

Supporting Information

Uniform, High Aspect Ratio Fiber-like Micelles and Block Co-Micelles with a Crystalline π -Conjugated Polythiophene Core by Self-Seeding

Jieshu Qian,¹ Xiaoyu Li,¹ David J. Lunn,¹ Jessica Gwyther,¹ Zachary M. Hudson,¹

Emily Kynaston,¹ Paul A. Rugar,^{1,3} Mitchell A. Winnik,^{*2} and Ian Manners^{*1}

Experimental

Materials. In general polymer synthesis, Tetrahydrofuran (THF) was purified by using double alumina and alumina/copper catalyst drying columns from Anhydrous Engineering Inc. before use. For anionic polymerization, cyclohexane was distilled from CaH_2 and THF was distilled from sodium benzophenone prior to use. 2,5-Dibromo-3-hexylthiophene, *tert*-butyl-magnesium chloride (1.0 M in THF), [(1,3-diphenylphosphino)propane]-dichloronickel $[\text{Ni}(\text{dppp})\text{Cl}_2]$, ethynylmagnesium chloride (0.5 M in THF), pentamethyldiethylenetriamine (PMDETA), copper(I) bromide, *sec*-butyllithium (1.4 M in hexanes), *n*-butyllithium (1,6 M in hexanes), sodium azide, and *n*-butyl acetate (BuAc, anhydrous, > 99 %) were purchased from Sigma-Aldrich and used without further purification. 1,1-diphenylethylene (DPE) and 1,3-dibromopropane (DBP) were purchased from Sigma-Aldrich and dried and purified before use. For anionic polymerization of styrene, styrene monomer (> 99 %, Sigma-Aldrich) was dried over CaH_2 and purified by distillation under reduced pressure.

Instrumentation. ^1H NMR spectra were recorded using a Varian 500 MHz instrument with chemical shifts referenced to tetramethylsilane (TMS) in CDCl_3 .

Gel permeation chromatography (GPC) measurements were carried out on a Viscotek GPCmax equipment with a UV detector at 450 nm and refractometer. A flow rate of 1.0 mL/min was used with THF as the eluent at 35 °C. Calibration was performed with polystyrene standards (Viscotek).

UV-vis data were acquired from a Lambda 35 spectrometer using standard quartz cells from wavelength of 300 nm to 700 nm.

Fluorescence data were obtained from a Perkin Elmer LS 45 Fluorescence Spectrometer.

Confocal fluorescence images were taken using a Leica SP5 system attached to a Leica DMI6000 inverted epifluorescence microscope and equipped with an Argon laser operating at 488 nm. A 63×(NA 1.4) oil immersion objective was used and parameters selected to optimize resolution. A Micelle concentration of 0.03 mg/mL was used for imaging experiments.

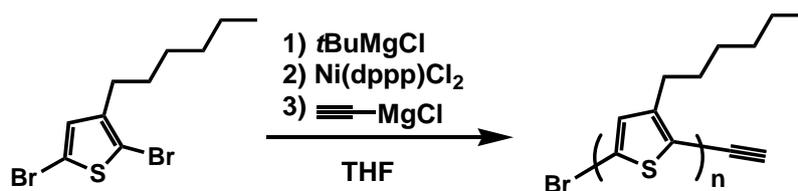
Transmission electron microscopy (TEM) images were taken using a JEOL JEM 1200 EX microscope operating at 120 kV. Micelle length distributions were determined using the software program ImageJ from the U.S. National Institutes of Health. For each sample, ca. 100 micelles in several images were traced by hand in order to obtain the length information. The number average micelle length (L_n) and weight average micelle length (L_w) were calculated using eq. S1 from measurements of the contour lengths (L_i) of individual micelles, where N_i is the number of micelles of length L_i , and n is the number of micelles examined in each sample.

$$L_n = \frac{\sum_{i=1}^n N_i L_i}{\sum_{i=1}^n N_i} \quad L_w = \frac{\sum_{i=1}^n N_i L_i^2}{\sum_{i=1}^n N_i L_i} \quad (\text{S1})$$

The distribution of micelle lengths is characterized by both L_w/L_n and the ratio σ/L_n , where σ is the standard deviation of the length distribution.

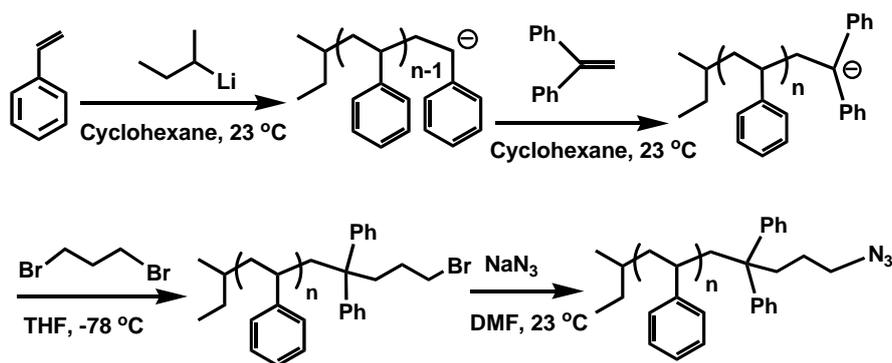
Polymer synthesis.

Synthesis of alkyne-terminated P3HT₃₄. The synthesis of regioregular P3HT was carried out using standard Schlenk technique to ensure oxygen and water-free environment. We used the Grignard metathesis method for the synthesis of P3HT, as reported previously.¹ The alkyne end group was introduced by using a second Grignard reagent, ethynylmagnesium chloride, to quench the polymerization, resulting in the *in situ* end-capping of the living chain ends. The synthetic procedure of P3HT is shown in Scheme S1. In a three-neck round-bottom flask, 2,5-dibromo-3-hexylthiophene (5.0 g, 15.3 mmol) was dissolved in 150 mL THF and stirred at 23 °C under N₂. *tert*-Butylmagnesium chloride (15.3 mL, 1.0 M in THF) was added to the flask, and the mixture was stirred at 23 °C under N₂ for 2 h. Ni(dppp)Cl₂ (130 mg, 0.24 mmol) was then added into the reaction mixture as one portion. The mixture was stirred for 8 min at 23 °C, followed by adding ethynylmagnesium chloride (2.5 mL, 0.5 M in THF) via syringe. The mixture was stirred at 23 °C for additional 6 min and then poured into methanol to precipitate the product. The polymer product was then transferred into an extraction thimble and washed by Soxhlet extraction with methanol, hexanes, and chloroform. A purple polymer powder (1.2 g, yield = 24 %) was obtained from drying the chloroform fraction. From the ¹H NMR spectra of the product as shown in Figure S1, the degree of polymerization was estimated to be 34.



Scheme S1. Synthesis of alkyne-terminated P3HT ($n = 34$).

Synthesis of azide-terminated PS₁₇₅. The synthetic procedure of azide-terminated PS₁₇₅ is shown in Scheme S2.



Scheme S2. Synthesis of azide-terminated PS ($n = 175$).

