

Supporting Information for

Cylindrical Micelles of Controlled Length with a π -Conjugated Polythiophene Core via Crystallization-Driven Self-Assembly

Sanjib K. Patra,¹ Rumman Ahmed,¹ George R. Whittell,¹ David J. Lunn,¹ Emma L. Dunphy,¹ Mitchell A. Winnik,^{*2} and Ian Manners^{*1}

¹*School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK.*

²*Department of Chemistry, University of Toronto, M5S 3H6, Canada.*

*Corresponding authors: Ian.Manners@bristol.ac.uk; mwnnik@chem.utoronto.ca

Index

1. Equipment and materials.....	S2
2. Experimental and syntheses.....	S4
3. Characterization and properties of P3HT-OH and P3HT- <i>b</i> -PDMS.....	S6
4. Self-assembly of P3HT- <i>b</i> -PDMS.....	S14
5. References.....	S21

Experimental Details

General Considerations: Equipment and Materials

All reactions were carried out under atmospheres of either dry nitrogen or dry argon using standard Schlenk line techniques or an MBraun MB150B-G glove box. All chemicals were purchased from Aldrich and were used as received unless otherwise stated. For general synthesis dry N₂-saturated THF, toluene and hexane were obtained from a Grubbs-type solvent system¹ using filtration through an alumina column impregnated with deoxygenated catalysts. CHCl₃ was purified by distillation from CaH₂ under nitrogen. For the anionic polymerization of hexamethylcyclotrisiloxane (D₃), the THF was pre-dried with Na before being distilled from Na/benzophenone under nitrogen. The D₃ was purified by stirring a solution in dry hexanes over CaH₂ for 12 h, removing the solvent and distilling the siloxane *in vacuo*. The distillate was then sublimed at room temperature under static vacuum. Triethylamine was dried over CaH₂ and distilled over 3 Å molecular sieves. Methylisopropyldichlorosilane and trimethylchlorosilane were distilled under nitrogen prior to use. All of the self-assembly experiments were performed in HPLC grade solvents that were acquired from Fisher.

NMR spectra were recorded at ambient temperatures on a Varian 500 (¹H: 499.9 MHz, ¹³C: 125.7 MHz, ²⁹Si: 99.3 MHz) spectrometer with all resonances referenced to residual NMR solvent resonances (¹H and ¹³C). Molecular weights of P3HT homopolymer and polydispersity indices ($PDI = M_w/M_n$) of all the polymers were obtained by Gel Permeation Chromatography (GPC) using a Viscotek VE 2001 Triple-Detector Gel Permeation Chromatograph equipped with automatic sampler, pump, injector, inline degasser, column oven (30 °C), styrene/divinylbenzene columns with pore sizes of 500 Å and 100,000 Å, VE 3580 refractometer, four-capillary differential viscometer and 90° angle laser and low angle laser (7°) light scattering detector (VE 3210 & VE270). THF stabilized with 0.025 % butylated hydroxytoluene (Fisher) was used as the chromatography eluent, at a flow rate of 1.0 mL/min. Samples were dissolved in the eluent (1 mg/mL) and filtered with a Ministart SRP 15 filter (polytetrafluoroethylene membrane of 0.45 µm pore size) before analysis. Calibration of all three detectors (refractive index, laser light scattering and viscometry) was performed using polystyrene standards (Viscotek). This equipment allows the absolute measurement of homopolymer molecular weights and PDIs. The molecular weights of the diblock copolymers were then determined by combining the

molecular weight M_n of the first block from GPC measurements with the block ratio obtained by integrating the ^1H NMR spectroscopic signal intensities of the respective blocks.

Transmission Electron Microscopy (TEM). The samples for electron microscopy were prepared by drop-casting one drop (*ca.* 10 μL) of the micelle colloidal solution onto a carbon coated copper grid which was placed on a piece of filter paper to remove excess solvent. Bright field TEM micrographs were obtained on a JEOL1200EX II microscope operating at 120 kV and equipped with an SIS MegaViewIII digital camera. No staining of the samples was necessary. Images were analyzed using the ImageJ software package developed at the US National Institute of Health.² For the statistical length analysis, 220 - 250 cylinders were carefully traced by hand to determine the contour length. From this data L_n and L_w of each sample of monodisperse cylindrical micelles was calculated as shown below (L = length of object, N = number).

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

$$L_w = \frac{\sum_{i=1}^n N_i L_i^2}{\sum_{i=1}^n N_i L_i} \quad (\text{S2})$$

The standard deviations (σ) of the measured lengths are related to length dispersity (L_w/L_n) through the following expression^{3,4}.

$$\frac{L_w}{L_n} - 1 = \left(\frac{\sigma}{L_n} \right)^2 \quad (\text{S3})$$

Atomic Force Microscopy (AFM). Atomic force microscopy (AFM) images were obtained using a Multimode AFM equipped with a Nanoscope V controller (Veeco Instruments). The micelle samples were prepared by drop-casting 0.05 mg/mL solution of micelles (toluene/ Et_2O) onto freshly cleaved highly ordered pyrolytic graphite (HOPG). Imaging was conducted in air at ambient temperature. All AFM images from which dimensions were determined were obtained with a new SSS-NCL (SuperSharpSilicon) long cantilever-type probe with a 10 nm tip radius from Nanosensors. The dimensions quoted in the text have not been corrected for tip effects, which are expected to be negligible. Images were analyzed using Gwyddion, an open source software program for SPM images (www.gwyddion.net).

Wide Angle X-ray Scattering (WAXS). X-ray powder diffraction data were collected with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) on a Bruker D8 Advance powder diffractometer fitted with a 0.6 mm fixed divergence slit, knife-edge collimator and a LynxEye area detector. Data were

collected between 5 - 30 degrees (2θ) with a step width of 0.02 . The samples were drop cast from chloroform solution onto silicon wafers prior to analysis.

UV-vis and Photoluminescence. UV-vis data were obtained on a Lambda 35 spectrometer employing standard quartz cells (1 cm) from 200 to 800 nm. Fluorescence data were obtained using Perkin Elmer LS 45 Fluorescence Spectrometer.

Laser Confocal Fluorescence Microscopy (LCFM). Laser Confocal fluorescence micrographs were obtained using a Leica TCS-SP2-AOBS confocal laser scanning microscope attached to a Leica DM IRE2 inverted epifluorescence microscope equipped with several lasers. The 458 nm line of the Argon laser was used for excitation of the samples examined here, with emission detection from 500 – 617 nm. The samples for LCFM were prepared by placing two drops of P3HT-*b*-PDMS micelle solution in THF/*n*-hexane (85% *n*-hexane v/v) on a microscope slide. A cover slip was placed on top. Epoxy was then applied around the cover slip to prevent solvent evaporation. Similar CFM data was obtained irrespective of whether the cylinder sample was subjected to dialysis to remove any unimers prior to data collection.

Dynamic Light Scattering (DLS). Dynamic light scattering (DLS) was carried out using Malvern Zeta sizer Nano series equipped with a laser with wavelength of 633 nm and a detector oriented 173° to the incident radiation.

Thermal Analysis. Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC Q100 apparatus coupled to a refrigerated cooling system (RCS90). Both heating and cooling scans were performed at 10 °C/min under an N₂ atmosphere with the samples contained in standard aluminium pans.

Experimental

Synthesis of regioregular vinyl terminated P3HT. The vinyl terminated P3HT was synthesized following a literature procedure developed by McCullough and coworkers.⁵ ¹H NMR (499.9 MHz, CDCl₃, ppm): δ = 6.99 ppm (s, thiophene), 6.83 (m, *vic*-vinyl), 5.52 (d, J = 11 Hz, *gem*-vinyl), 5.14 (d, J = 11 Hz, *gem*-vinyl), 2.82 (t, J = 7 Hz, -hexyl), 1.72 (m, -hexyl), 1.45 (m, -hexyl), 1.37 (m, -hexyl), 0.93 (t, J = 7 Hz, -hexyl). M_n (GPC) = 8.40 kDa, PDI = 1.08. GPC analysis revealed DP_n as 48 which was in reasonable agreement with the value calculated from end-group analysis (40).

