Supplementary Information (SI) for Soft Matter.

# Supporting Information

## Morphological Transitions in the Crystallization-Driven Self-Assembly of Narrowly Distributed π-Conjugated Triblock Copolymer

*Bin Huang, Donglai Tian, Zhubin Liu, Yanchen Deng, Guiyou Wang*, Aiguo Hu**

Shanghai Key Laboratory of Advanced Polymeric Materials, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai, 200237, China.

*Corresponding Authors: hagmhsn@ecust.edu.cn (AH), guiyouwang@ecust.edu.cn (GW)

## Materials and Methods

Unless otherwise noted, all reagents were purchased from commercial sources (Titan, Shanghai, China) and used without further purification. N, N-dimethylacetamide (DMAc) and dichloromethane (DCM) were distilled over calcium hydride before use. THF was distilled from Na/benzophenone under nitrogen before use. CuBr was purified by stirring with glacial acetic acid, washing with ethanol, and then drying under vacuum at 70 °C. 2-(Dimethylamino)ethyl methacrylate (DMAEMA) was distilled at reduced pressure to remove inhibitor. 1,4-bis(2-ethylhexyloxy)-2,5-diiodobenzene[1-2], Pd@SBA-15[3-4] were synthesized according to literature procedures. Self-assembly experiments were performed using HPLC grade solvents.

**Gel Permeation Chromatography (GPC).** Number-averaged molecular weight ($M_n$) and dispersity ($Đ$) were measured by a gel permeation chromatography (GPC) system, equipped with a Waters 1515 isocratic HPLC pump and a Waters 2414 refractive index detector. Narrowly distributed polystyrene (PS) was used as the standard. THF was chosen as the eluent (1 mL/min, 40 °C) for the measurement of all samples.

**Nuclear Magnetic Resonance Spectroscopy (NMR).** $^1$H NMR spectra were obtained from a Bruker AVANCE FT NMR spectrometer in $CDCl_3$ equipped with a TXIZ probe head (600 MHz) or a Bruker AVANCE FT NMR spectrometer in $CDCl_3$ equipped with broadband high resolution probe head (400 MHz).

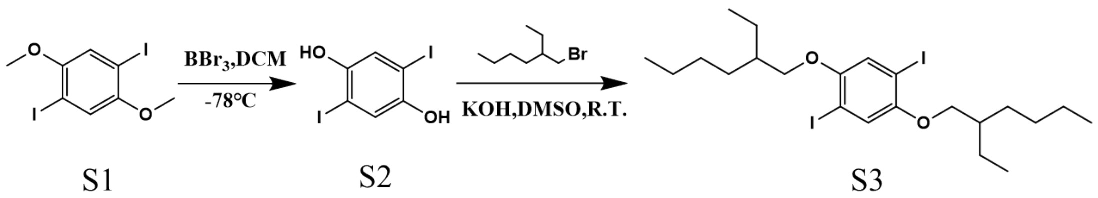
**Transmission Electron Microscopy (TEM).** The TEM images were recorded through a JEM-2100 microscope (JEOL, Japan) at an acceleration voltage of 200 kV. TEM samples were prepared by dropping 4 μL of the micellar solution onto carbon-coated copper grids; then, the samples were negatively stained with phosphotungstic acid (PTA) aqueous solution. Images were analyzed with the software Image J (NIH). For the statistical analyses, more than N = 100 micelles in several images were traced by the software to obtain the length or width information. The number average micelle length/width ($L_n/W_n$) and weight average micelle length/width ($L_w/W_w$) were calculated as shown below.

$$L_n = \frac{\sum_i^n N_i L_i}{\sum_i^n N_i}, \quad L_w = \frac{\sum_i^n N_i L_i^2}{\sum_i^n N_i L_i}$$

**UV/Vis absorption spectroscopy (UV-vis).** UV/vis data were recorded by an Evolution 201 UV spectrophotometer (Thermo fisher, USA) employing quartz cells (1 cm x 0.1 cm) from 200 to 800 nm. Experiments were conducted at a concentration of 0.05 mg mL$^{-1}$ to allow for convenient monitoring of micelle formation and dissolution.

**Atomic Force Microscopy (AFM).** AFM measurements were performed on a Bruker MultiMode 8 using tapping mode at room temperature. The samples for AFM were prepared on a silicon wafer by drop-casting the micelle solution (20 μL, 0.05 mg mL$^{-1}$) onto the clean silicon wafer. The silicon wafer was gently dried from the sides with a filter paper and dried via vacuum desiccation.

## Experimental Procedures



Scheme S1. Synthesis of Monomers

**Synthesis of 2,5-diiodobenzene-1,4-diol (S2)**[1]: 1,4-diiodo-2,5-dimethoxybenzene (S1, 8.0 g, 0.02 mol) placed into a 250 mL Schlenk flask, which was evacuated and purged with argon three times. Anhydrous DCM (100 mL) was then added, and the flask was immersed in a dry ice/acetone bath. After stirring for 15 min, $BBr_3$ in DCM (1.0 M, 80 mL, 0.08 mol) was added via syringe. The solution was allowed to return to room temperature and stirred for 16 h. The reaction mixture was then poured into ice water, resulted in a white precipitate. The mixture was filtered, washed with dichloromethane three times, and vacuum-dried to remove residual solvent, yielding the product as a white powder (6.95 g, 96%).

**Synthesis of 1,4-bis((2-ethylhexyl) oxy)-2,5-diiodobenzene (S3)[1-2]:** S2 (6.95 g, 19.20 mmol) and KOH (4.85g, 86.4mmol) were added to a 100 mL round-bottom flask containing anhydrous DMSO (30 mL). The reaction mixture was stirred at room temperature under a nitrogen atmosphere for 1 h. Using a syringe, 2-ethylhexyl bromide (8.16 g, 42.26 mmol) was added, and the reaction continued for 24 h. The reaction mixture was then poured into saturated brine (200 mL) and extracted with DCM (100 mL) for three times. The DCM phase was collected and the solvent was removed. After removal of solvent, the crude product was purified by silica gel column chromatography with hexane as eluent to get S3 (8.10 g, 72%) as a colorless oil. $^1H$ NMR (400 MHz, $CDCl_3$) δ: 7.16 (s, 2H) 3.81 (d, J = 5.5 Hz, 4H) 1.73 (m, 2H) 1.61-1.29 (m, 16H) 0.99 - 0.83 (m, 12H).