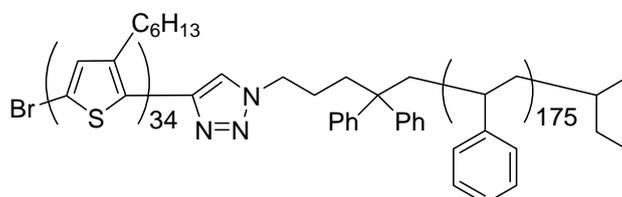
Synthesis of bromo-terminated PS₁₇₅. Polystyrene was synthesized using an anionic polymerization method inside a glovebox. Styrene monomer (1.56 g, 15 mmol) was added into cyclohexane (6 mL) and stirred in a 28 mL vial. *sec*-Butyllithium (93 μL , 1.4 M in hexanes) was added into the reaction and the mixture was stirred in 23 °C for 1 h. The solution was diluted with 6 mL THF. Five minutes later, DPE (24 μL , 0.14 mmol) was added into the reaction and the solution was then cooled to -78 °C. Ten minutes later, the living PS solution was added dropwise to a solution of excess DBP (210 μL , 2 mmol) in THF (6 mL) at -78 °C to quench the polymerization. The polymer was removed from the glovebox, precipitated into methanol, and dried overnight at 40 °C in a vacuum oven (1.26 g, yield = 81 %). Bromo-terminated polystyrene with $M_n = 18,610$ g/mol and PDI = 1.07 (GPC) was obtained, the degree

of polymerization of which was calculated to be 175. In another batch of anionic polymerization, polystyrene with $M_n = 90,320$ g/mol and PDI = 1.10 (GPC) was synthesized, the degree of polymerization of which was calculated to be 865.

Synthesis of azide-terminated PS₁₇₅-N₃. Sample PS₁₇₅-Br (1.13 g, 60 μ mol) was dissolved in dimethylformamide (DMF, 10 mL) with sodium azide (26 mg, 0.4 mmol) added. The reaction was allowed to stir overnight at 23 °C. The product was precipitated into methanol and dried overnight at 40 °C in a vacuum oven (1.02 g, yield = 91 %). The ¹H NMR spectra of this sample is shown in Figure S2

Synthesis and characterization of P3HT₃₄-*b*-PS₁₇₅. The alkyne-P3HT₃₄ (48 mg, 8 μ mol), PS₁₇₅-N₃ (200 mg, 11 μ mol), and PMDETA (23 μ L, 11 μ mol) was dissolved in THF (10 mL) in a Schlenk tube equipped with a magnetic stir bar. After three cycles of freeze-pump-thaw, the solution was moved into a glovebox. A small spatula of CuBr was then added into the reaction and the solution was allowed to stir for 48 h at 40 °C. Cu/PMDETA was removed by passing the solution through an alumina column. In order to remove possible unreacted PS homopolymer, the polymer was precipitated by dropping into acetone and dried overnight at 40 °C in a vacuum oven. In order to remove unreacted P3HT homopolymer, the product was dissolved in THF and purified by passing through a size exclusion chromatography column three times. The ¹H NMR spectra of the final product (40 mg, yield = 25 %) is shown in Figure S3, from which the block ratio of the P3HT₃₄-*b*-PS₁₇₅ was estimated to be 1:5. The number-averaged molecule weight of the P3HT₃₄-*b*-PS₁₇₅ was estimated to be $M_n = 24,300$ g/mol. From the GPC analysis relative to polystyrene standards, the

P3HT₃₄-*b*-PS₁₇₅ sample possessed PDI = 1.05. The GPC traces of the P3HT₃₄-*b*-PS₁₇₅ block copolymer with its homopolymer precursors are shown in Figure S4. The chemical structure of the P3HT₃₄-*b*-PS₁₇₅ block copolymer is presented in Scheme S3.



Scheme S3. Chemical structure of the P3HT₃₄-*b*-PS₁₇₅ diblock copolymer.

Synthesis of azide-terminated PDMS₂₃₆. Azide-terminated PDMS was synthesized following the same procedures as reported previously.² In a glove box under an argon atmosphere, 1.6 M n-butyllithium (37.5 μ L, 0.06 mmol) was added into a solution of hexamethylcyclotrisiloxane (0.89 g, 4.00 mmol) in dry THF (5 mL), and allowed to stirred at 23 °C for 2 h. The reaction mixture was removed from the glove box and set up under a nitrogen atmosphere and quenched with a 5-fold excess of (bromomethyl)chlorodimethylsilane. The solution was precipitated into a vigorously stirring mixture of methanol (100 mL) and triethylamine (10 mL), and centrifuged to isolate the crude polymer. The product was precipitated twice more in methanol and dried overnight at 40 °C in a vacuum oven to afford bromide-terminated PDMS as a colorless viscous liquid. To a solution of bromide-terminated PDMS (0.4 g) in THF (5 mL) was added sodium azide (15 mg, 0.23 mmol) and tetrabutylammonium bromide (75 mg, 0.23 mmol). The resulting mixture was sealed in a vial and heated at 40 °C with stirring for 24 h. The reaction mixture was precipitated three times in methanol, collected via centrifugation and dried at 40 °C in a vacuum oven to afford azide-terminated PDMS as a colorless viscous liquid (0.79 g, yield = 89 %, see GPC

trace in Figure S5). The azide-terminated PDMS has $M_n = 17,600$ g/mol and PDI = 1.1, relative to PS standard, the degree of polymerization of the polymer was calculated to be 236.

Synthesis and characterization of P3HT₃₄-*b*-PDMS₂₃₆. The alkyne-P3HT₃₄ (12 mg, 2 μ mol), PDMS₂₃₆-N₃ (35 mg, 2 μ mol), and PMDETA (4 μ L, 2 μ mol) was dissolved in THF (5 mL) in a Schlenk tube equipped with a magnetic stir bar. After three cycles of freeze-pump-thaw, the solution was moved into a glovebox. A small spatula amount of CuBr was then added into the reaction and the solution was allowed to stir for 48 h at 40 °C. Cu/PMDETA was removed by passing the solution through an alumina column. In order to remove possible unreacted PDMS homopolymer, the polymer was precipitated by dropping methanol into the THF solution. The precipitate was collected and dried overnight at 40 °C in a vacuum oven. In order to remove unreacted P3HT homopolymer, the product was dissolved in THF and purified by passing through a size exclusion chromatography column three times. The ¹H NMR spectra of the final product (ca. 20 mg, yield = 43 %) is shown in Figure S6, from which the block ratio of the P3HT₃₄-*b*-PDMS₂₃₆ was estimated to be ca. 1:7.2. From the GPC analysis as shown in Figure S5, the number-averaged molecule weight of the P3HT₃₄-PDMS₂₃₆ was estimated to be $M_n = 25,100$ g/mol with PDI = 1.13 relative to polystyrene standards.

Self-assembly of P3HT₃₄-*b*-PS₁₇₅ in BuAc.

Formation of fiber-like micelles from the self-assembly of P3HT₃₄-*b*-PS₁₇₅.

