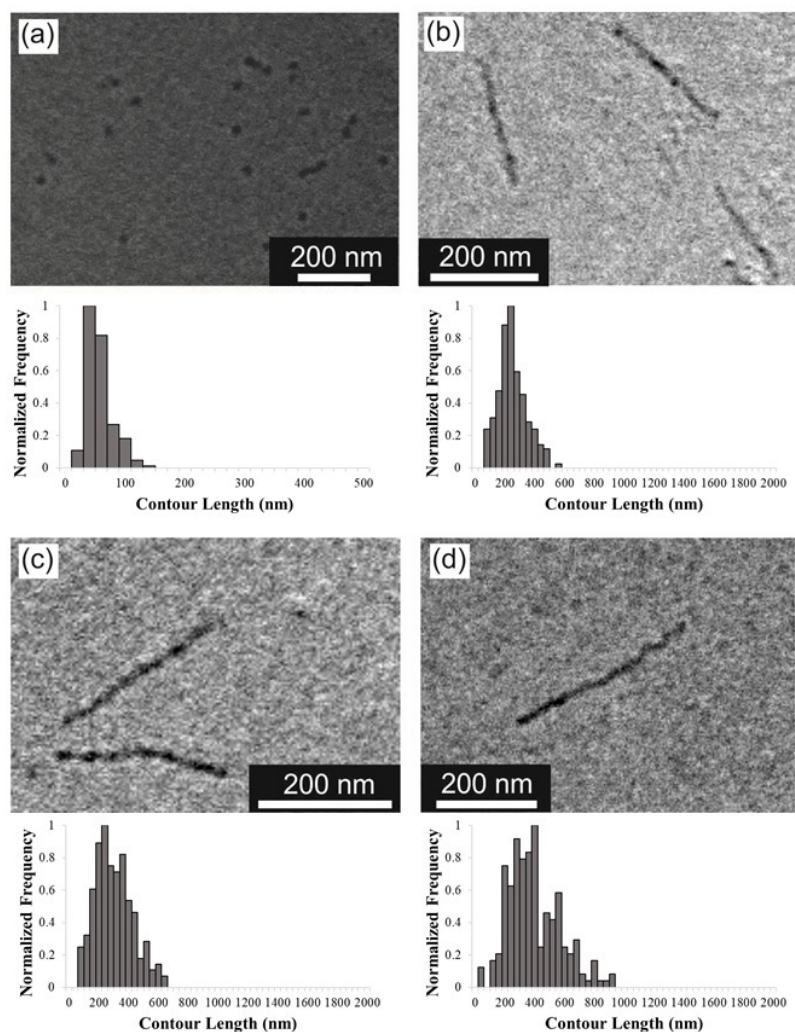


Figure S22. (a) TEM micrograph and corresponding histogram of P3OT₂₆-*b*-PDMS₅₀ seed micelles prepared by adding small amounts of unimer as a 10 mg mL⁻¹ THF solution to an excess of decane at a temperature of 0°C. TEM micrographs and histograms for the P3OT₂₆-*b*-PDMS₅₀ fiber-like micelles which were obtained from adding P3OT₂₆-*b*-PDMS₅₀ unimer in THF to P3OT₂₆-*b*-PDMS₅₀ seed micelles, prepared without the use of sonication (see a), in decane (b) or in a decane/THF solvent mixture with THF fractions of 6% (c) and 9% (d) at 22°C. For all seeded growth experiments the unimer-to-seed mass ratio was 10.