**Synthesis of Pd@SBA15**

**SBA-15**: A 1000 mL round-bottom flask was charged with P123 ($EO_{20}$-$PO_{70}$-$EO_{20}$, $M_n$ = 5800, 10.0 g), which was dissolved in deionized water (320 mL) and concentrated hydrochloric acid (53 mL). The solution was stirred slowly at 40 °C until clear. Tetraethyl orthosilicate (22.2 mL) was then added dropwise, causing the solution to gradually turn white. The mixture was stirred for an additional 20 h, then transferred to a PTFE-lined container. This container was placed in a stainless steel autoclave and subjected to crystallization at 100 °C for 20 h. After cooling to room temperature, the mixture was filtered. The resulting solid was washed with deionized water and ethanol, and then dried under vacuum at 60 °C to obtain SBA-15 as a white powder (7.25 g).

**Re-SBA-15**: In a 250 mL round-bottom flask, SBA-15 (7.25 g) and P123 (29.0 g) were added, followed by absolute ethanol (110 mL). The mixture was stirred at room temperature for 24 hours. The product was then filtered, and the resulting white powder was dried under vacuum at 60 °C to obtain Re-SBA-15 (10.6 g).

**HMDS-Re-SBA-15**: Re-SBA-15 (10.0 g) and hexamethyldisilazane (HMDS) (125 mL) were added to a 250 mL round-bottom flask and stirred at room temperature for 3 h. The mixture was filtered, washed with n-hexane, and then dried under vacuum at 60 °C to obtain HMDS-Re-SBA-15 (34.7 g).

**EX-HMDS-Re-SBA-15:** The HMDS-Re-SBA-15 was Soxhlet-extracted with ethanol for 7 days, and then dried under vacuum at 60 °C to obtain EX-HMDS-Re-SBA-15.

**SBA-15-$NH_2$:** EX-HMDS-Re-SBA-15 (7.0 g) was placed in a 250 mL round-bottom flask, to which anhydrous toluene (84 mL) and 3-aminopropyltriethoxysilane (APTES, 24.5 mL) were added. The mixture was refluxed under nitrogen atmosphere for 48 h. Subsequently, it was washed three times with acetone and chloroform, and then dried in a vacuum oven at 60 °C to give SBA-15-$NH_2$ (5.5 g).

**Pd@SBA-15:** SBA-15-$NH_2$ (2.0 g) was placed in a 250 mL flask, to which DMF (100 mL) was added, and the mixture was sonicated for 15 min. At room temperature, the mixture was stirred vigorously for 10 min while a solution of $H_2PdCl_4$ (10 mM, 6 mL) was added dropwise. After sonication for 15 min, the mixture was stirred for 4 h. A freshly prepared $NaBH_4$ solution (1 M, 5 mL) was then added dropwise to the solution, and stirring continued for an additional 12 h. The product was filtered, washed three times each with deionized water and ethanol, and then dried in a vacuum oven at 60 °C to obtain Pd@SBA-15 (1.85 g).

### Synthesis of conjugated polymers and triblock copolymers

**PPP**: A mixture of 1,4-bis(2-ethylhexyloxy)-2,5-diiodobenzene (586.3 mg, 1 mmol), 1,4-benzenediboronic acid bis(pinacol) ester (330.0 mg, 1 mmol), Pd@SBA15 (177.4 mg, 0.01 mmol), $Cs_2CO_3$ (977.5 mg, 3 mmol) and N,N-dimethylacetamide (DMAc, 10 mL) was added to a 25 mL Schlenk flask. After three freeze-pump-thaw cycles, the tube was sealed under nitrogen atmosphere and stirred at 80 °C for 3 days. Subsequently, 1,4-benzenediboronic acid bis(pinacol) ester (165 mg, 0.5 mmol) and NHC-Pd[5] (7 mg, 0.01 mmol) were added *in situ*, and the reaction was continued for 24 h. The product was washed with methanol and collected with filtration to obtain pale yellow solid (318.6 mg, 78 %).