Synthesis of hydroxyethyl terminated P3HT-OH and -OSiCl end-capped P3HT-O(ⁱPr)MeSiCl. The vinyl terminated P3HT was converted to hydroxyethyl terminated P3HT-

OH following the procedure described in literature.⁴ The complete disappearance of vinyl protons (signals at 5.52 and 5.14 ppm as doublets) and the appearance of signals at 3.89 (m) and 3.06 (t) ppm in ¹H NMR spectrum confirmed the complete conversion of vinyl to hydroxyethyl terminated P3HT. ¹H NMR (499.9 MHz, CDCl₃, ppm): δ = 6.99 ppm (s, thiophene), 3.89 (m, -CH₂CH₂O), 3.06 (t, -CH₂CH₂), 2.82 (t, J = 7 Hz, -hexyl), 1.72 (m, -hexyl), 1.45 (m, -hexyl), 1.37 (m, -hexyl), 0.93 (t, J = 7 Hz, -hexyl). *M_n* (GPC) = 8.40 kDa, PDI = 1.08.

0.20 g (0.024 mmol) of P3HT-OH was dissolved in 5.0 mL of dry toluene in a greaseless Schlenk tube under the inert atmosphere of Ar in a glove box. To that 0.50 mL (3.58 mmol) of dry triethylamine and 0.50 mL (3.25 mmol) of methylisopropyldichlorosilane (excess) were added. After few minutes, turbidity was observed due to the formation of triethylamine hydrochloride salt. The reaction mixture was stirred for 12 h at RT. The Schlenk tube was removed from the glove box and placed on a Schlenk line. After removing all volatiles in vacuum at 40 °C for 6 h, the Schlenk tube was brought into the glove box. The purple residue was dissolved in 5 mL of dry toluene and filtered through a short (3 cm) pre-dried celite column prepared from a Pasteur pipette. The red filtrate of P3HT-O(ⁱPr)MeSiCl was collected in another greaseless Schlenk tube, dried in vacuum and used immediately for the next reaction. Yield 0.18 g (90%). ¹H NMR (499.9 MHz, CDCl₃, ppm): δ = 6.99 ppm (s, thiophene), 3.95 (t, -CH₂CH₂O), 3.04 (t, -CH₂CH₂O), 2.81 (t, J = 7 Hz, -hexyl), 1.86 (m, -CH, ⁱPr), 1.72 (m, -hexyl), 1.45 (m, -hexyl), 1.37 (m, -hexyl), 1.07 (d, -CH₃, ⁱPr) 0.92 (t, J = 7 Hz, -hexyl), 0.41 (s, *Me*).

Synthesis of P3HT-*b*-PDMS diblock copolymer. To a solution of hexamethylcyclotrisiloxane, D₃, (800 mg, 3.6 mmol) in THF (2.0 mL) was added 10 μL of 1.6 M *n*-BuLi (0.016 mmol) solution in hexanes and polymerization was allowed to proceed in a glove box for 18 h at 0 °C. 0.50 mL of the solution was withdrawn and quenched with Me₃SiCl to characterize the PDMS homopolymer. 100 mg of P3HT-OSiCl (0.012 mmol, *M_n* (GPC) = 8.40 kDa) was then added to the remainder of the solution and stirred for 6 h at RT in the glove box. The excess living anionic PDMS was quenched by adding few drops of Me₃SiCl and precipitated in methanol to get a dark purple residue of rrP3HT-*b*-PDMS. The purple residue was then treated with minimum amount (ca. 5.0 mL) of methyl ethyl ketone (MEK) and centrifuged to remove PDMS homopolymer. The washing step was repeated an additional two times and finally the residue was dried in vacuum for 12 h to give a purple elastomeric material in 72% (450 mg) yield. ¹H NMR (499.9 MHz, CDCl₃, ppm): δ = 6.99 ppm (s, thiophene), 2.80 (t, J = 7 Hz, -hexyl), 1.70 (m, -hexyl), 1.44 (m, -hexyl), 1.35 (m, -

hexyl), 0.92 (t, $J = 7$ Hz, -hexyl), 0.08 (s, -SiMe₂). ²⁹Si-DEPT NMR (99.3 MHz, CDCl₃) - 21.1 ppm. $M_n = 49.15$ kDa (calculated from the combination of GPC analysis of P3HT-OH homopolymer and the ¹H NMR analysis of P3HT-*b*-PDMS diblock copolymer), PDI = 1.05.

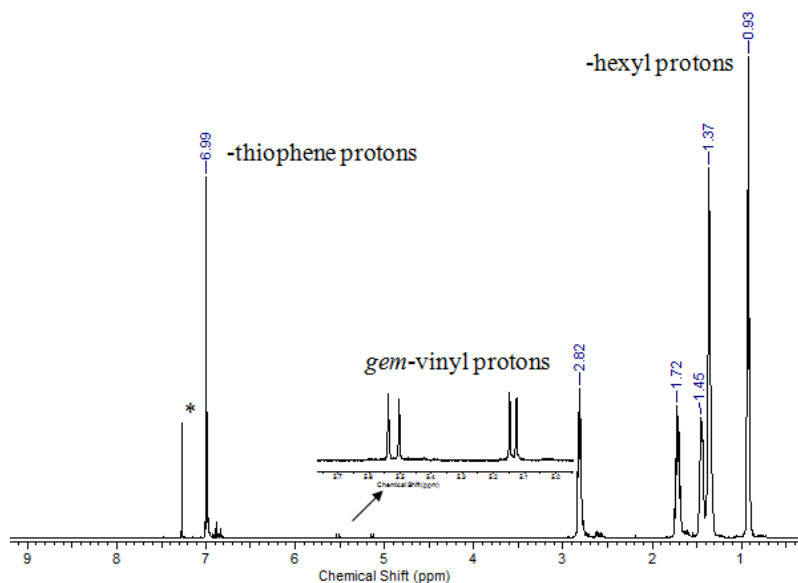


Figure S1: ¹H NMR spectrum of vinyl terminated P3HT in CDCl₃. The asterisk denotes residual solvent signal. The signals in the range of 2.82 – 0.93 ppm are for hexyl protons.

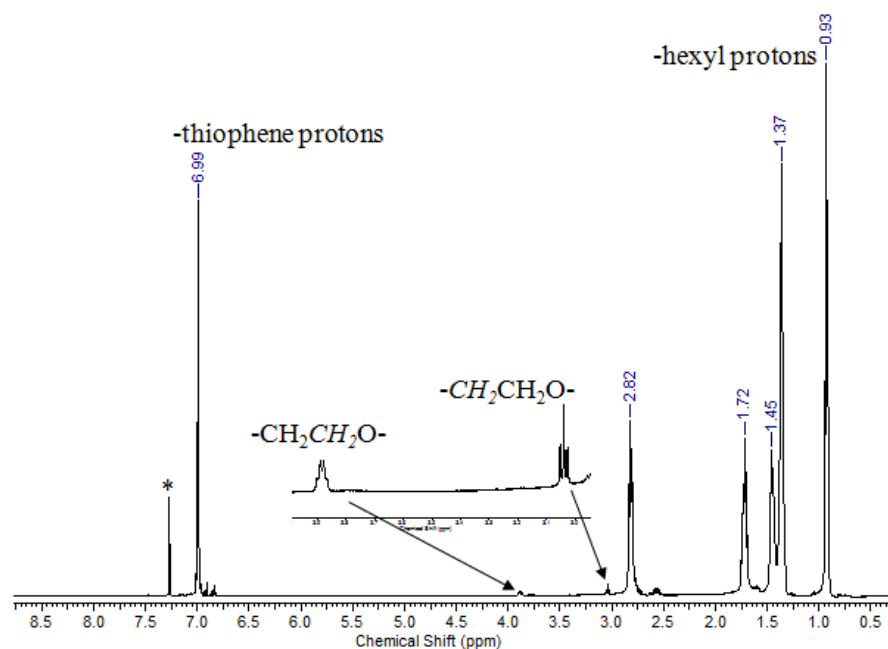


Figure S2: ^1H NMR spectrum of hydroxyethyl terminated P3HT in CDCl_3 . The complete disappearance of vinyl protons (signals at 5.52 and 5.14 ppm) and appearance of signals at 3.89 and 3.06 ppm in ^1H NMR spectrum confirms the complete conversion of vinyl to hydroxyethyl terminated P3HT. The asterisk denotes residual solvent signal. The signals in the range of 2.82 – 0.93 ppm are for hexyl protons of P3HT.