A mixture of P3HT₃₄-*b*-PS₁₇₅ polymer (3.0 mg) and BuAc (10.0 mL, $c = 0.30$ mg/mL) was heated to 100 °C in an oil bath on top of a hotplate for 2 h, followed by cooling to 23 °C slowly (ca. 1.5 °C/min). The temperature of the oil bath was controlled by a IKATRON ETS-D5 (Germany) thermometer with a temperature fluctuation of 0.1 °C. One day later, sample for TEM measurement was prepared by drop casting a drop of the solution onto a carbon-coated copper grid, which was placed on a filter paper to remove excess solvent. However, we observed a problem of sample aggregation on carbon film. Thus, we modified slightly the sample preparation for TEM analysis. For all samples containing only P3HT-PS block copolymer that are described in this paper, a drop of the sample solution was mixed with another drop of BuAc solution containing the PS₈₆₅ homopolymer ($c = 1$ mg/mL), followed by drop casting onto a carbon-coated copper grid. In order to obtain micelle fragments, the solution was placed in a water bath of a 160 watt ultrasonic cleaning apparatus (BANDELIN, Germany) and sonicated at 23 °C for two 15 min intervals.

Temperature-induced self-seeding of P3HT₃₄-*b*-PS₁₇₅. Eight equivalent batches (300 μL) of the BuAc solutions containing P3HT₃₄-*b*-PS₁₇₅ micelle fragments were transferred into new vials. These solutions were annealed in an oil bath at various temperatures. After 30 min, each solution was quenched into another oil bath at 35 °C and allowed to age at 35 °C for 24 h. Afterwards, these samples were allowed to age at 23 °C for at least 24 h before grids for TEM measurements were prepared.

Solvent-induced self-seeding of P3HT₃₄-*b*-PS₁₇₅. Eight equivalent batches (500 μ L) of the BuAc solutions containing P3HT₃₄-*b*-PS₁₇₅ micelle fragments were transferred into new vials, followed by the addition of different amounts of THF, 200, 250, 300, 350, 400, 500, 600, and 800 μ L. Two hours after the addition of THF, the caps of these vials were removed to let the THF evaporate slowly. Two days later, samples were examined by TEM by drop casting an aliquot of each of the solutions onto TEM grids.

Preparation of triblock co-micelles. Uniform P3HT₃₄-*b*-PS₁₇₅ micelle sample generated from the self-seeding process was used as the precursor for the preparation of triblock co-micelles. Specifically, we used the P3HT₃₄-*b*-PS₁₇₅ micelles obtained by annealing the micelle fragments in BuAc (0.3 mg/mL) at 60 °C for 30 min, followed by annealing at 35 °C for 24 h and cooling to 23 °C. The solution was diluted by BuAc to 0.05 mg/mL. To the BuAc solution of P3HT₃₄-*b*-PS₁₇₅ (0.50 mL, 0.05 mg/mL) was added the THF solution of P3HT₃₄-*b*-PDMS₂₃₆ (0.25 mL, 0.8 mg/mL). The vial containing the solution was allowed to age at 23 °C in air without a cap in order to let the THF evaporate slowly for at least 24 h. Aliquots of the solution were then taken for TEM measurements. The copper grid for TEM measurements was exposed to RuO₄ vapor for 2 h.

Supporting Figures and Tables and Additional Discussion

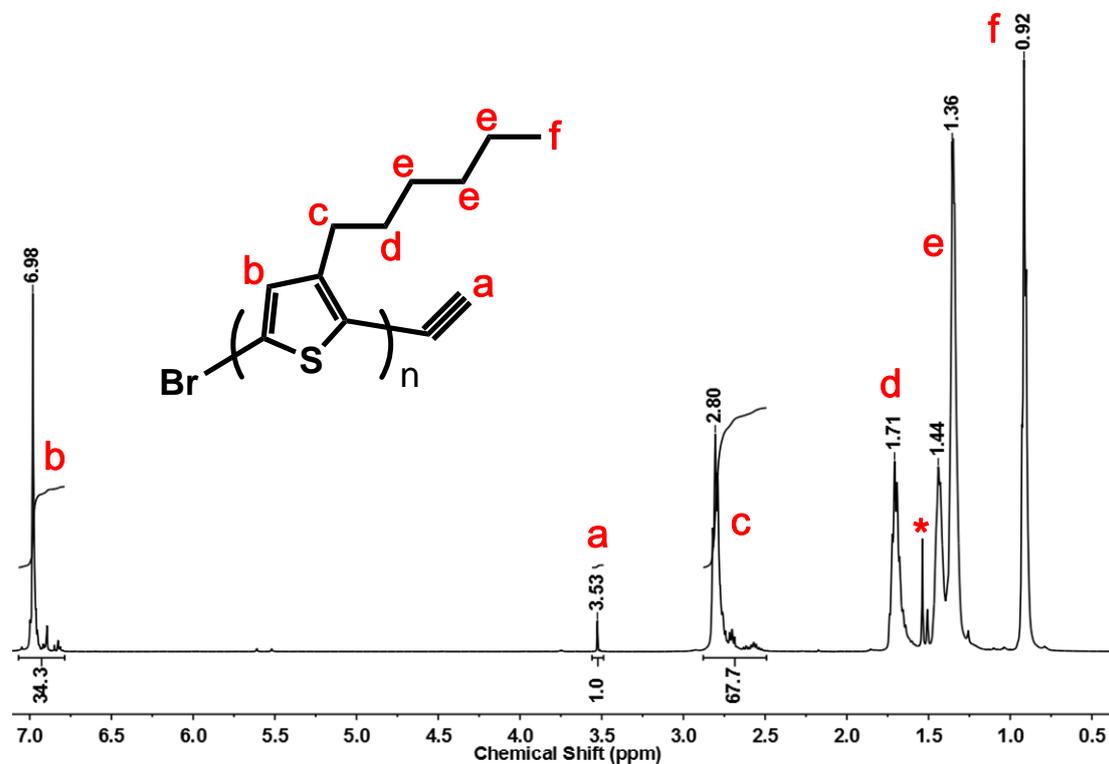


Figure S1. ¹H NMR spectrum of alkyne-P3HT₃₄ in CDCl₃/TMS. The asterisk denotes the proton signal from H₂O. By comparing the proton on the alkyne end (proton a, $\delta = 3.53$ ppm, integration of 1.0) to the proton on the thiophene ring (proton b, $\delta = 6.98$ ppm, integration of 34.3), the degree of polymerization of the polymer was estimated to be 34.