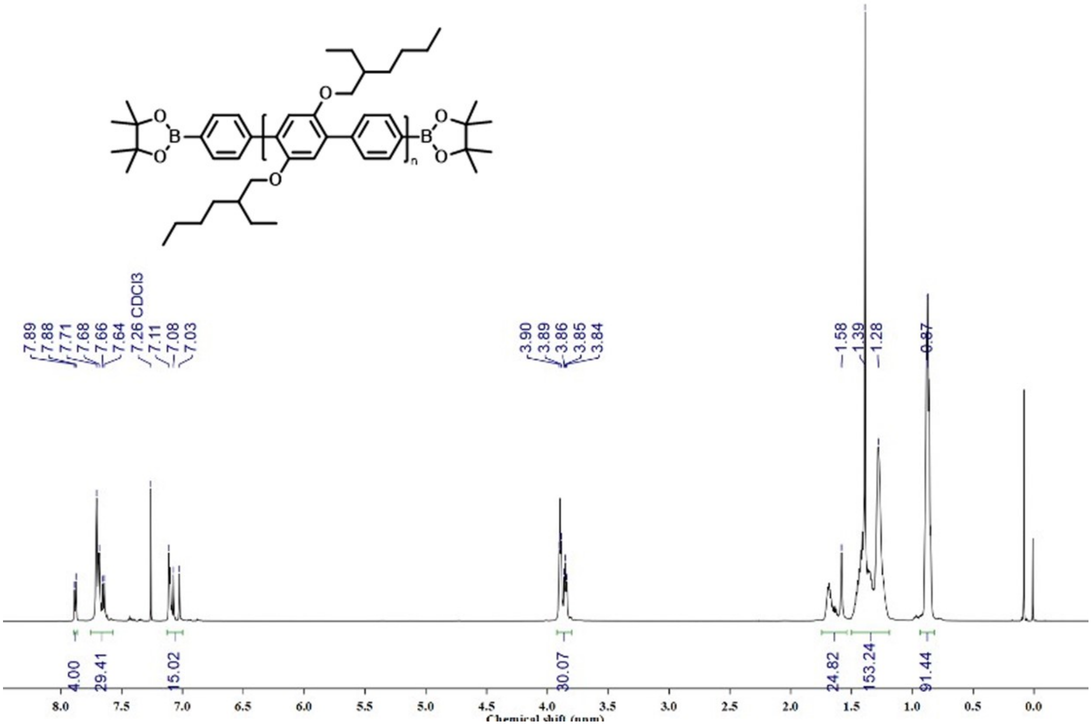


Figure S1. $^1H$ NMR spectrum of PPP

**HO-PPP-OH:** A mixture of PPP (258 mg, 0.07 mmol), hydrogen peroxide (6.5 ml, *wt* = 30%), NaOH (130 mg, 3.25 mmol) and THF (25 mL) were added to a 100 mL round-bottom flask. The mixture was stirred vigorously at room temperature for 10 h, and then concentrated under reduced pressure to remove residual THF. The crude residue was dissolved in DCM (30 mL), and the solution was washed with saturated aqueous NaCl solution (20 mL × 3). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated under vacuum to afford a white solid (212.1 mg, 85%).

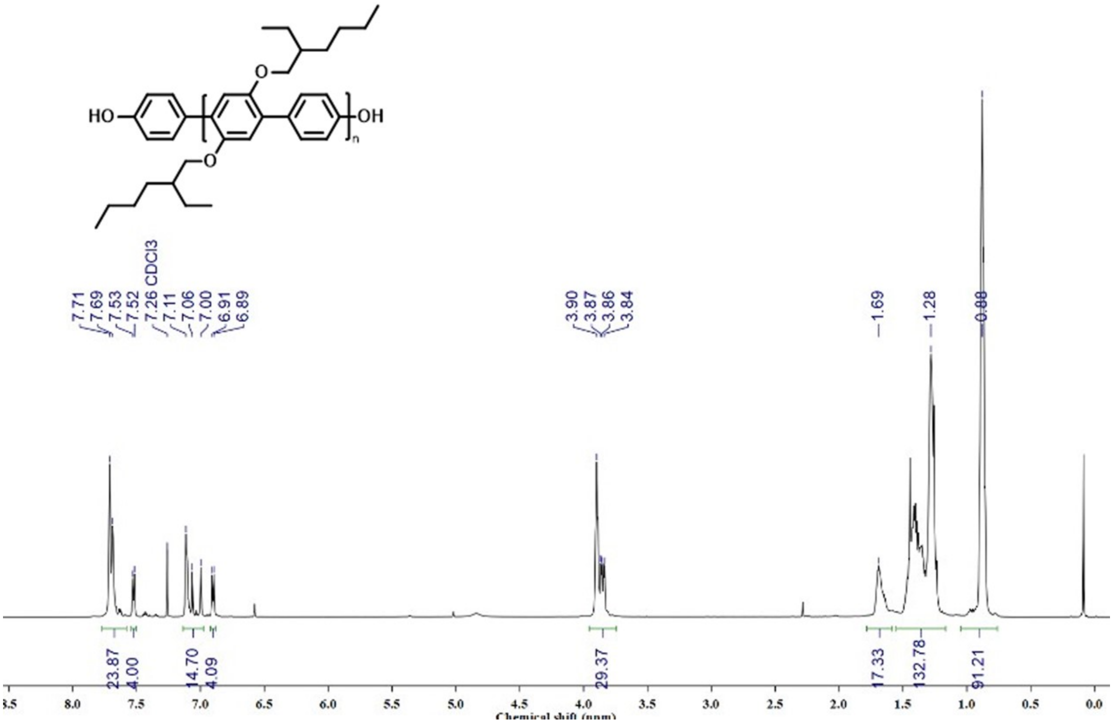


Figure S2. $^1H$ NMR spectrum of HO-PPP-OH

**Br-PPP-Br:** A mixture of HO-PPP-OH (212.1 mg, 0.07 mmol), DMAP (3.1 mg, 0.5 mmol), triethylamine (0.14 mL, 2 mmol) and DCM (10 mL) was placed in a 25 mL round-bottom flask cooled in an ice-water bath (0 °C). After stirring for 15 min, 2-bromoisobutyryl bromide (0.1 mL) was added dropwise, and the reaction was allowed to proceed at room temperature for 2 h. Upon completion, the mixture was precipitated with methanol, centrifuged, and the collected solid was dried under vacuum to afford the product as a light-yellow flaky solid (187 mg, 88% yield).