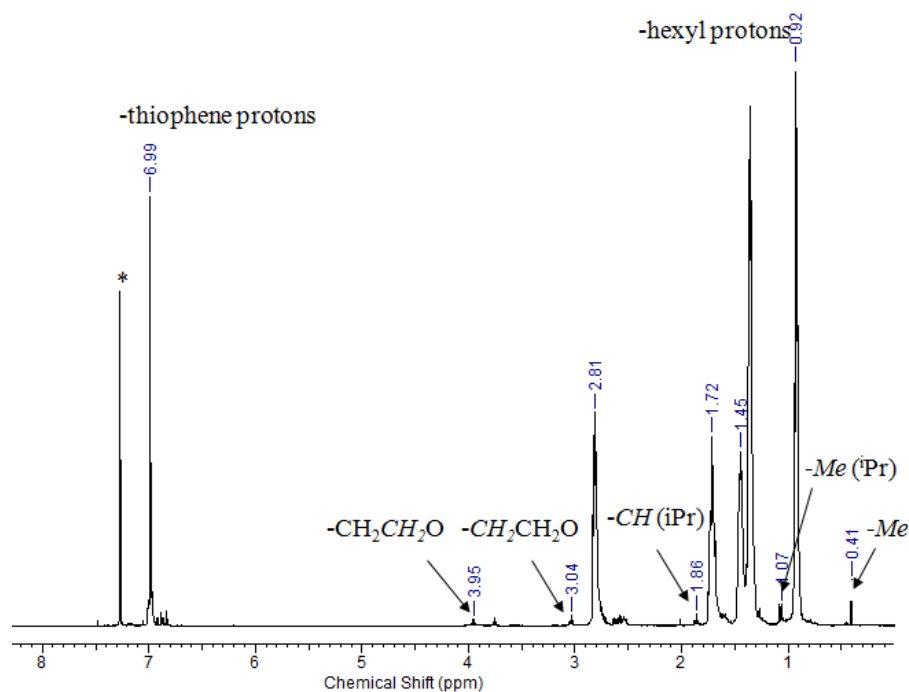


Figure S3: ^1H NMR spectrum P3HT-OSiCl in CDCl_3 . The signals at 2.81, 1.72, 1.45, 1.37 and 0.92 ppm are for hexyl protons of P3HT. The asterisk denotes residual solvent signal.

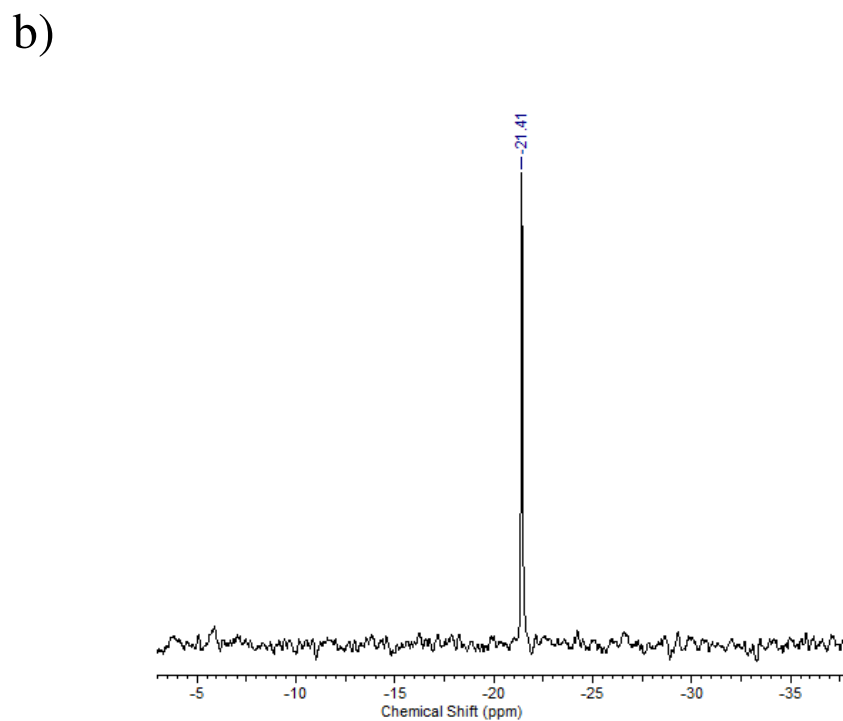
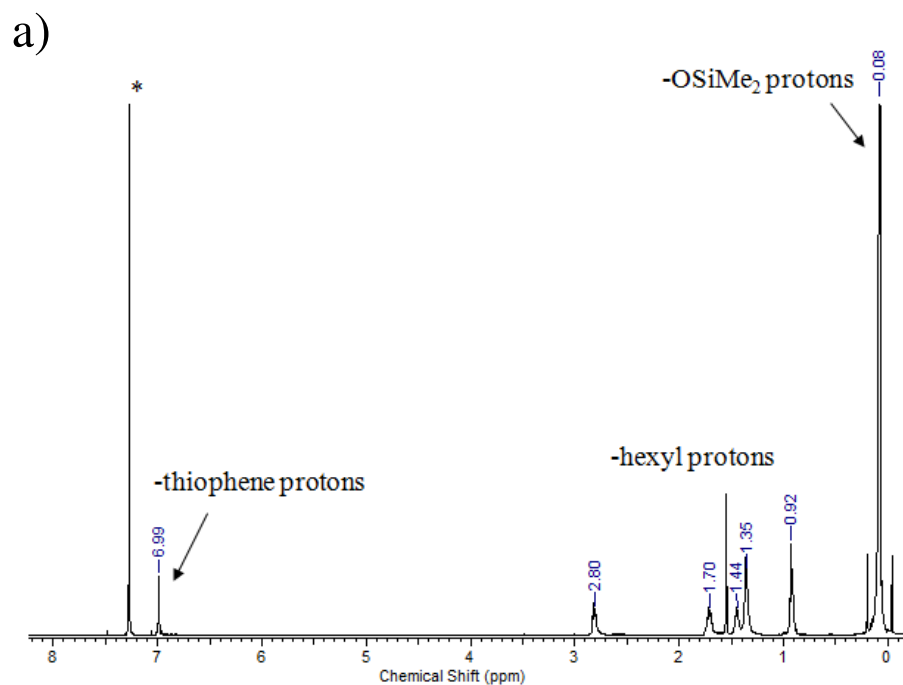


Figure S4. (a) ^1H NMR spectrum of P3HT-*b*-PDMS. The signals in the range of 2.80 – 0.92 ppm are for hexyl protons of P3HT block. The asterisk denotes residual solvent signal. (b) ^{29}Si -DEPT NMR spectrum of P3HT-*b*-PDMS in CDCl_3 .

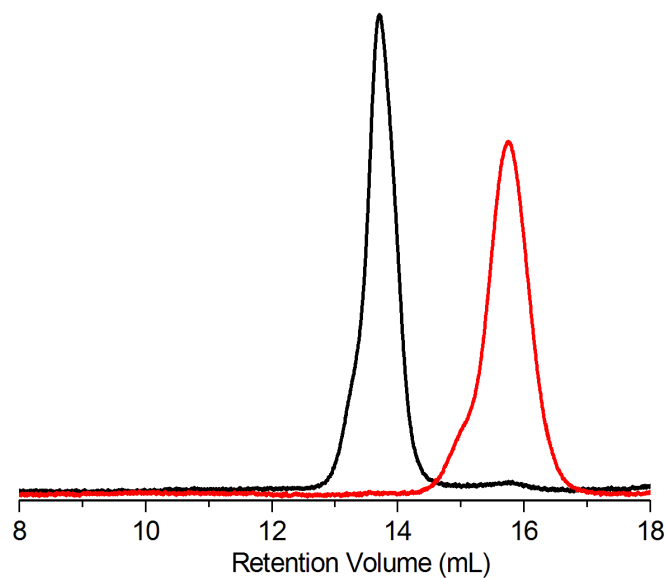


Figure S5. GPC trace (Refractive Index response) of P3HT-*b*-PDMS diblock copolymer (black) and the corresponding hydroxyethyl terminated P3HT-OH homopolymer (red) using THF as eluent. PDIs (M_w/M_n) of P3HT-OH and P3HT-*b*-PDMS were found to be 1.08 and 1.05 respectively.

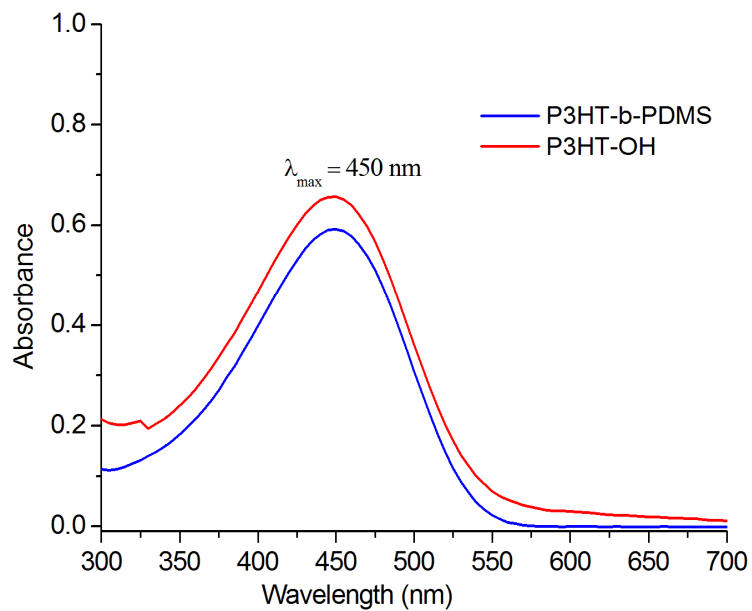


Figure S6: UV-vis absorption spectra of P3HT-OH (0.10 mg/mL) and P3HT-*b*-PDMS (0.50 mg/mL) in toluene in a quartz cell (10 mm).