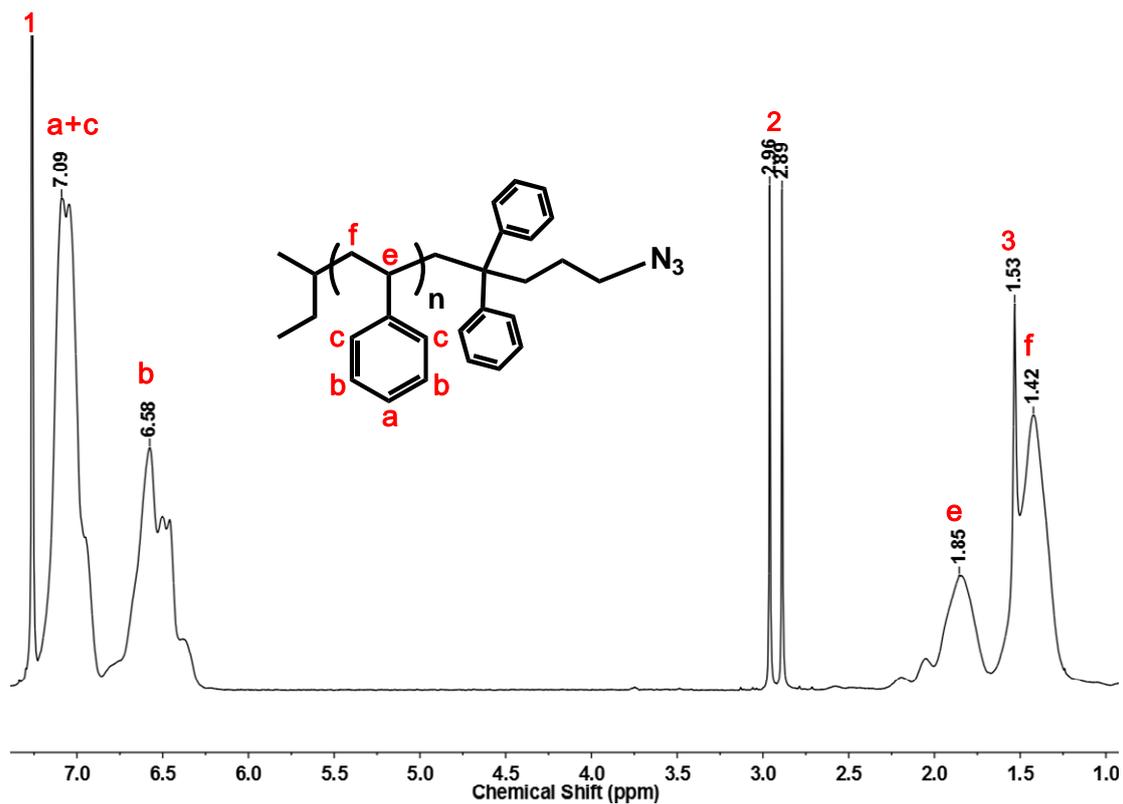


Figure S2. ¹H NMR spectrum of azide-PS₁₇₅ in CDCl₃/TMS. Peak 1 is proton signal from residual CHCl₃. Peaks 2 are proton signals from DMF. Peak 3 is proton signal from H₂O.

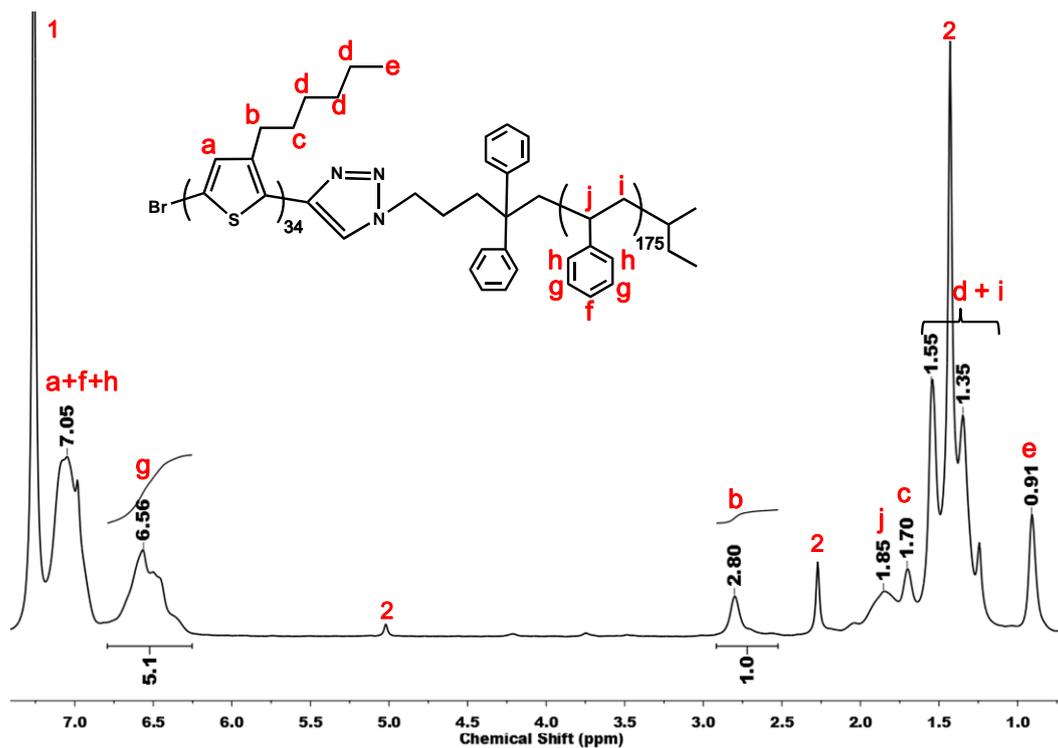


Figure S3. ^1H NMR spectrum of P3HT₃₄-*b*-PS₁₇₅ in CDCl₃/TMS. Peak 1 is proton signal from residual CHCl₃. Peaks 2 are proton signals from BHT. By comparing the hexyl protons in P3HT (protons b, $\delta = 2.80$ ppm, integration of 1.0) to the aromatic protons in PS (protons g, $\delta = 6.56$ ppm, integration of 5.1), the block ratio of P3HT to PS was estimated to be 1:5.

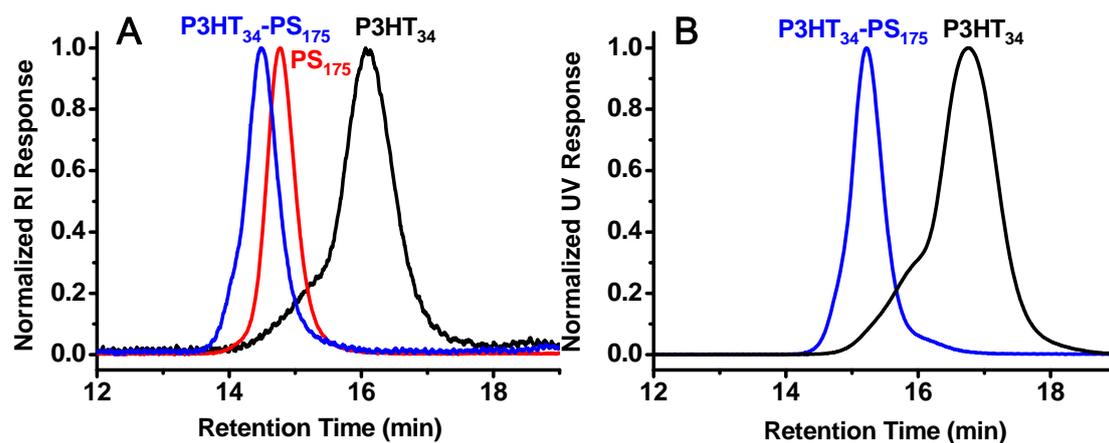


Figure S4. Normalized GPC (A) refractive index (RI) and (B) UV (450 nm) traces for P3HT₃₄ homopolymer (black), PS₁₇₅ homopolymer (red), and P3HT₃₄-PS₁₇₅ diblock copolymer (blue). The PDI of P3HT₃₄-*b*-PS₁₇₅ was calculated to be 1.05 relative to polystyrene standards.