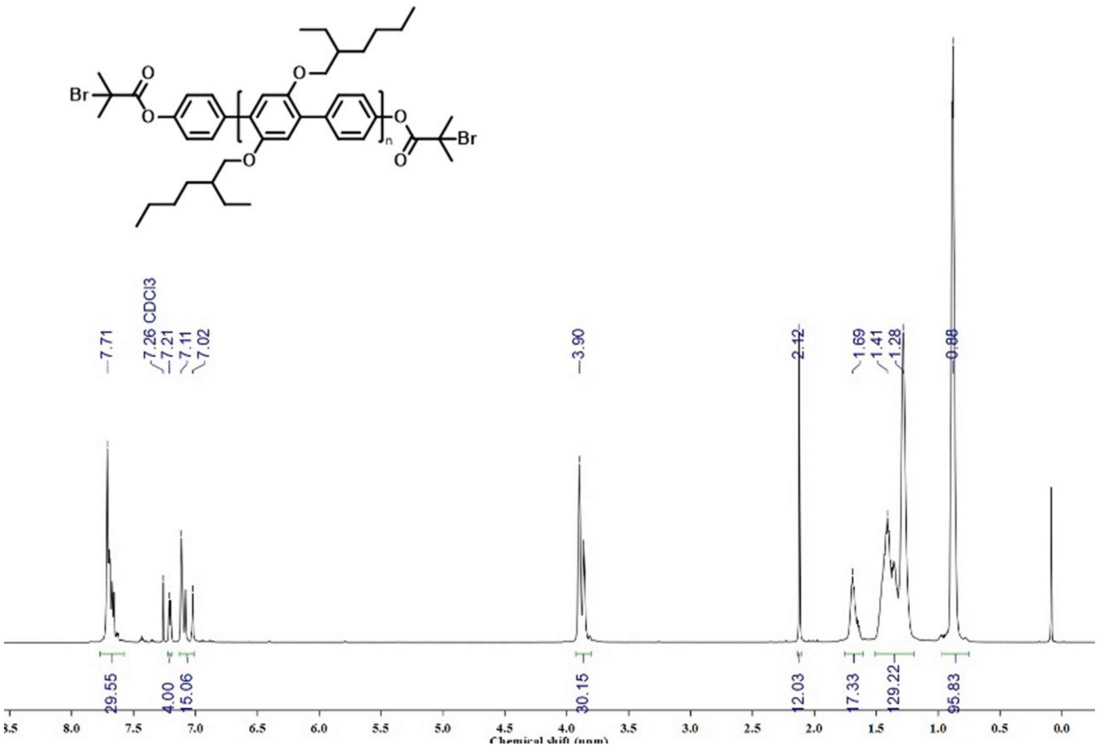


Figure S3. $^1$H NMR spectrum of Br-PPP-Br

**PDMAEMA-PPP-PDMAEMA:** Synthesis of PDMAEMA-PPP-PDMAEMA was given by taking PDMAEMA$_{12}$-PPP$_{16}$-PDMAEMA$_{12}$ as an example. In a 10 mL Schlenk flask, the macroinitiator Br-PPP-Br (35 mg, 0.01 mmol), DMAEMA (55 mg, 0.35 mmol), and HMTETA (6.9 mg, 0.03 mmol) were dissolved in anhydrous toluene (2 mL). The mixture was degassed by three freeze-pump-thaw cycles, after which CuBr (2.86 mg, 0.02 mmol) was added. The reaction was then stirred at 60 °C under a nitrogen atmosphere. After stirred for 20 h, it was rapidly cooled in an ice bath. The mixture solution was dialyzed by water to remove the residual Cu complexes and monomer and so on. After dialysis, the mixture solution was turned to a white emulsion. The product PDMAEMA-PPP-PDMAEMA was collected by freeze drying. Triblock copolymers with varying PDMAEMA block lengths were prepared by adjusting the monomer-to-macroinitiator feed ratio. Monomer : macroinitiator = 1:20 (BCP1), 1:35 (BCP2), 1:50 (BCP3), 1:80 (BCP4), 1:120 (BCP5), 1:200(BCP6).

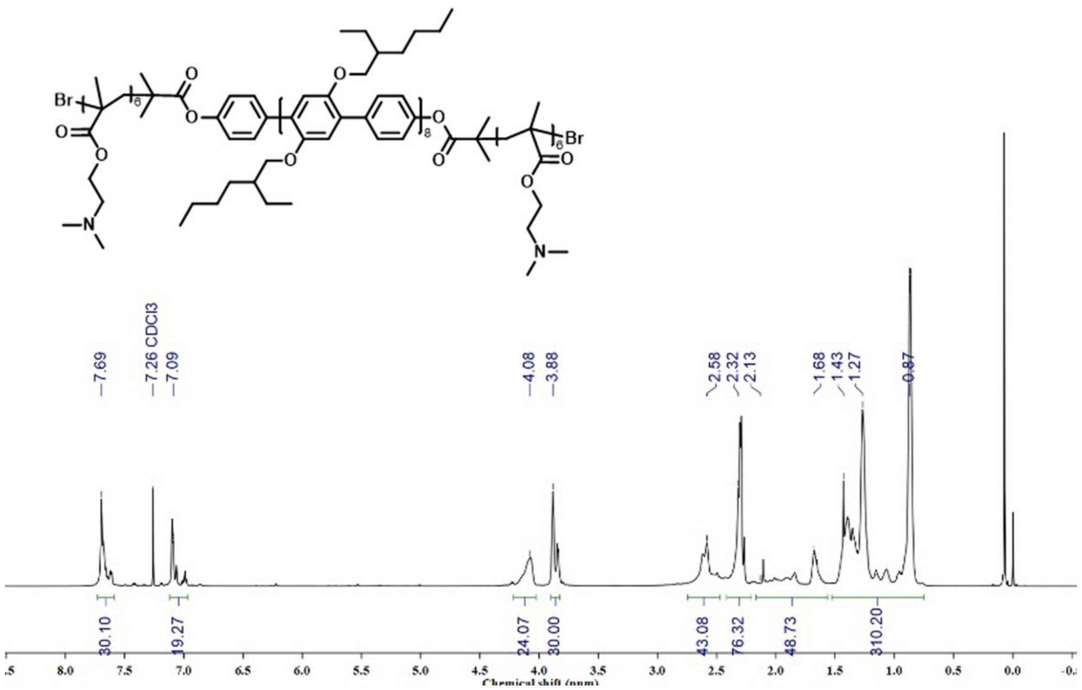


Figure S4.1. $^{1}$H NMR spectrum of BCP1.