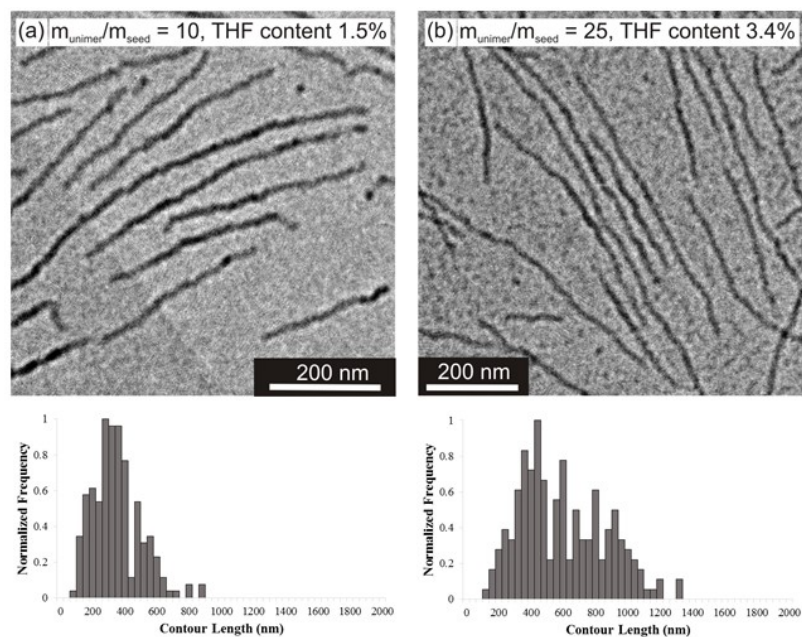


Figure S23. TEM micrographs and corresponding histograms for the P3OT₂₆-*b*-PDMS₅₀ fiber-like micelles which were obtained from adding 60 μg (a), and 150 μg (b) P3OT₂₆-*b*-PDMS₅₀ unimer to 6 μg of P3OT₂₆-*b*-PDMS₅₀ seed micelles in decane at 35°C.

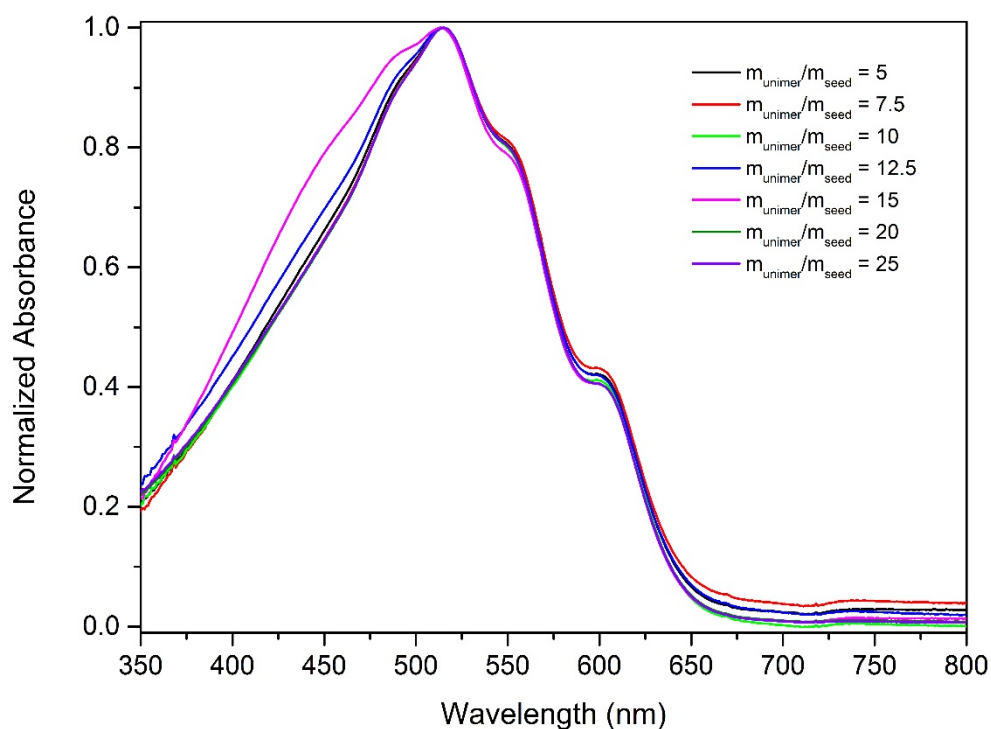


Figure S24. UV/vis spectra of P3OT₂₆-*b*-PDMS₅₀ micelle solutions obtained from adding the respective amount of P3OT₂₆-*b*-PDMS₅₀ unimer to 6 μg of P3OT₂₆-*b*-PDMS₅₀ seed micelles in decane at 35°C, micelles aged at 35°C for two days.