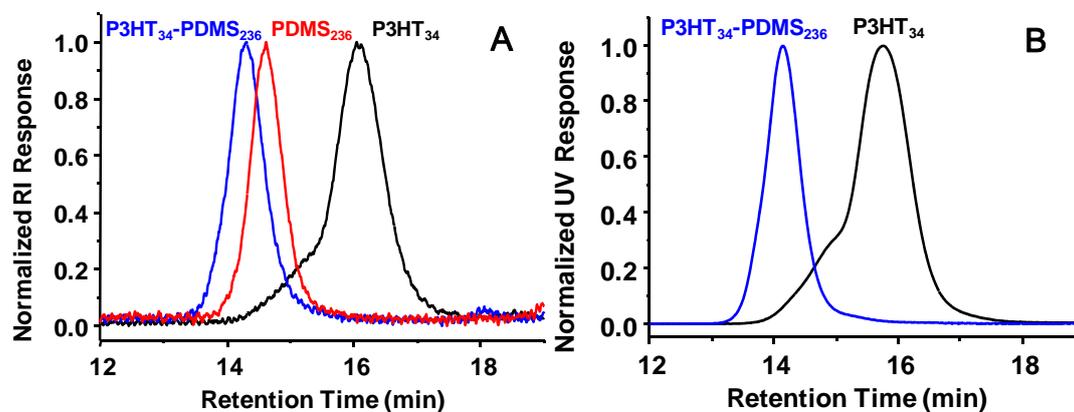


Figure S5. Normalized GPC (A) refractive index (RI) and (B) UV (450 nm) traces for P3HT₃₄ homopolymer (black), PDMS₂₃₆ homopolymer (red), and P3HT₃₄-*b*-PDMS₂₃₆ diblock copolymer (blue). The PDI of P3HT₃₄-*b*-PDMS₂₃₆ was calculated to be 1.13 relative to polystyrene standards.

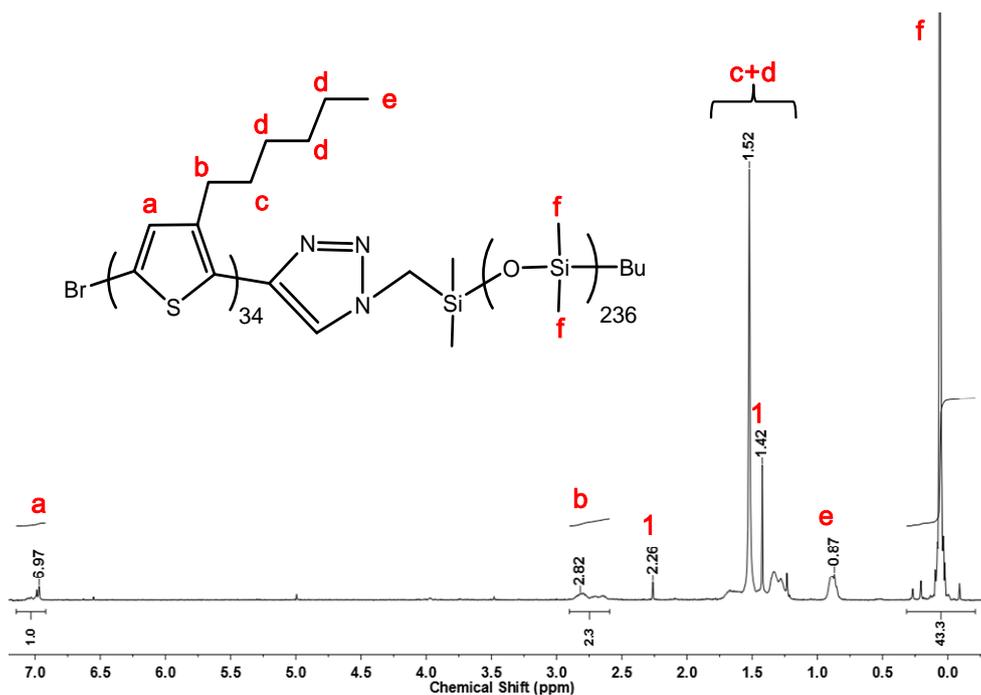


Figure S6. ¹H NMR spectrum of P3HT₃₄-b-PDMS₂₃₆ in CDCl₃/TMS. Peaks 1 are proton signals from BHT. By comparing the proton in P3HT (protons a, $\delta = 6.97$ ppm, integration of 1.0) to the methyl protons in PDMS (protons f, $\delta = 0.06$ ppm, integration of 43.3), the block ratio of P3HT to PDMS was estimated to be 1:7.2.

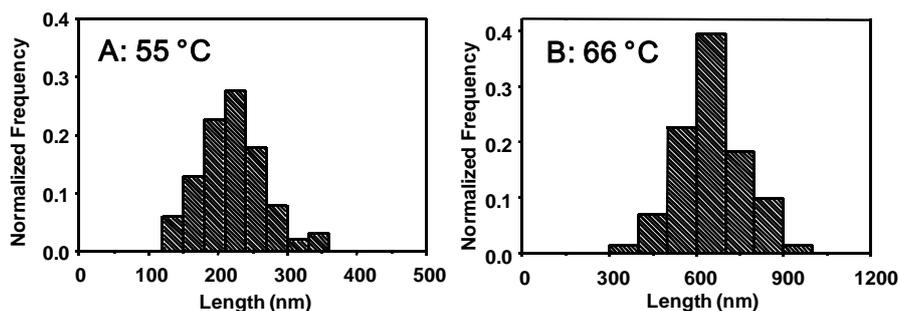


Figure S7. Histograms of length distribution of the P3HT-PS micelles obtained by annealing the micelle fragments in BuAc at (A) 55 and (B) 66 °C for 30 min, followed by annealing at 35 °C for 24 h and cooling to 23 °C. (A) $L_n = 224$ nm, $L_w = 235$ nm, $L_w/L_n = 1.05$, $\sigma/L_n = 0.228$. (B) $L_n = 656$ nm, $L_w = 673$ nm, $L_w/L_n = 1.03$, $\sigma/L_n = 0.163$.

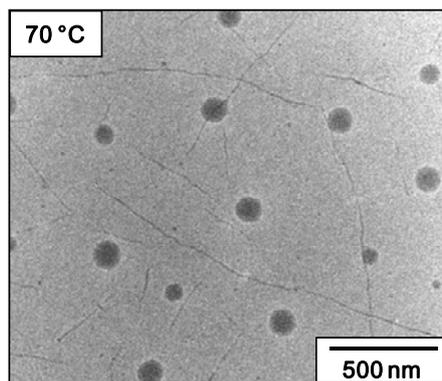


Figure S8. TEM image of the P3HT-PS micelles obtained by annealing the micelle fragments in BuAc at 70 °C for 30 min, followed by annealing at 35 °C for 24 h and cooling to 23 °C. Sample was prepared by drop casting aliquots of a mixture of the micelle solution (50 μ L) with BuAc containing PS homopolymer (50 μ L, $c = 1$ mg/mL) onto the carbon film of the copper grid.