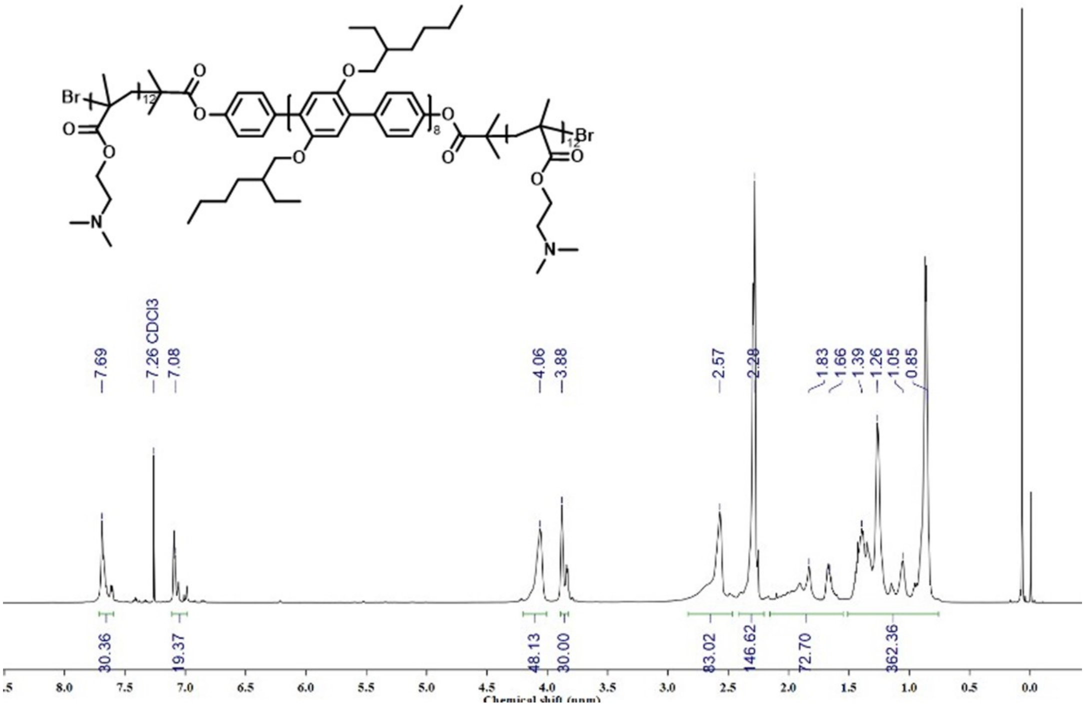


Figure S4.2. $^{1}$H NMR spectrum of BCP2.

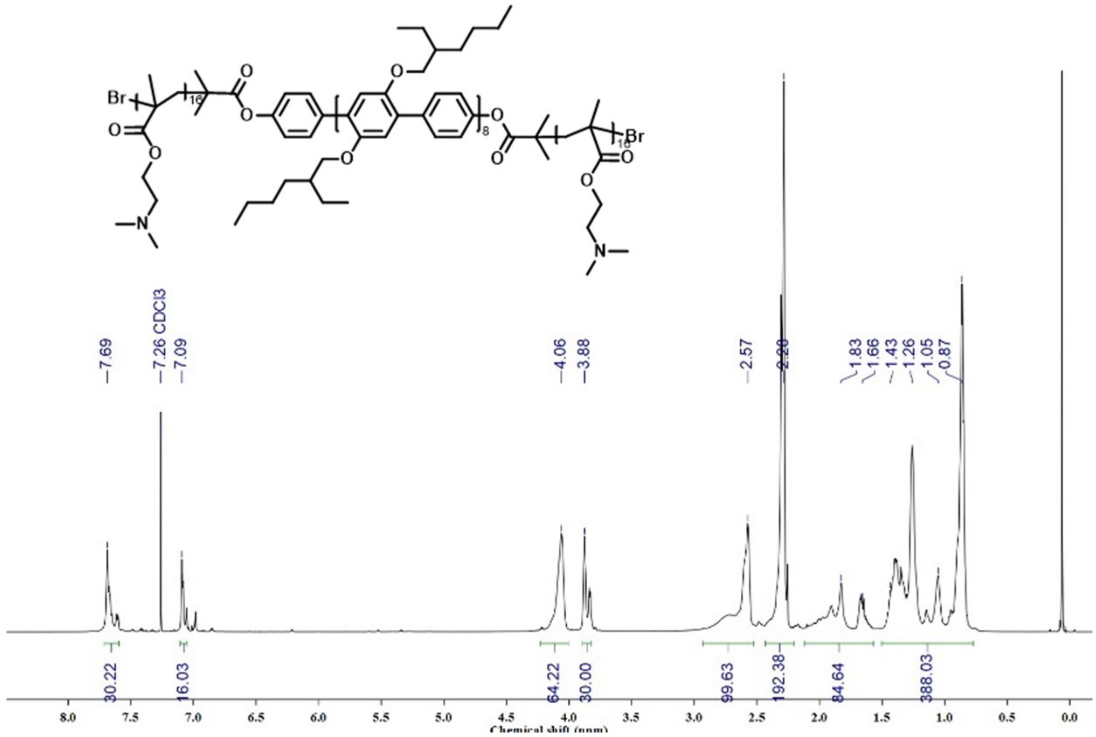


Figure S4.3. $^1$H NMR spectrum of BCP3.