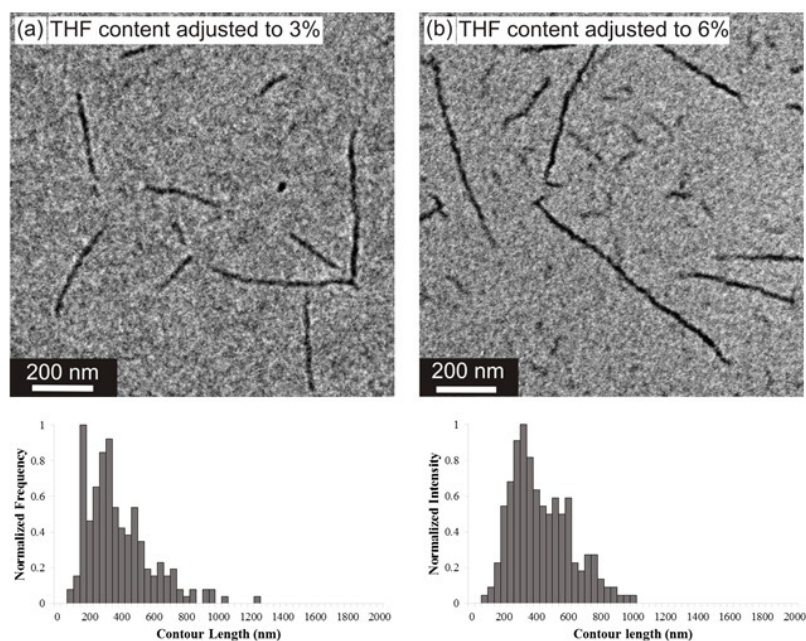


Figure S25. TEM micrographs and corresponding histograms for the fiber-like P3OT₂₆-*b*-PDMS₅₀ micelles which were obtained from adding 60 μ g P3OT₂₆-*b*-PDMS₅₀ unimer to 6 μ g of P3OT₂₆-*b*-PDMS₅₀ seed micelles in a decane/THF solvent mixture with final THF fractions of 3% (a) and 6% (b) at 35°C.