Additional Discussion for Figure 2C in the Main Text.

In Figure 2C in the main text, we present a plot showing the average contour length vs. annealing temperature. This data illustrates that the length of the micelles increases with the annealing temperature, giving fibers up to values of ca. 700 nm with a narrow length distribution ($L_w/L_n < 1.05$).

Since the mass of polymer m in solution is constant, the length of micelles L_n is connected to the total number of micelles N by equation (S2), if we assume i) the concentration of free polymer chains at 23 °C is negligible, ii) the mass of polymer per unit length M_L remains constant.

$$L_n = (1/M_L)(m/N) \quad (\text{S2})$$

However for the first assumption, based on the photoluminescence data in Figure S12B, we could not rule out the possibility of the presence of unimers in the micelle solution. Nevertheless, we checked the micelle solutions that were subjected to the annealing treatment six months after the sample preparation and found only a slight

increase of the micelle length. For example, one day after sample preparation, micelles formed after the fragment solution was annealed at 60 °C were characterized by $L_n = 382$ nm and $L_w/L_n = 1.03$, these values changed to $L_n = 410$ nm and $L_w/L_n = 1.02$ six months after sample preparation. There was only ca. 7 % increase of the L_n value over a period of six months, while the length distribution remained narrow. These results suggest that the concentration of unimers in solution at 23 °C remained almost constant, having little effect on the length of micelles. Those unimers are no longer active for the micelle growth. Thus in Equation S2, the mass of polymer m should be represented by apparent mass of polymer m_{app} that can grow onto micelles, which remains constant.

Based on Equation S2, we could calculate the fraction of seeds that survived the annealing at each temperature by taking into account the initial length of the fragments and the final length after annealing. The results are summarized in Figure S9.

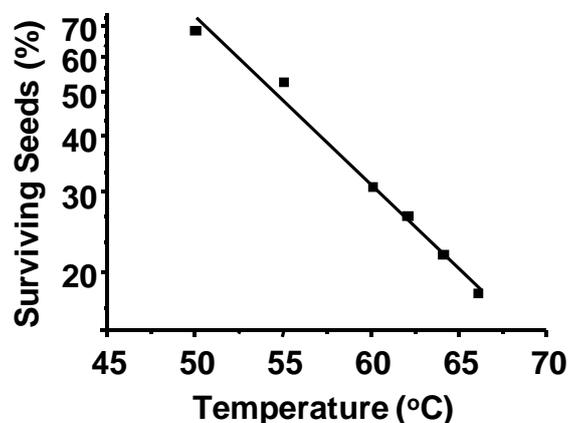


Figure S9. Semilogarithmic plot of percentage of surviving seeds vs. annealing temperature. Solid line represents the linear best fit for the data.

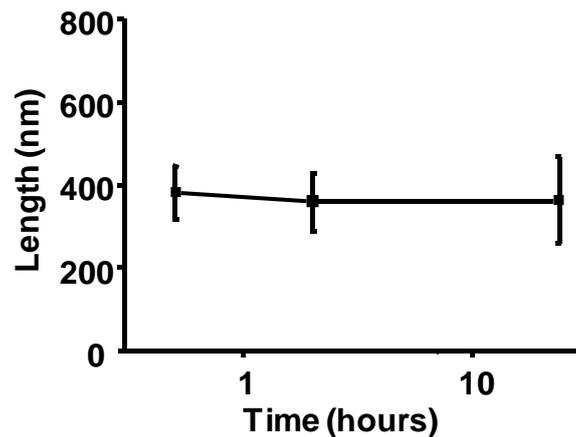


Figure S10. Time dependence of length L_n of the P3HT-PS micelles obtained by annealing the micelle fragments in BuAc at 60 °C, followed by annealing at 35 °C for 24 h and cooling to 23 °C. The error bars are the standard deviations σ in length for each sample. The solid line is a guide for the eye. The details of the length information of all the three samples are summarized in Table S2.

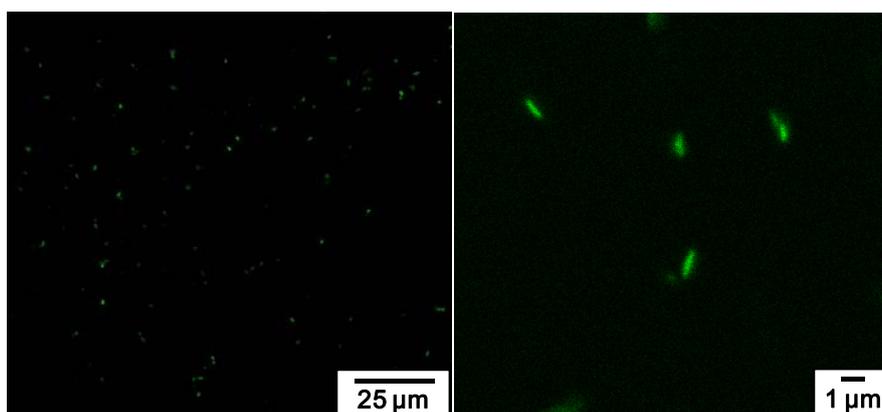


Figure S11. Confocal fluorescence images with different magnifications of the P3HT-PS micelles in BuAc (0.03 mg/mL) obtained by annealing the micelle fragments in BuAc at 66 °C for 30 min, followed by annealing at 35 °C for 24 h and cooling to 23 °C.

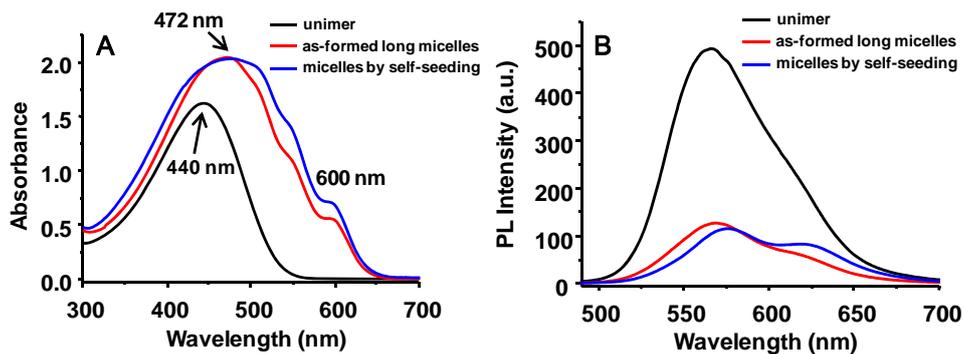


Figure S12. (A) UV/Vis spectra of P3HT-PS unimers (black line, 0.3 mg/mL in THF), as-formed long micelles (red line, 0.3 mg/mL) in BuAc, and micelles obtained by self-seeding (blue line, 0.3 mg/mL, annealing temperature: 60 °C). (B) Solution PL spectra (excited at 365 nm) of the corresponding samples in (A).

Additional Results and Discussion for Solvent-induced Self-seeding of

P3HT-*b*-PS Block Copolymer.