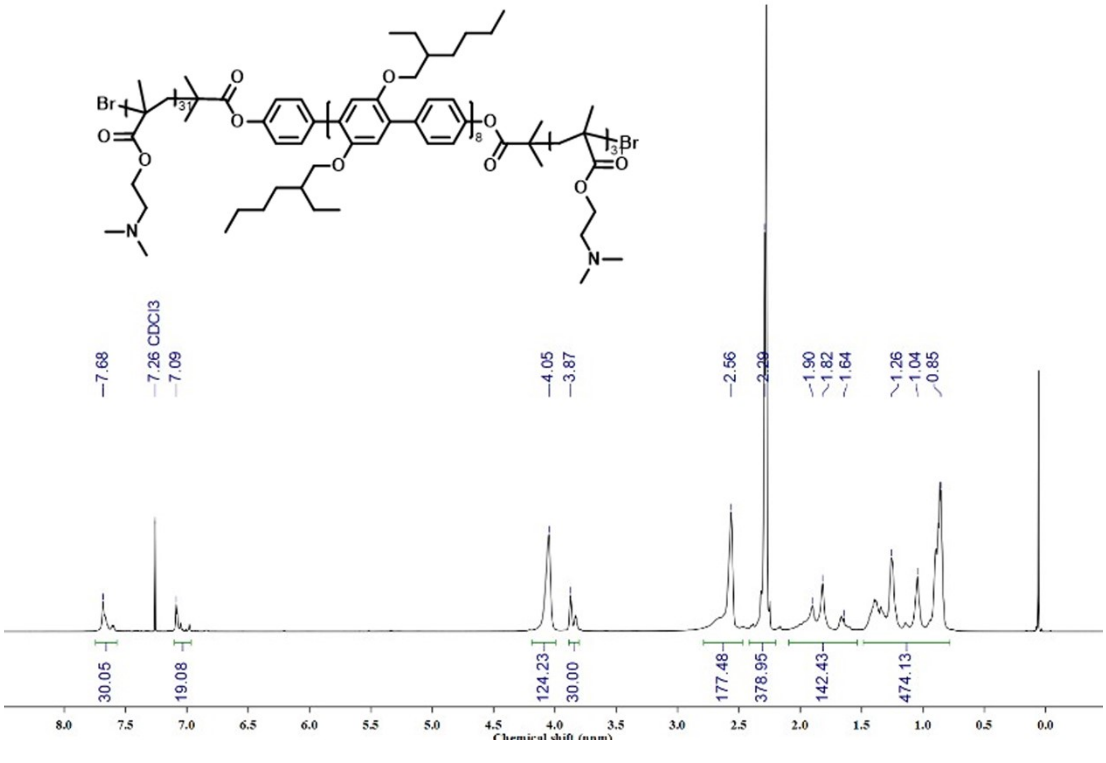


Figure S4.4. $^1$H NMR spectrum of BCP4.

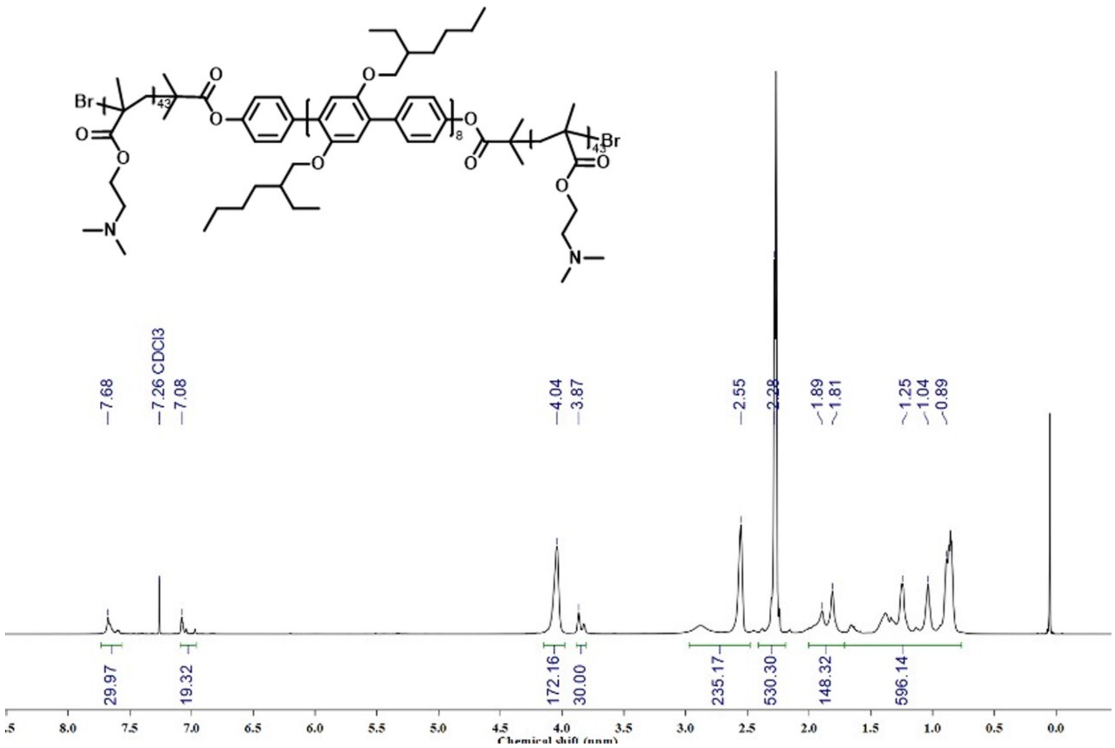


Figure S4.5. $^1$H NMR spectrum of BCP5.

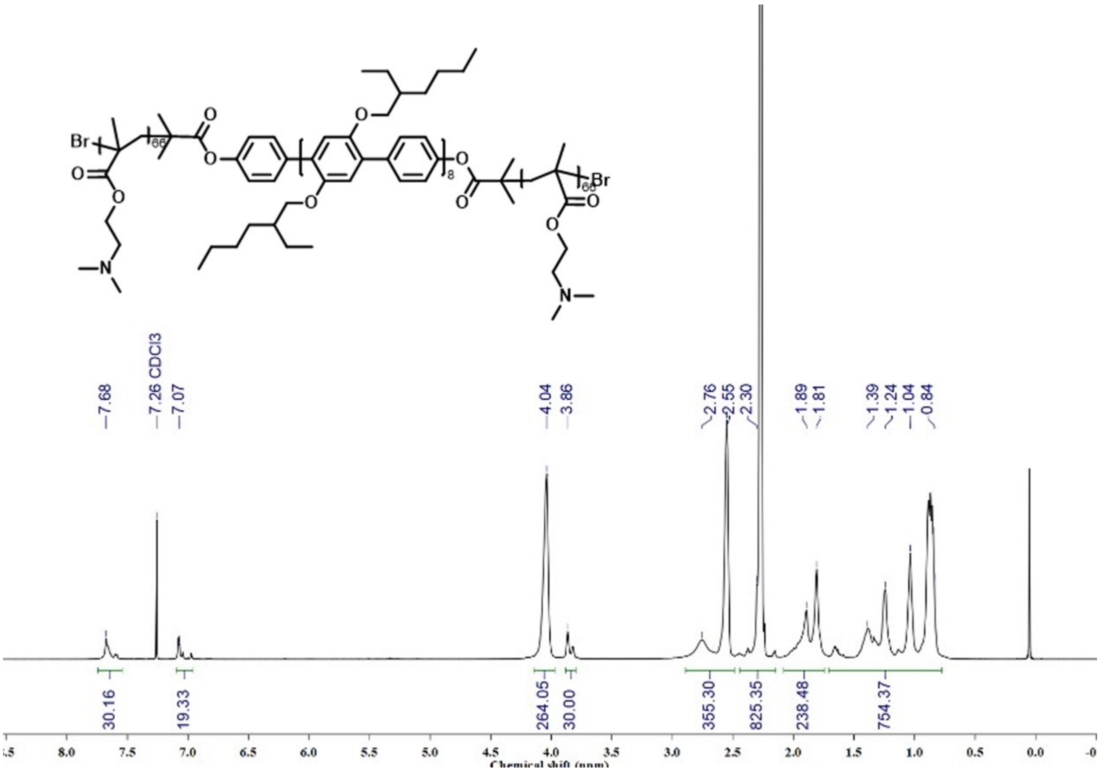


Figure S4.6. $^1$H NMR spectrum of BCP6.