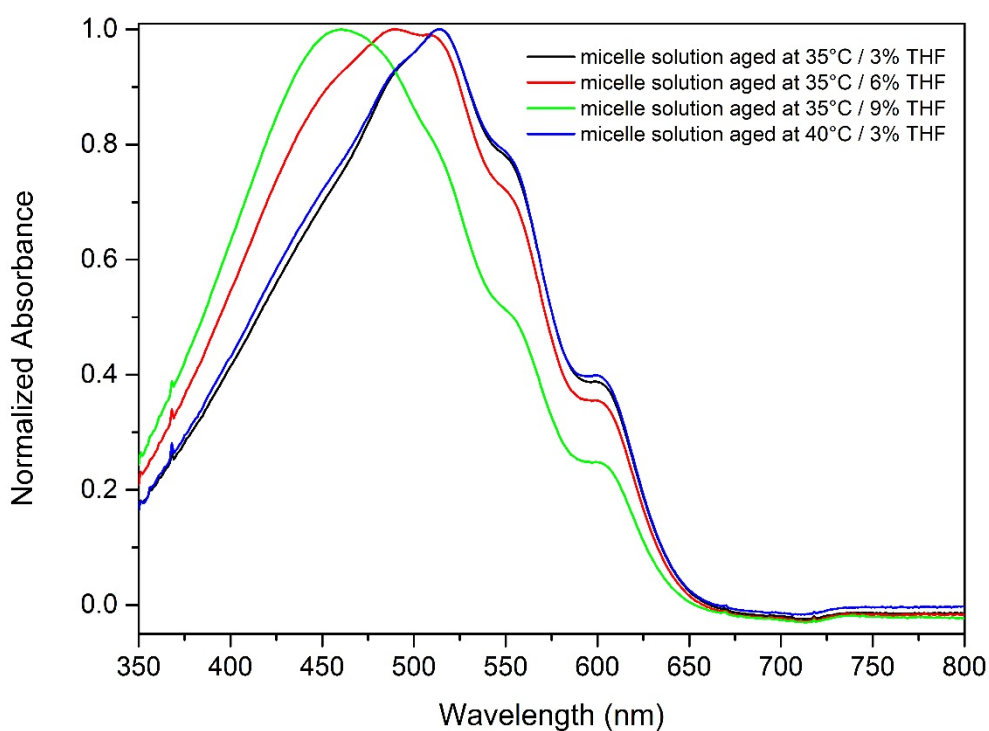


Figure S26. UV/vis spectra of P3OT₂₆-*b*-PDMS₅₀ micelle solutions obtained from adding 60 μ g P3OT₂₆-*b*-PDMS₅₀ unimer to 6 μ g of P3OT₂₆-*b*-PDMS₅₀ seed micelles in a decane/THF solvent mixture with final THF fractions of 3%, 6%, and 9% at 35°C or 40°C, micelles aged at the respective temperature for two days.

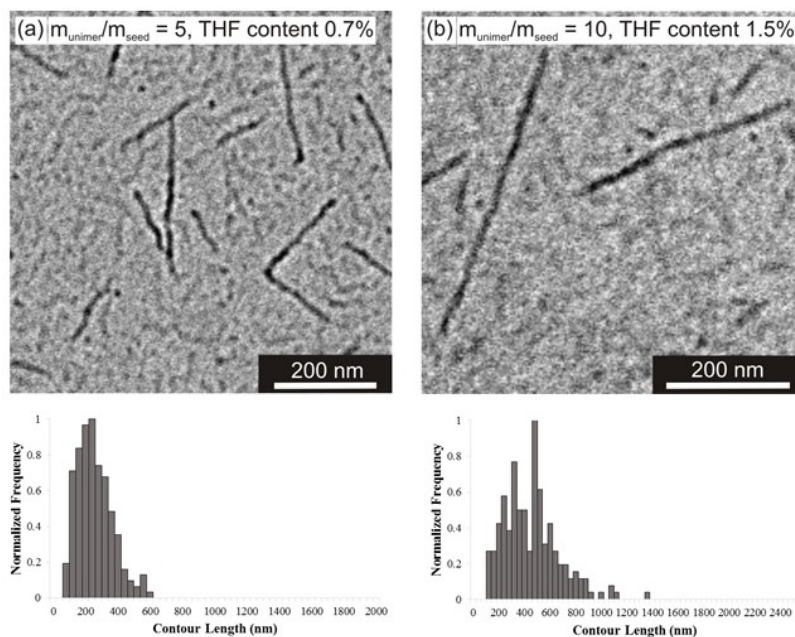


Figure S27. TEM micrographs for the fiber-like P3OT₂₆-*b*-PDMS₅₀ micelles which were obtained from adding 30 μ g (a) and 60 μ g (b) P3OT₂₆-*b*-PDMS₅₀ unimer to 6 μ g of P3OT₂₆-*b*-PDMS₅₀ seed micelles in decane at 40°C. For discussion see page S10/11.