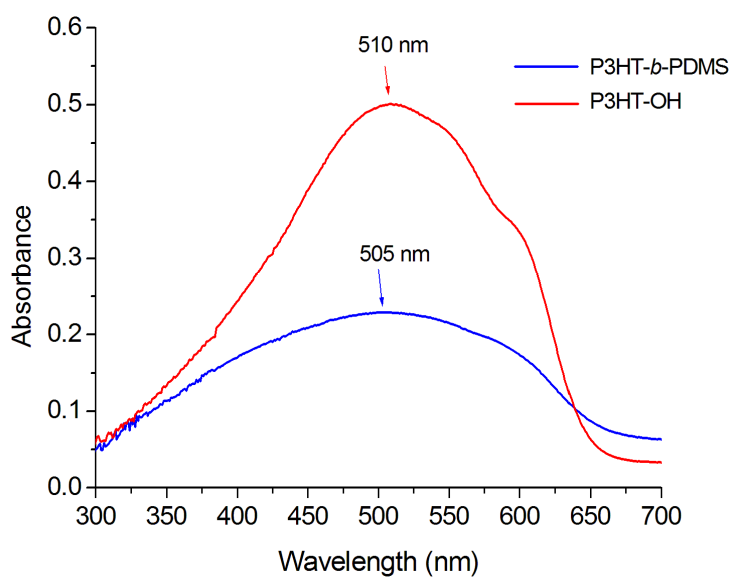


Figure S7: UV-vis absorption spectra of thin films (on quartz discs) of P3HT-OH and P3HT-*b*-PDMS.

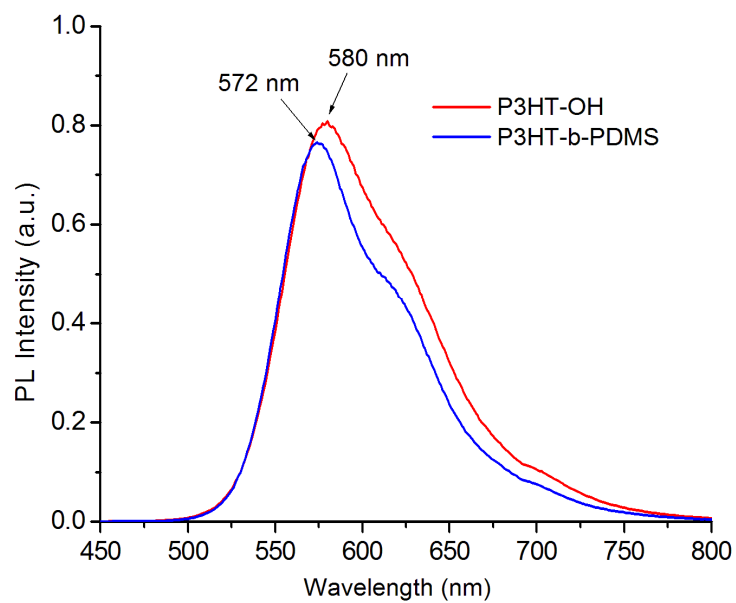


Figure S8: Photoluminescence (PL) spectra (excited at 440 nm) of P3HT-OH (0.05 mg/mL) and P3HT-*b*-PDMS (0.10 mg/mL) in toluene using quartz cell (10 mm).

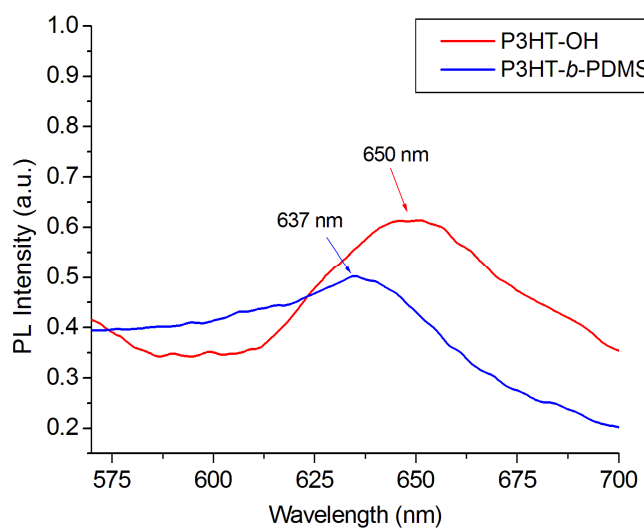


Figure S9: PL spectra (excited at 440 nm) of films (on quartz disc) of P3HT-OH and P3HT-*b*-PDMS.

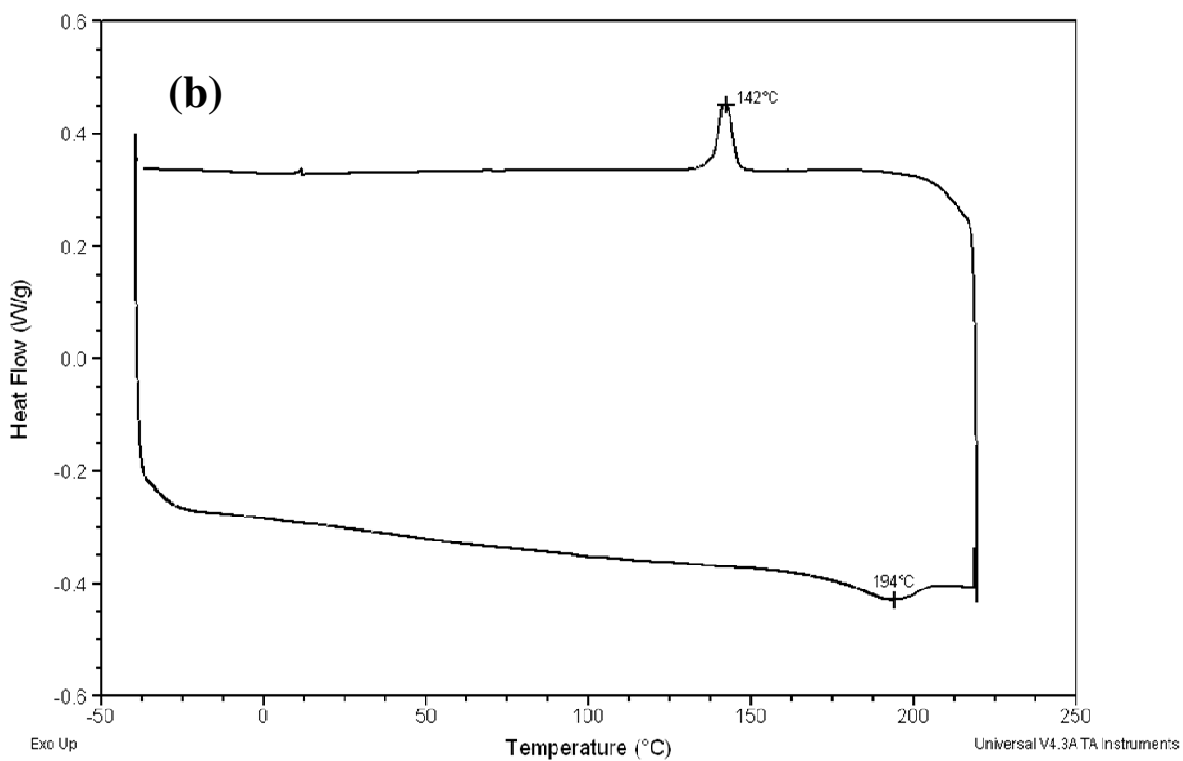
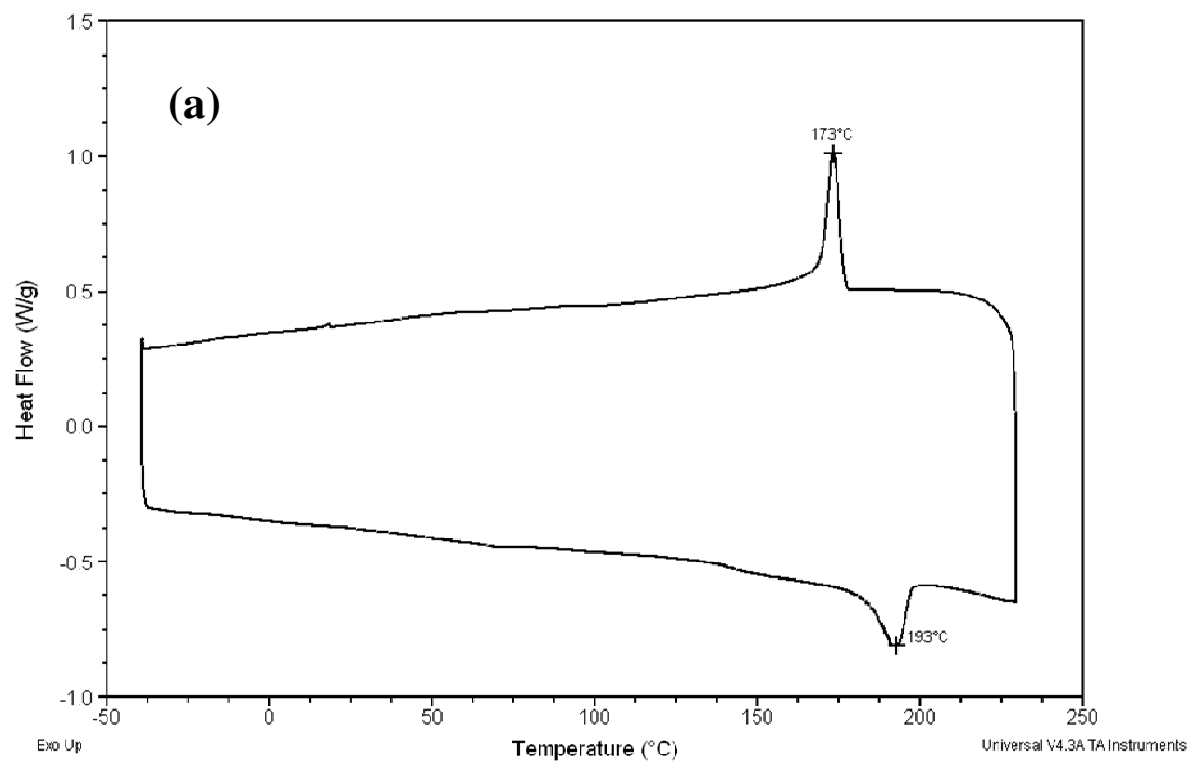