## Crystallization-Driven Self-Assembly

### General self-assembly procedure for preparation of the micellar solutions

The micellar solution was prepared by first dissolving the PDMAEMA-b-PPP-b-PDMAEMA copolymer (0.25 mg $mL^{-1}$) in THF (1.2 mL), a good solvent for both blocks. Distilled water (1.8 mL) was then added dropwise (3ml $h^{-1}$) under vigorous stirring. This yielded a final micellar dispersion with a polymer concentration of 0.1 mg $mL^{-1}$ in a THF/water mixture (THF volume fraction $f_{THF} = 0.4$). Micellar solutions at different pH values were prepared analogously. The assembly pH was adjusted using aqueous NaOH or HCl, while a neutral reference was obtained using aqueous NaCl.

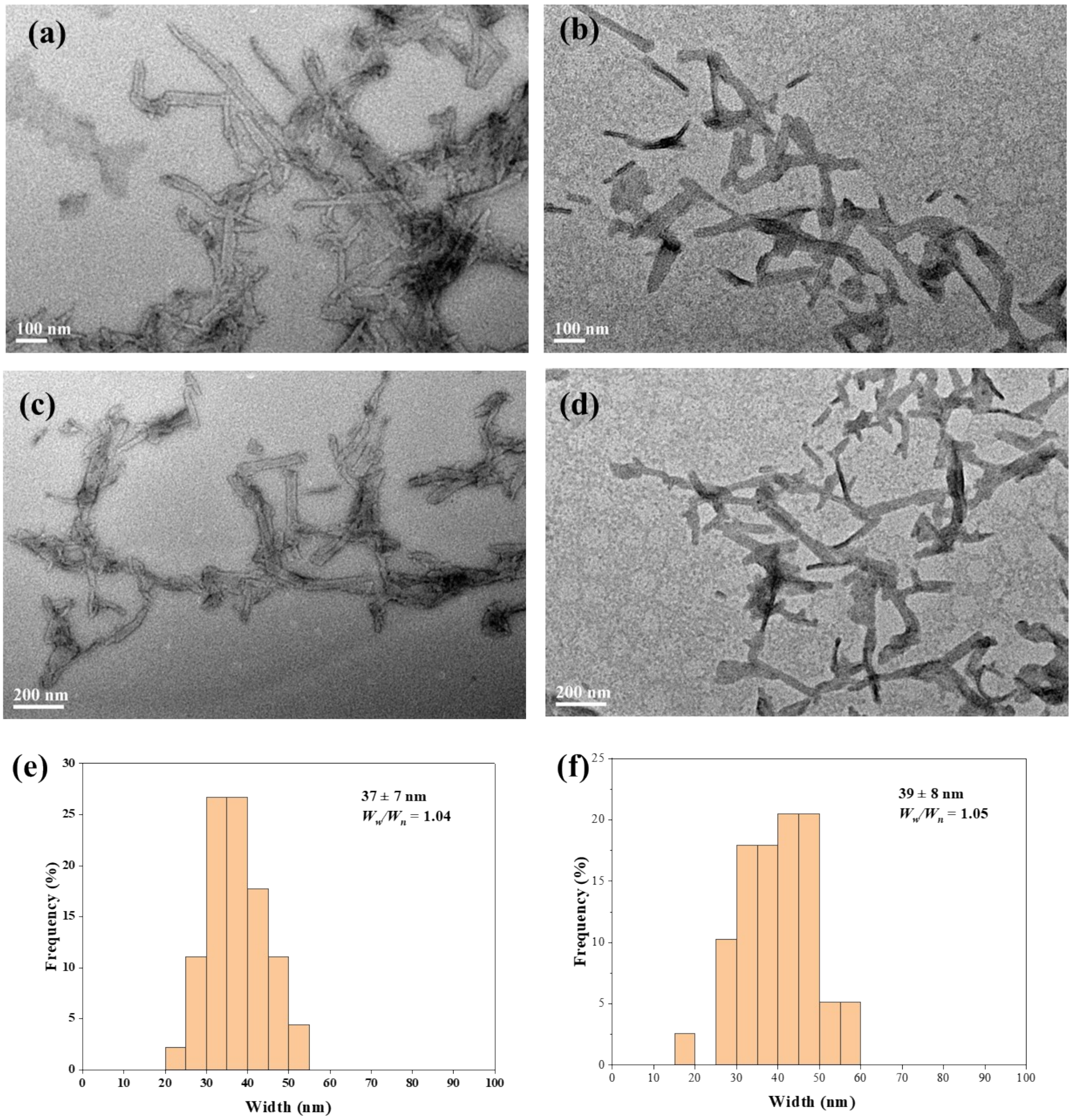


Figure S5. (a) and (c) TEM image of BCP1 micelle solution (0.1 mg mL$^{-1}$) in THF/$H_2O$ mixed solution. (b) and (d) TEM image of BCP2 micelle solution (0.1 mg mL$^{-1}$) in THF/$H_2O$ mixed solution. (e) Histogram showing the width distribution of BCP1. (f) Histogram showing the width distribution of BCP2.