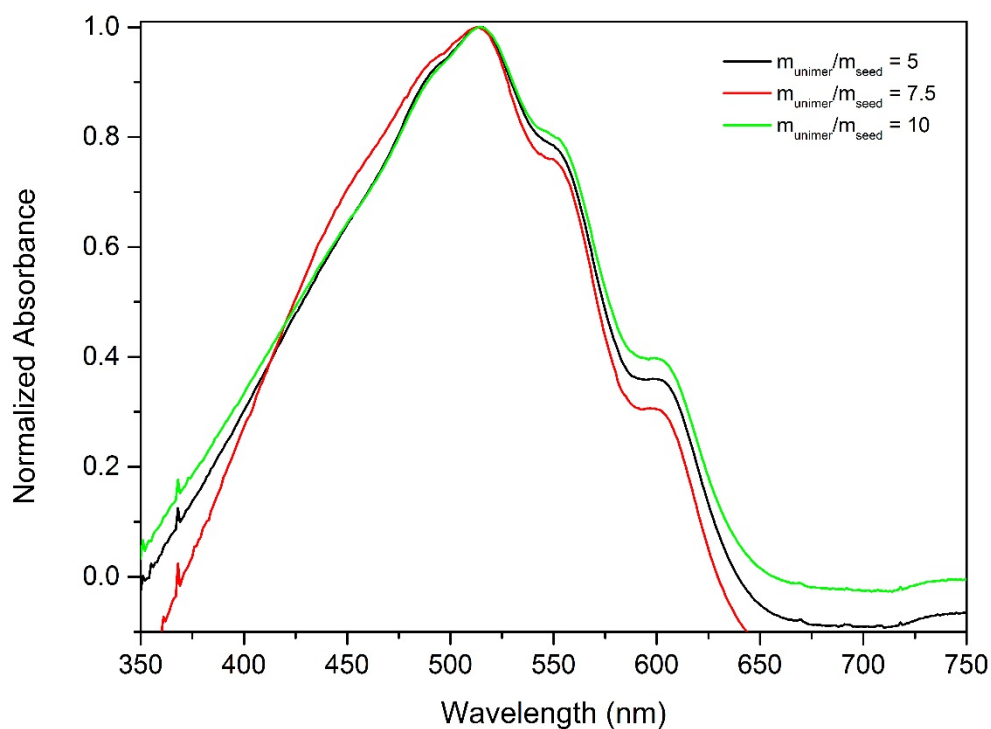


Figure S28. UV/vis spectra of P3OT₂₆-*b*-PDMS₅₀ micelle solutions obtained from adding the respective amount of P3OT₂₆-*b*-PDMS₅₀ unimer to 6 μ g of P3OT₂₆-*b*-PDMS₅₀ seed micelles in decane at 40°C, micelles aged at 40°C for two days. For discussion see page S10/11.

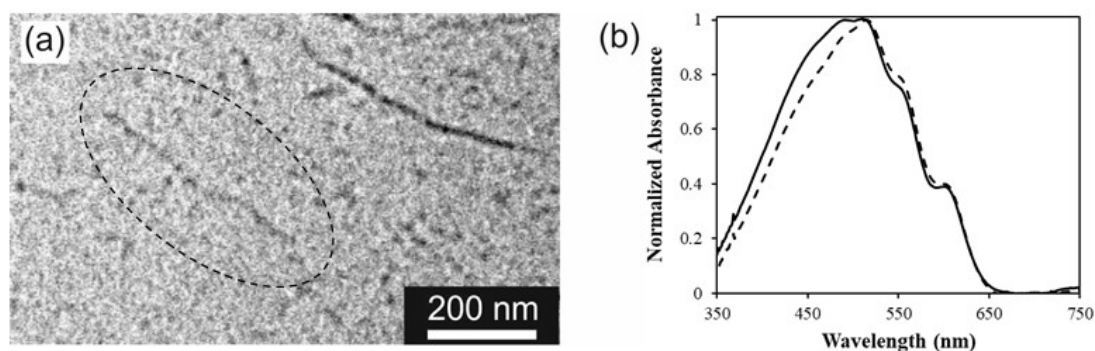


Figure S29. (a) TEM micrograph for the fiber-like P3OT₂₆-*b*-PDMS₅₀ micelles which were obtained from adding 60 μ g P3OT₂₆-*b*-PDMS₅₀ unimer to 6 μ g of P3OT₂₆-*b*-PDMS₅₀ seed micelles in a decane/THF solvent mixture with final THF fractions of 6% at 40°C. The contour of some micelles incorporated in higher amounts of unimer film became blurred (circled micelle). (b) UV/vis spectra of P3OT₂₆-*b*-PDMS₅₀ micelle solutions obtained from adding 60 μ g P3OT₂₆-*b*-PDMS₅₀ unimer to 6 μ g of P3OT₂₆-*b*-PDMS₅₀ seed micelles in a decane/THF solvent mixture with a final THF fraction of 6% at 22°C (dotted line) and 40°C (solid line). Micelles were aged at the respective temperature for two days. An increased amount of unimer was detected for micelle solutions which were aged at an elevated temperature of 40°C in the presence of an increased THF fraction. For discussion see page S10/11.