Figure S10: DSC thermogram of (a) P3HT-OH homopolymer and (b) P3HT-*b*-PDMS diblock copolymer at a scan rate of 10 °C/min. The degree of crystallinity for P3HT-OH and P3HT-*b*-PDMS were found to be ca. 45% and ca. 10% respectively as measured from DSC studies. The melting enthalpy for 100% crystalline P3HT was taken as 99 J/g.⁶

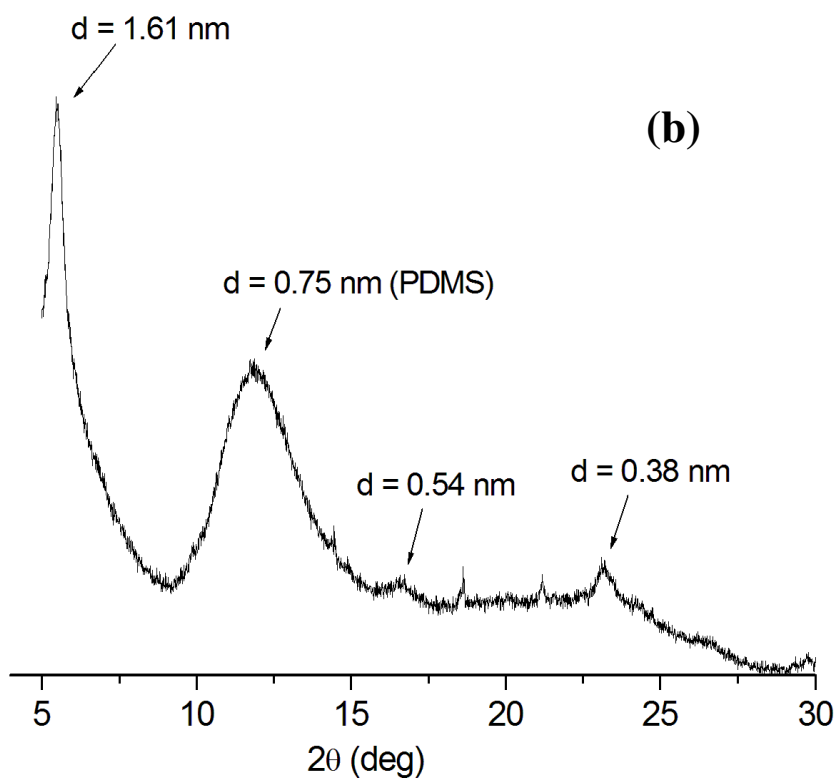
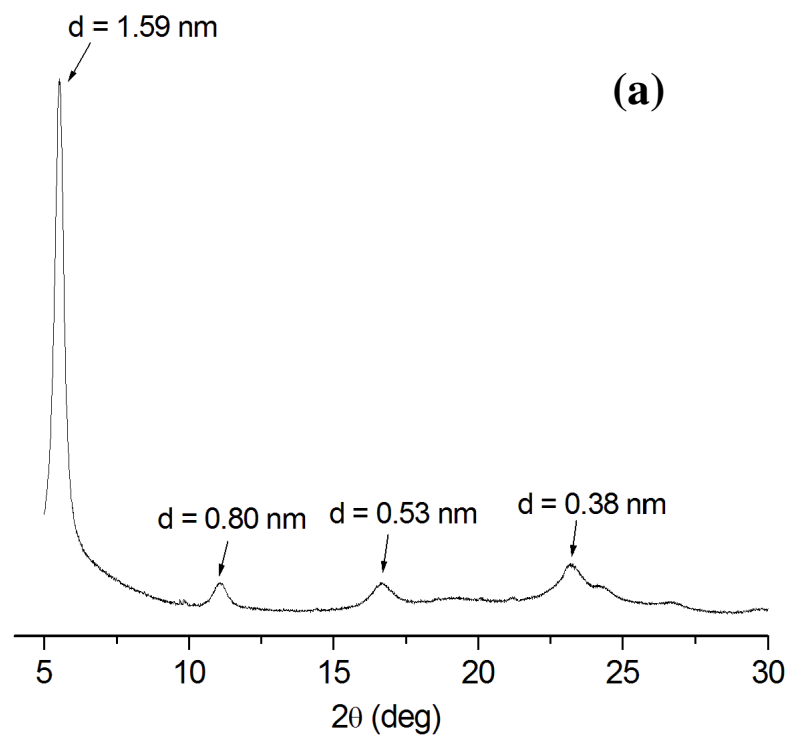


Figure S11: WAXS diffraction pattern of (a) P3HT-OH homopolymer and (b) P3HT-*b*-PDMS diblock copolymer (measured on film cast from chloroform solution in a 2θ interval from 5° to 30°). The broad signal at 11.79° ($d = 0.75$ nm) is the amorphous halo due to the PDMS block.⁷

Self-assembly of P3HT-*b*-PDMS diblock copolymer.

Self-assembly in neat solvents (*n*-hexane and Et₂O). P3HT-*b*-PDMS was dissolved in *n*-hexane or Et₂O, which are selective solvents for the PDMS block (0.30 mg/mL). This afforded clear orange solutions at room temperature, which became red in colour after *ca.* 2 days. Analysis by bright field TEM indicated the presence of polydisperse cylindrical micelles. Figure S12 shows the representative TEM images of the micelles formed in *n*-hexane and in Et₂O.