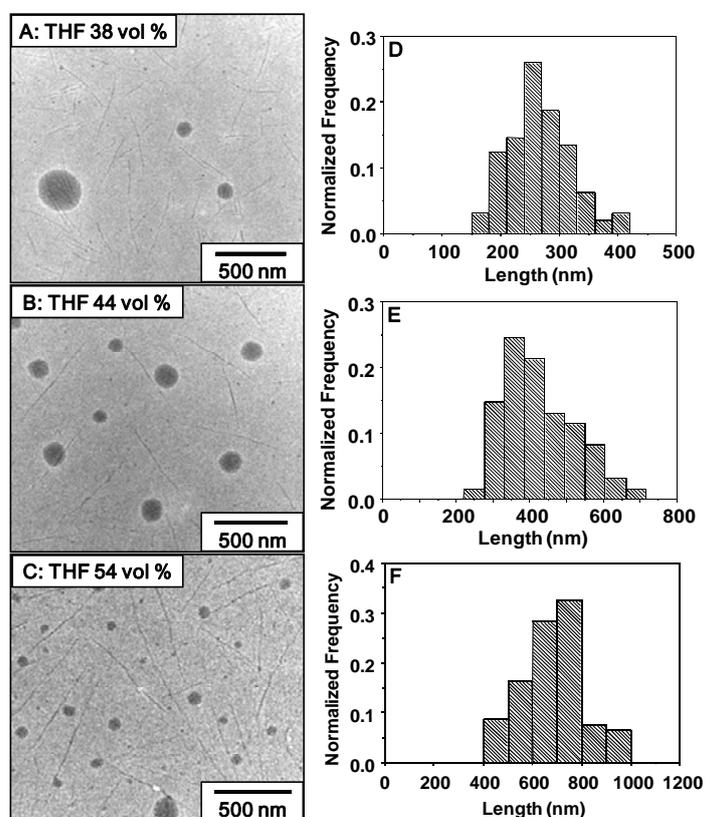


Figure S13. (A-C) TEM images and (D-F) the corresponding length distribution histograms of the P3HT-PS micelles obtained by adding various amounts of THF into the BuAc solutions (500 μ L) of micelle fragments, followed by slow evaporation of the THF in air for 2 days. The initial THF volume fraction of THF is indicated in each figure. The micelles in (A) were characterized by $L_n = 266$ nm, $L_w = 276$ nm, $L_w/L_n = 1.04$, $\sigma/L_n = 0.195$. The micelles in (B) were characterized by $L_n = 429$ nm, $L_w = 453$ nm, $L_w/L_n = 1.05$, $\sigma/L_n = 0.235$. The micelles in (C) were characterized by $L_n = 687$ nm, $L_w = 712$ nm, $L_w/L_n = 1.04$, $\sigma/L_n = 0.194$. Sample was prepared by drop casting aliquots of a mixture of the micelle solution (50 μ L) with BuAc containing PS homopolymer (50 μ L, $c = 1$ mg/mL) onto the carbon film of the copper grid.

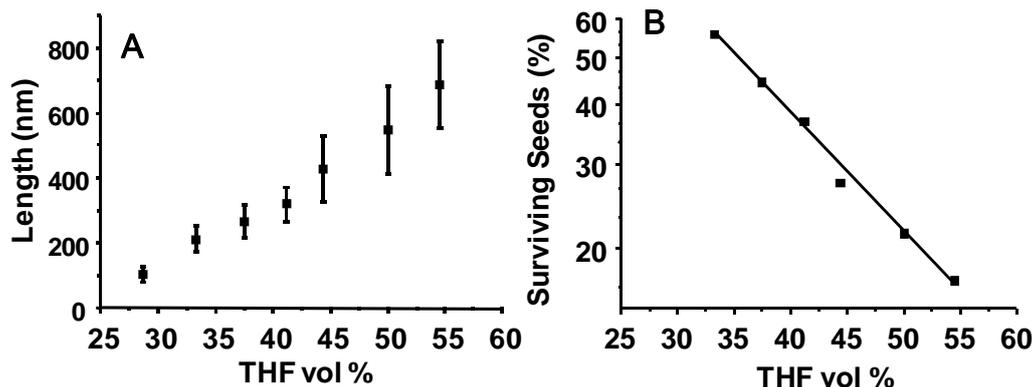


Figure S14. (A) Number-average length L_n of the P3HT-PS micelles obtained after the evaporation of THF vs. the volume fraction of THF in the micelle fragment solution before the evaporation of THF. (The error bars are the standard deviations σ for the length distribution.) (B) Semilogarithmic plot of percentage of surviving seeds vs. volume fraction of THF. Solid line represents the linear best fit for the data.

Additional Discussion for Figure S14.

In Figure S14A, we show the length L_n of the micelles obtained after the evaporation of THF vs. the volume fraction of THF that was initially present in the solution. The data show that as the fraction of THF increased, longer micelles with narrow length distribution were obtained. At volume fractions of THF above 60%, much longer micelles ($> 1 \mu\text{m}$, see Figure S15) that resembled those of the initially prepared micelles (see Figure 1B in the main text) were obtained. We suspect that the micelle fragments dissolved completely at this solvent composition.

The dependence of micelle length on the solvent composition resembles that of the solvent-induced one-dimensional self-seeding of PFS block copolymer micelles.³ THF is a good solvent for both blocks in the P3HT-*b*-PS material and the addition of THF into the solution of micelle fragments increases its solubility. This leads to the dissolution of the fraction of the micelle fragments with the lowest crystallinity, resulting in the formation of unimers. With an increasing proportion of THF in the

solution, a greater fraction of the micelle fragments dissolved. As the THF evaporated, the solubility of the polymer decreased and the addition of unimers to the living ends of the remaining micelles became possible. The Semilogarithmic plot in Figure S14B shows the percentage of surviving micelle fragments vs. the volume fraction of THF in the initial solutions, evaluated via Equation S1. We can see that the fraction of surviving fragments decreased exponentially with an increasing volume fraction of THF.

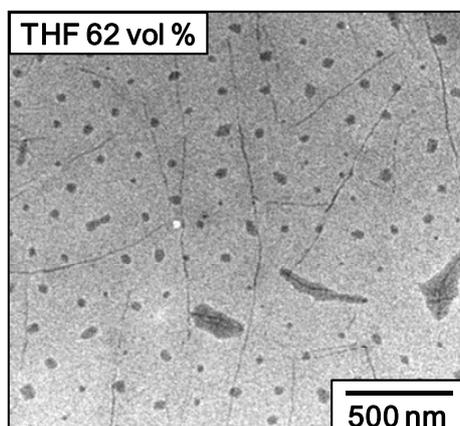


Figure S15. TEM image of the P3HT-PS micelles obtained by adding 800 μL THF into the BuAc solution (500 μL) of micelle fragments, followed by slow evaporation of the THF in air for 2 days. The sample was prepared by drop casting aliquots of a mixture of the micelle solution (50 μL) with BuAc containing PS homopolymer (50 μL , $c = 1 \text{ mg/mL}$) onto the carbon film of the copper grid.