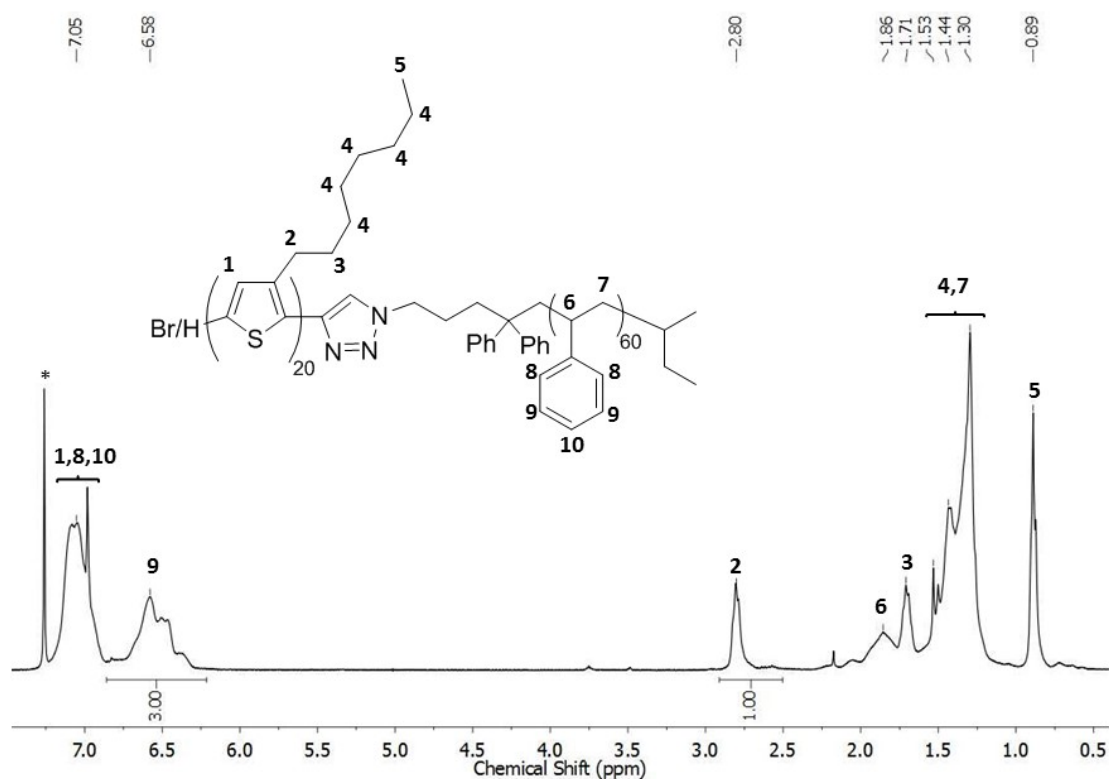


Figure S30. ¹H NMR spectrum of P3OT₂₀-*b*-PS₆₀ in CDCl₃. The asterisk denotes residual protonated solvent signal.