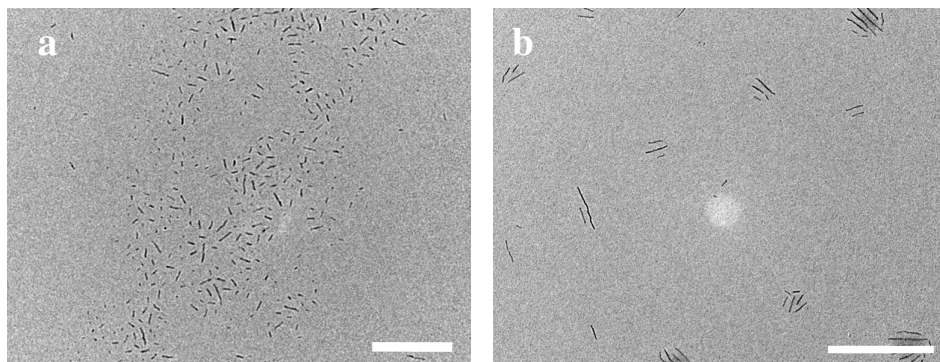


Figure S12: Bright field TEM image of P3HT-*b*-PDMS cylindrical micelles formed in (a) *n*-hexane (0.30 mg/mL) and (b) Et₂O (0.30 mg/mL), scale bar: 500 nm

Self-assembly in the mixed solvent systems. A solution containing 1 mg of P3HT-*b*-PDMS in 0.5 mL of toluene was prepared in a small sample vial and 2.5 mL of Et₂O was added dropwise. The clear yellow-orange solution was allowed to age for 48 h at which time the colour of the solution had turned red. Figure S13 shows TEM and AFM images of the resulting micelles.

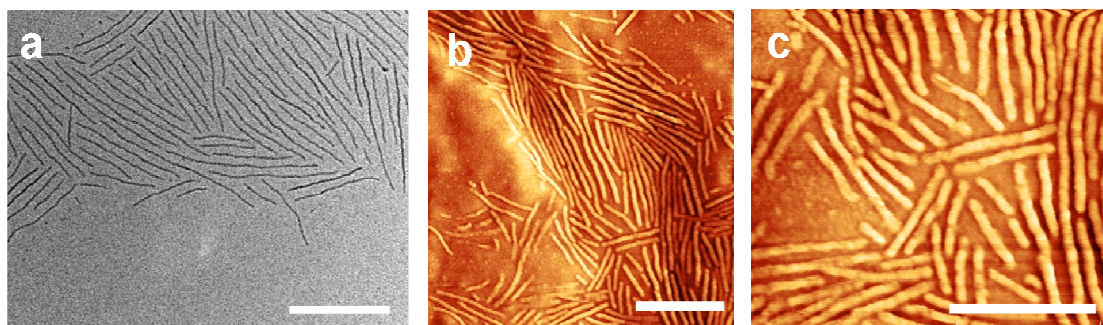


Figure S13: (a) Bright field TEM image of P3HT-*b*-PDMS cylindrical micelles formed in toluene/Et₂O mixture (85% Et₂O v/v), scale bar: 1000 nm; (b) and (c) AFM phase images of P3HT-*b*-PDMS cylindrical micelles formed in toluene/Et₂O mixture (85% Et₂O v/v); scale bar: 500 nm (b) and 400 nm (c).

In a similar manner to above, well-defined cylindrical micelles of P3HT-*b*-PDMS were prepared in THF/*n*-hexane solvent system. 1 mg of P3HT-*b*-PDMS was dissolved in 0.5 mL of THF. 2.5 mL of *n*-hexane was then added dropwise. The clear yellow-orange solution was allowed to age for 48 h at which time the colour of the solution became reddish-purple. Figure S15a (*vide infra*) shows well-defined polydisperse cylindrical micelles with uniform diameter.

Preparation of P3HT-*b*-PDMS seed micelles. A vial containing the micelle colloidal solution (in toluene/Et₂O or THF/*n*-hexane system) was flushed with nitrogen and capped with a rubber septum. The sonotrode was introduced into the colloidal solution through the rubber septum before the solution was cooled to -5 °C. The colloidal solution was then subjected to ultrasound with stirring for 2.5 h (ultrasonic processor: Hielscher UP50H operating at 30 kHz and 50 W equipped with a Hielscher MS1 titanium sonotrode). TEM micrographs of the fragmented micelles (seed micelles) are shown in Figure S14 (in toluene/Et₂O) and S15b (in THF/*n*-hexane).

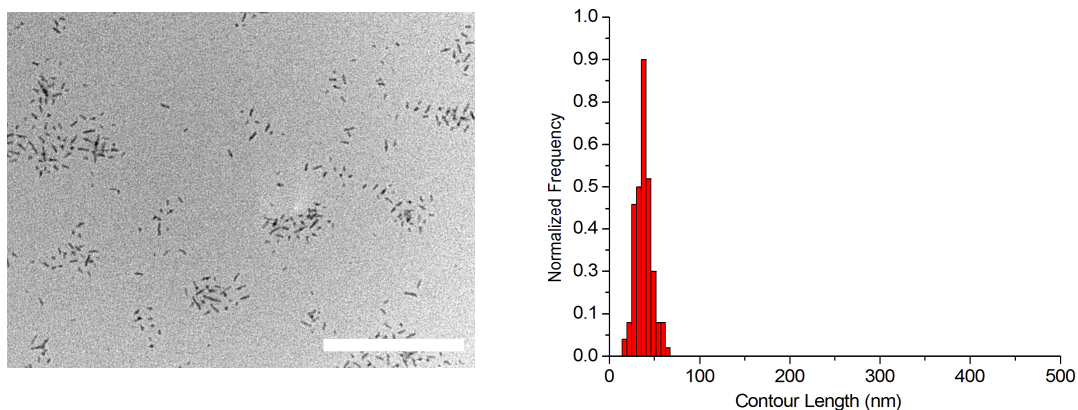


Figure S14: (left) Seed micelles prepared by sonication of the long cylindrical micelles formed in toluene/Et₂O, scale bar: 500 nm; (right) Histogram of the contour length distribution of the seed micelles ($L_n = 38$ nm, $L_w = 40$ nm, $L_w/L_n = 1.05$, $\sigma/L_n = 0.22$)

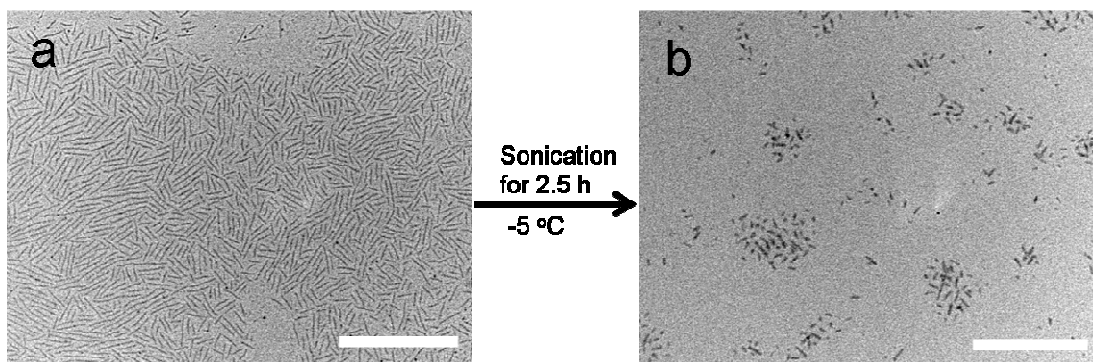


Figure S15: TEM images of (a) polydisperse P3HT-*b*-PDMS cylindrical micelles in THF/*n*-hexane mixture (85% *n*-hexane v/v) (b) Seed micelles ($L_n = 41$ nm, $L_w = 43$ nm, $L_w/L_n = 1.05$, $\sigma/L_n = 0.21$) prepared by sonication of micelles (a); scale bar: 500 nm.

Seeded growth of P3HT-*b*-PDMS cylindrical micelles

In the toluene/Et₂O system. In order to obtain monodisperse cylindrical micelles with controlled lengths, different quantities of P3HT-*b*-PDMS unimers (700, 1400, 2100 and 2800 μ g) were added as 7 mg/mL toluene solutions to a stirred (300 rpm) solution of the small P3HT-*b*-PDMS seed micelles (33 μ g in 100 μ L of 85% v/v Et₂O/toluene) diluted with a further 1.5 mL of Et₂O. After stirring for 10 s, the samples were aged for 2 days at 21 °C during which time the colour of the solutions changed from yellow to reddish purple. Contour lengths were measured from 220 - 250 micelles in multiple TEM images (Figure 2 in main text). These data are summarized in Table S1.

Table S1: Contour length data of monodisperse P3HT-*b*-PDMS cylindrical micelles (in toluene/Et₂O system grown from seed micelles) as measured from TEM images.