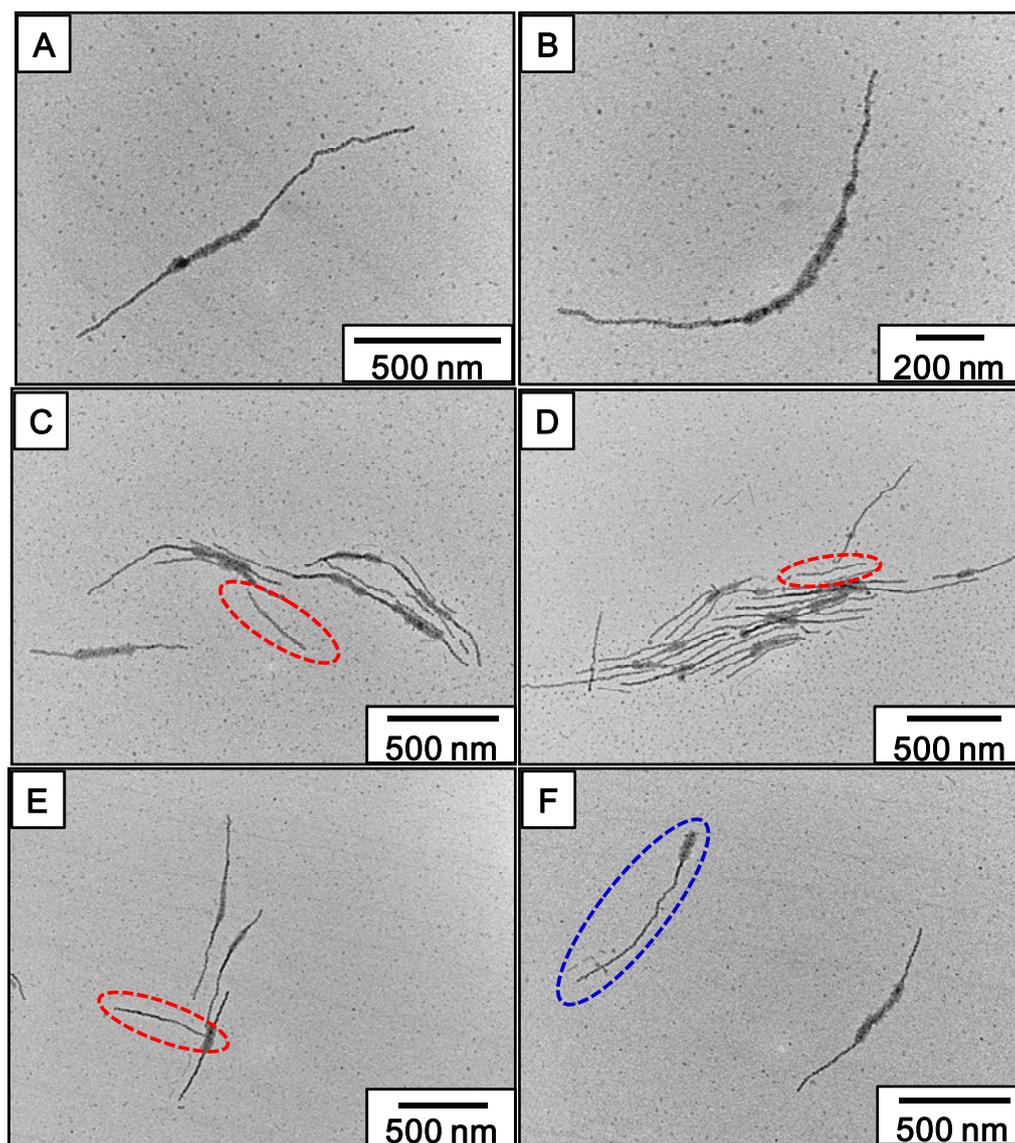


Figure S16. (A-F) TEM images of micelles formed by adding unimer of P3HT₃₄-*b*-PDMS₂₃₆ in THF (0.8 mg/mL, 0.25 mL) into BuAc solution of P3HT₃₄-*b*-PS₁₇₅ (0.05 mg/mL, 0.50 mL), followed by evaporation of THF in air for 24 h. The sample was stained by RuO₄ for 2 h. In the preparation of this sample for TEM measurements, no PS homopolymer was used. The black regions in all images are likely to be unimers that are non-active for growth. Red dashed lines in (C,D,E) highlight the micelles formed by the self-nucleation of P3HT-PDMS. Blue dashed line in (F) highlights the diblock co-micelle in which only one end of the P3HT-PS precursor was active for growth.

Additional Discussion for Figure S16.

Some features in Figure 3 and S16 are also important. Firstly, we notice some dark regions scattering on the carbon film in the magnified image in Figure 3B, we suspect that they are likely due to the staining of the residual unimers. Secondly, besides the triblock co-micelles we present in Figure 3, we also observe significant amount of P3HT-*b*-PDMS homo-micelles, which were formed by self-nucleation rather than epitaxial growth from P3HT-*b*-PS micelles. TEM images showing the coexistence of triblock co-micelles with P3HT-*b*-PDMS homomicelles are presented in Figure S16C-E. After surveying several TEM images, we estimate the number fraction of triblock co-micelles to be ca. 60 - 70 %. Thirdly, very rarely some diblock co-micelles were observed, indicating that only one end of the P3HT-*b*-PS precursor was active for the growth (See Figure S16F).

Table S1. Values of L_n , L_w , L_w/L_n , σ and σ/L_n of P3HT₃₄-*b*-PS₁₇₅ micelle fragments in BuAc and micelles formed after the solution of the fragments was annealed at different temperatures for 30 min followed by annealing at 35 °C for 24 h and cooling to 23 °C.

T (°C)	L_n (nm)	L_w (nm)	L_w/L_n	σ (nm)	σ/L_n
Fragments	118	124	1.05	26	0.220
35	114	119	1.05	25	0.219
50	173	178	1.03	29	0.168
55	224	235	1.05	51	0.228
60	382	392	1.03	64	0.168
62	445	463	1.04	90	0.202
64	542	563	1.04	108	0.199
66	656	673	1.03	107	0.163

Table S2. Values of L_n , L_w , L_w/L_n , σ and σ/L_n of P3HT₃₄-*b*-PS₁₇₅ micelles formed after the solution fragments in BuAc was annealed at 60 °C for different times followed by annealing at 35 °C for 24 h and cooling to 23 °C.

Time	L_n (nm)	L_w (nm)	L_w/L_n	σ (nm)	σ/L_n
30 min	382	392	1.03	64	0.168
2 h	360	374	1.04	71	0.197
24 h	363	392	1.08	104	0.287

Table S3. Values of L_n , L_w , L_w/L_n , σ and σ/L_n of P3HT₃₄-*b*-PS₁₇₅ micelles formed after the slow evaporation of THF versus the volume fractions of THF in the P3HT₃₄-*b*-PS₁₇₅ fragment in BuAc solutions before the evaporation of THF.

THF v %	L_n (nm)	L_w (nm)	L_w/L_n	σ (nm)	σ/L_n
28.6	105	109	1.05	22	0.210
33.3	212	219	1.03	39	0.184
37.5	266	276	1.04	52	0.195
41.2	320	330	1.03	54	0.169
44.4	429	453	1.05	101	0.235
50.0	548	580	1.06	135	0.261
54.5	687	712	1.04	133	0.194

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