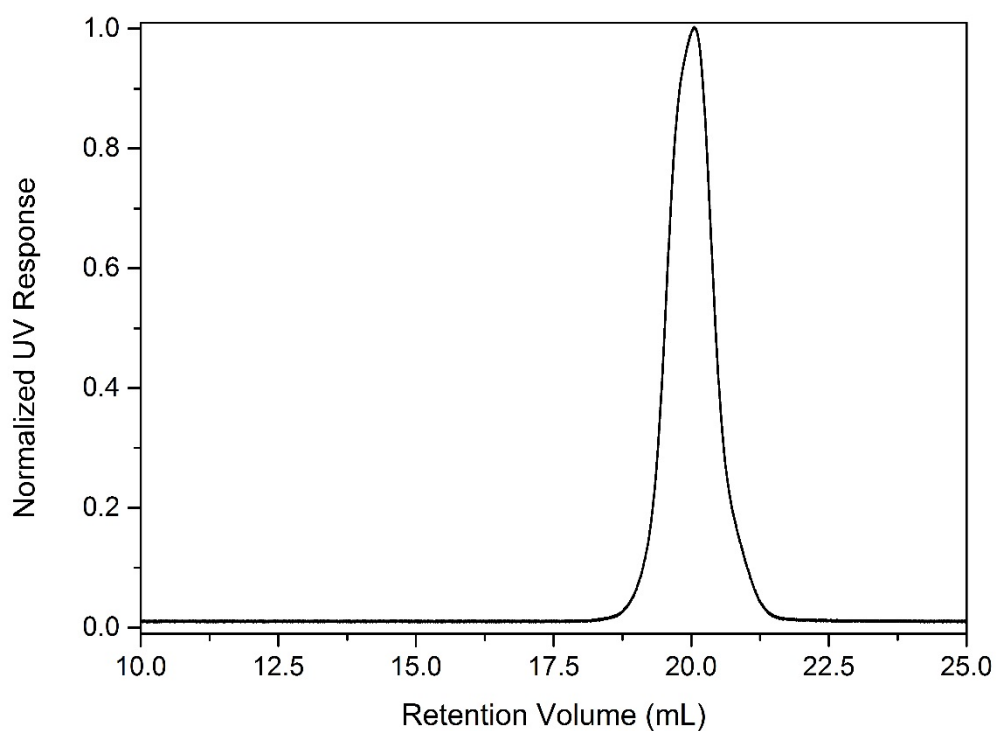


Figure S31. GPC trace (UV response, $\lambda = 440$ nm) of P3OT₂₀-*b*-PS₆₀ dissolved in THF relative to polystyrene standards.

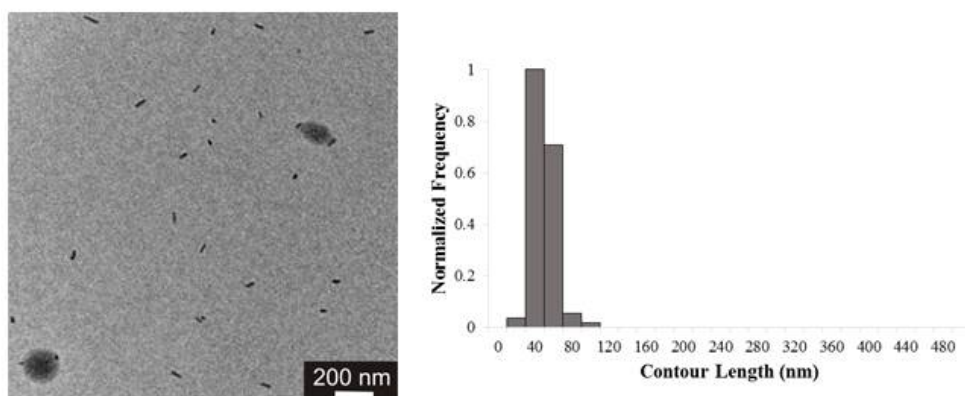


Figure S32. TEM micrograph and corresponding histogram of P3OT₂₀-*b*-PS₆₀ seed micelles obtained by sonication of multi-micron-long micelles at 0°C for 4 h. For TEM imaging, fibers were dispersed by PS₆₀ homopolymer to avoid severe agglomeration. The dark, spherical regions are aggregates of PS.