Sample	$m_{unimers}/m_{seed}$	L_n , nm	L_w , nm	L_w/L_n	σ	σ/L_n
A	21	83	87	1.05	18.6	0.22
B	43	128	135	1.06	31.3	0.25
C	64	155	163	1.05	32.6	0.22
D	85	217	234	1.08	61.4	0.28

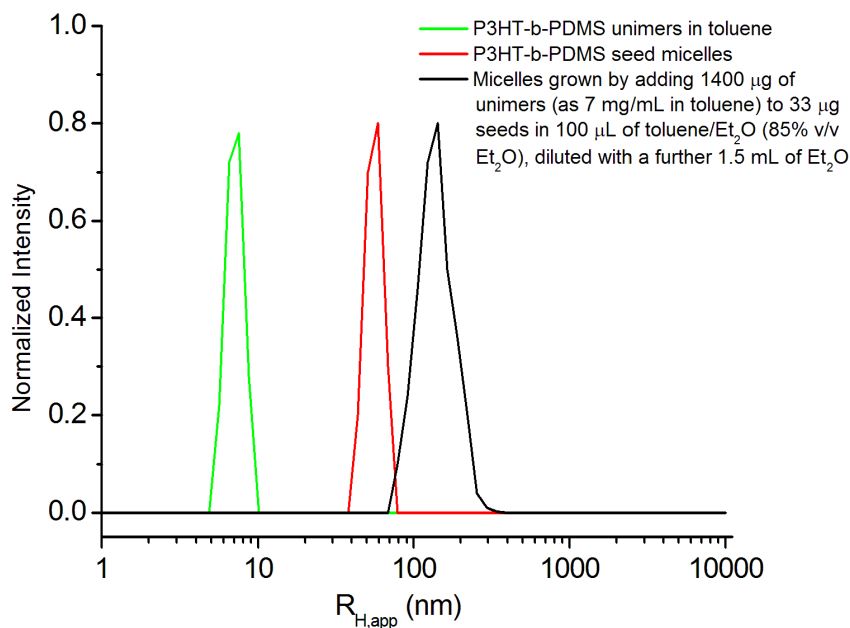


Figure S16: DLS volume distribution for (green) P3HT-*b*-PDMS unimers in toluene (1mg/mL); $R_{H,app}$ = 6.5 nm; (red) Seed micelles prepared from the micelles grown in toluene/Et₂O system (0.33 mg/mL), $R_{H,app}$ = 44 nm; (black) Micelles grown by adding 1400 μ g unimers (as 7 mg/mL in toluene) to 33 μ g of seeds in 100 μ L of toluene/Et₂O (85% v/v Et₂O), diluted with a further 1.5 mL of Et₂O, $R_{H,app}$ = 115 nm. Upon further addition of unimers no significant change in $R_{H,app}$ was detected. Presumably, this is due to the limitations of interpreting the diffusion of a rigid-rod system in solution by the Stokes-Einstein equation. Moreover, $R_{H,app}$ is derived from a hard sphere model, the value is highly inaccurate for a cylinder.

In the THF/*n*-hexane system. To a 75 μL (0.33 mg/mL in 85% v/v *n*-hexane/THF) of a freshly sonicated colloidal solution of P3HT-*b*-PDMS seed micelles (containing 25 μg of polymer) was added an additional 1.5 mL of *n*-hexane. As aliquots of this colloidal solution were stirred at 300 rpm, solutions of P3HT-*b*-PDMS (containing 500, 1000, 2000 and 4000 μg of unimers as 10 mg/mL in THF) were added dropwise. The solutions were allowed to stir for 10 s before being allowed to age for 2 days. Figure S17 and S18 show the TEM images and corresponding contour length distributions of the grown micelles. Contour length data of monodisperse P3HT-*b*-PDMS cylindrical micelles grown in THF/*n*-hexane system are listed in Table S2.

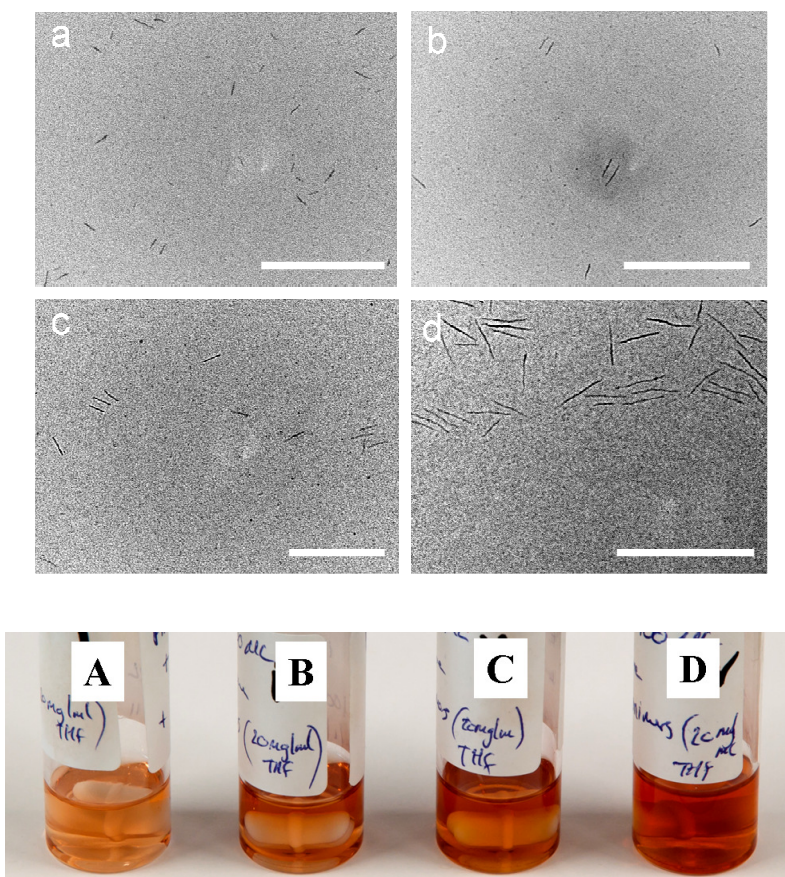


Figure S17: (a) – (d) Corresponding TEM images of micelles formed by homoepitaxial growth by adding increasing amounts of (A) 500, (B) 1000, (C) 2000 (D) 4000 μg of P3HT-*b*-PDMS unimers as 10 mg/mL in THF to 25 μg in 75 μL THF/*n*-hexane (85% v/v *n*-hexane), diluted with a further 1.5 mL of *n*-hexane, scale bar: 500 nm. The micelle solutions were aged for 2 days before sample preparations for TEM measurements. (Below) Photographs of the respective micelle solutions.

Table S2: Contour length data of monodisperse P3HT-*b*-PDMS cylindrical micelles (in THF/*n*-hexane system grown from seed micelles) as measured from TEM images.

$m_{unimers}/m_{seed}$	L_n , nm	L_w , nm	L_w/L_n	σ	σ/L_n
20	72	74	1.03	12.7	0.18
42	133	136	1.02	20.8	0.16
185	215	221	1.03	29.0	0.14
268	320	328	1.03	49.0	0.15

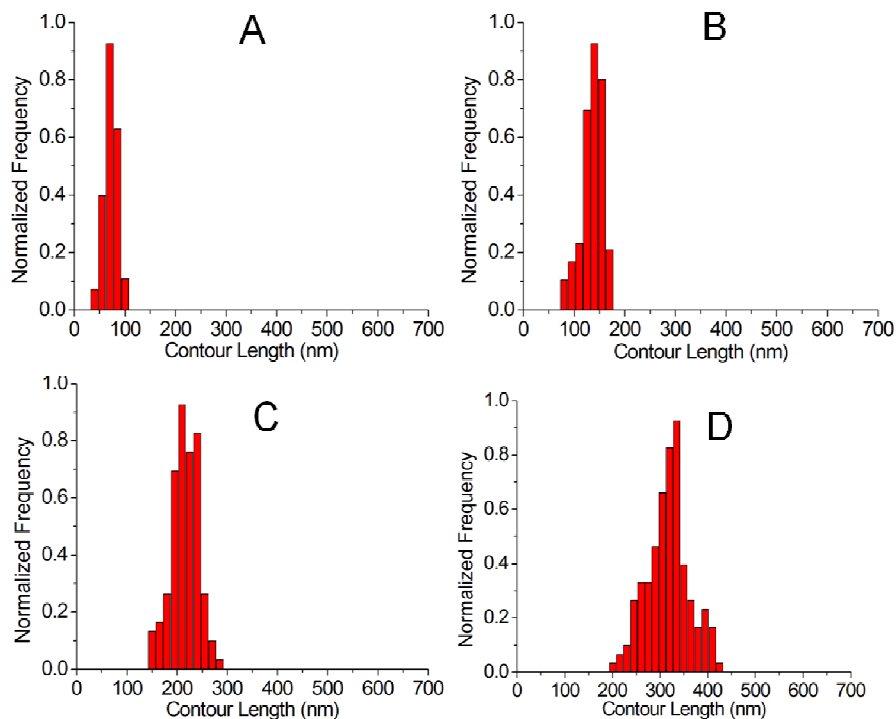


Figure S18: (A) – (D) Histograms of the contour length distribution (CLD) of samples A - D formed through CDSA. The CLDs were determined from analysis of multiple TEM images for each sample. (E) Linear dependence of the number-average length (L_n) of micelles on the unimer-to-seed ratio ($m_{unimers}/m_{seed}$).

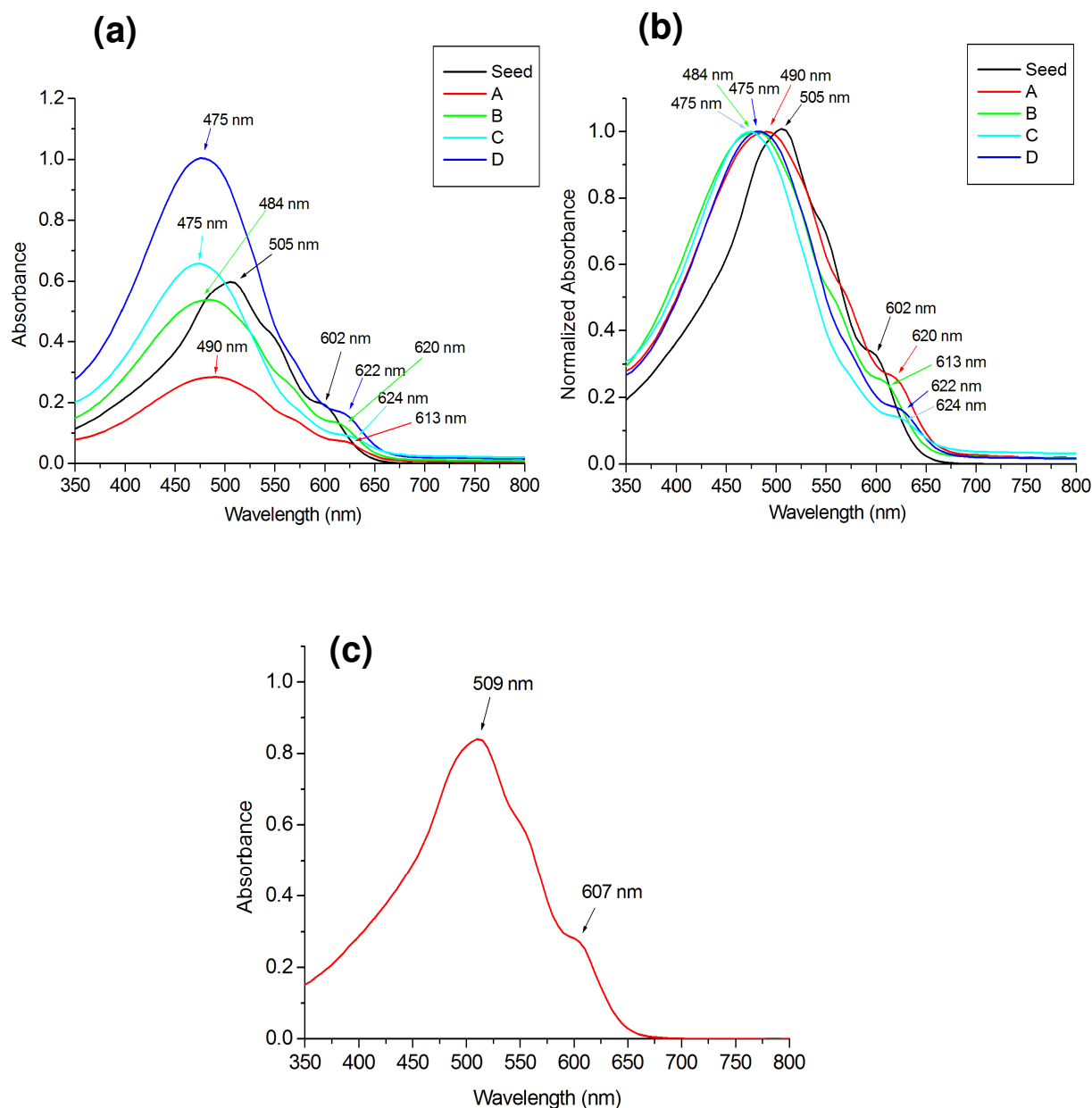


Figure S19: (a) and (b) UV-vis absorption spectra of seeds (0.33 mg/mL in toluene/Et₂O, 85% Et₂O v/v) and the samples of cylinder micelles A, B, C and D (Table S1) obtained by adding 700, 1400, 2100 and 2800 μ g as 7 mg/mL solution in toluene to 33 μ g of seed micelles. The absorptions at 602 – 624 nm (which appear as shoulders) are ascribed to the crystalline P3HT cores formed in solution. The blue shift of λ_{max} suggests that following addition of the solution of block copolymer in toluene, significant amounts of the polymer remain as unimers in solution and do not participate in addition to the seed micelles. For comparison, the absorbance for P3HT-*b*-PDMS unimers in toluene solution is at 450 nm, see Figure S6. (c) UV-vis absorption spectrum of a solution in toluene/Et₂O (85% Et₂O v/v) of the micelles formed by direct growth (see Figure S13 for TEM and AFM images).

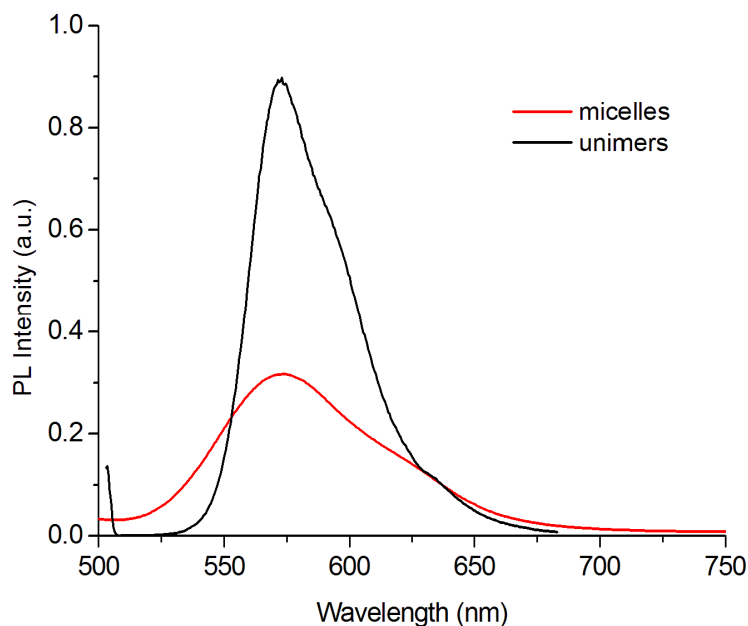


Figure S20: Solution PL spectra (excited at 440 nm) of unimers in toluene (0.10 mg/mL in toluene) and micelles (0.33 mg/mL in toluene/Et₂O, 85% Et₂O v/v) formed by direct growth (see Figure S13 for TEM and AFM images). The emission at $\lambda_{em} = 572$ nm may be due to the much stronger emission intensity of soluble unimers that are also present in the solution of micelles. The absorption spectra of the samples are shown in Figure S6 and in Figure S19C respectively.

References

1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
2. Rasband, W. S. ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, <http://imagej.nih.gov/ij/>, 1997-2011.
3. Rogošić, M.; Mencer, H. J.; Gomzi, Z.. *Polym. J.* **1996**, *32*, 1337.
4. Henderson, J. F.; Szwarc, M. *Macromol. Rev.* **1969**, 317.
5. (a) Jeffries-El. M.; Sauvé, G.; McCullough, R. D. *Macromolecules* **2005**, *38*, 10346. (b) Iovu, M. C.; Jeffries-El. M.; Sheina, E. E.; Cooper, J. R.; McCullough, R. D. *Polymer* **2005**, *46*, 8582.
6. Malik, S.; Nandi. A. K. *J. Polym. Sci. Part B: Polym. Phys.* **2002**, *40*, 2073.
7. Andrianov, K. A.; Slonimskit, G. L.; Zhdanov, A. A.; Levin, V. Y.; Godovskit, Y. K.; Moskalenko, V. A. *J. Polym. Sci., Part A-1*, **1972**, *10*, 1.