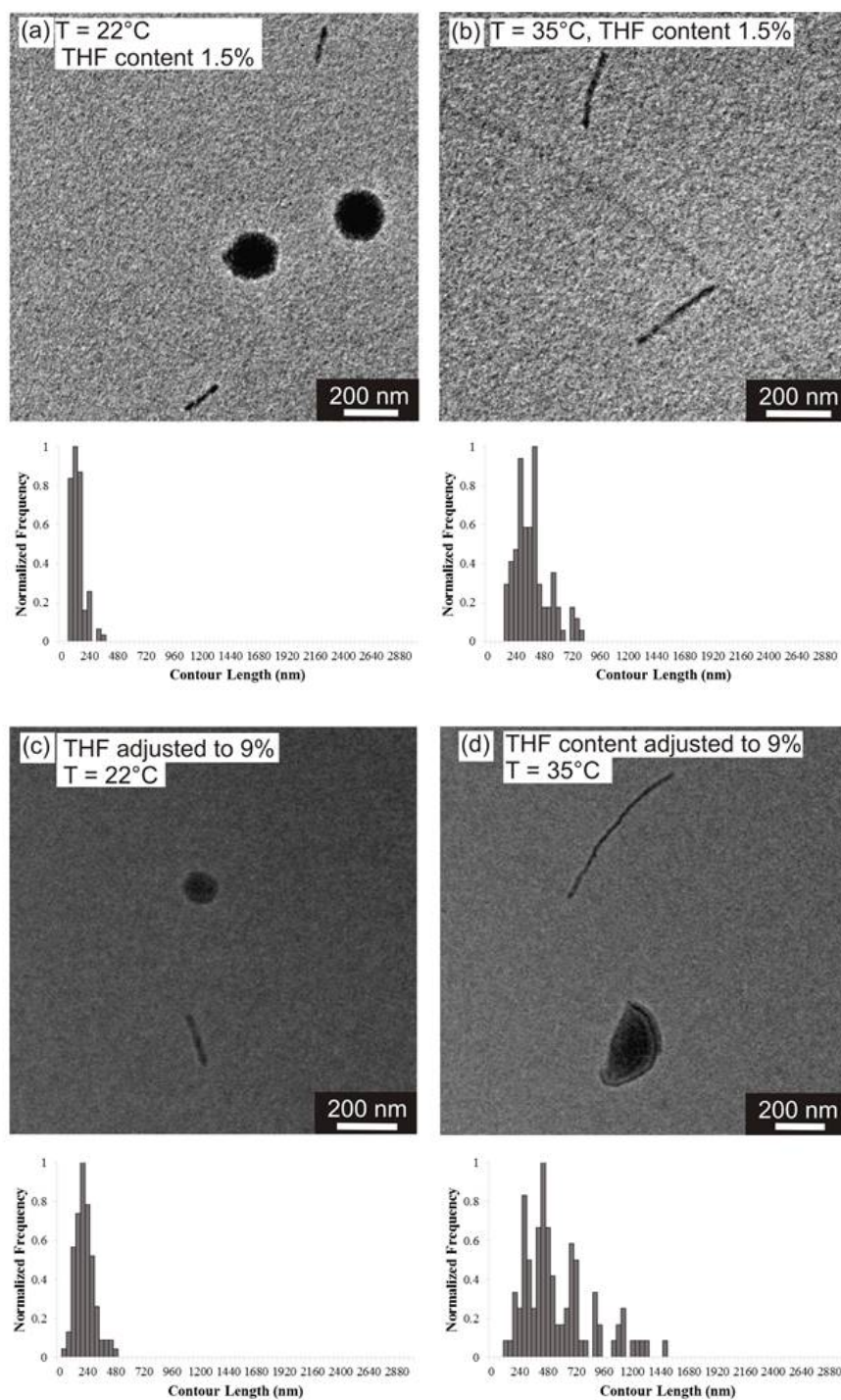


Figure S33. TEM micrographs of P3OT₂₀-*b*-PS₆₀ micelles obtained from adding 60 μ g unimer to 6 μ g of seed micelles in butyl acetate at 22°C (a) and 35°C (b) or a butyl acetate/THF solvent mixture with final THF fractions of 9% at 22°C (c) and 35°C (d). Micelles were aged at the respective temperature for two days. For TEM imaging, fibers were dispersed by PS₆₀ homopolymer to avoid severe agglomeration. The dark, spherical regions are aggregates of PS.

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