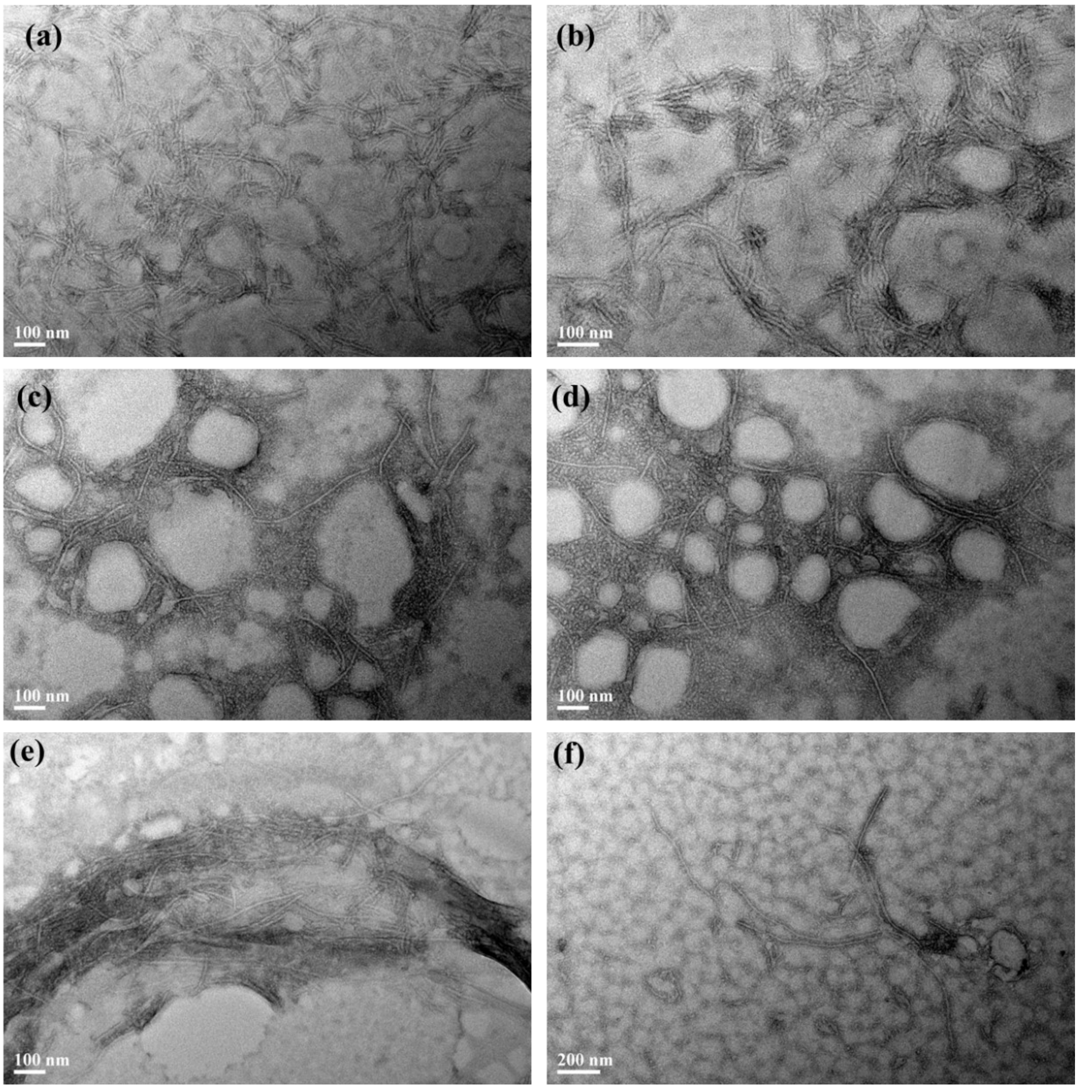


Figure S6. TEM images of the micelles of triblock copolymers dispersed in THF/water (0.1 mg $mL^{-1}$): BCP3 (a) and (b); BCP4 (c) and (d); BCP5 (e) and (f).

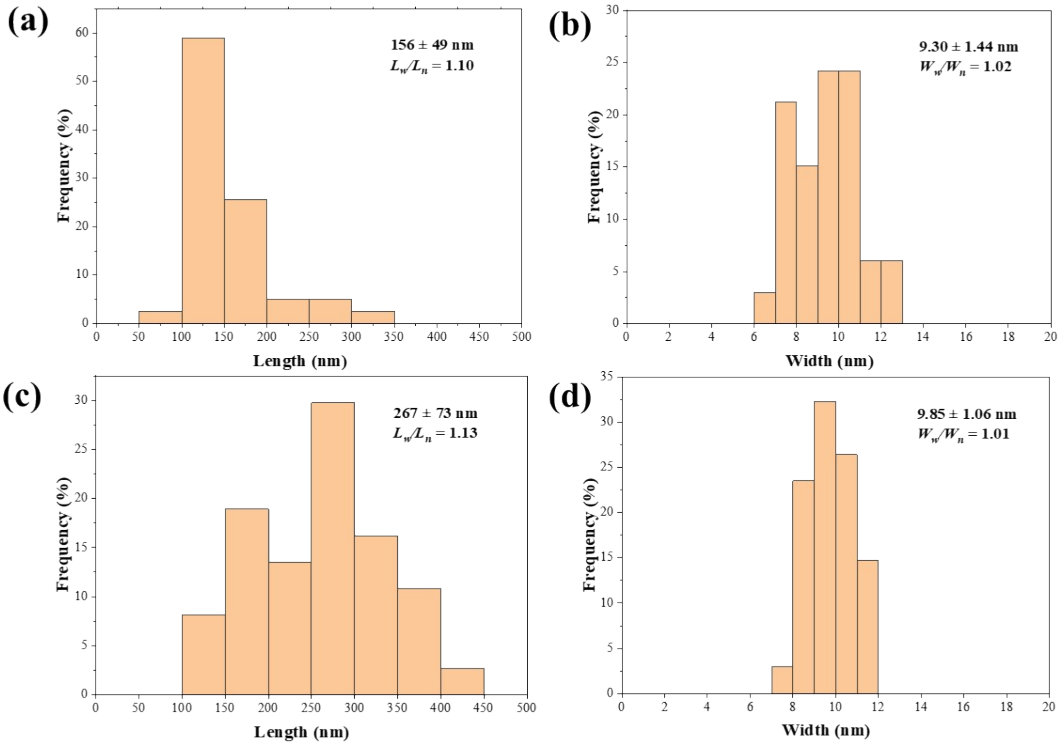


Figure S7. Histogram showing the length and width distribution of the fiber-like micelles. BCP3 (a) and (b); BCP4 (c) and (d).

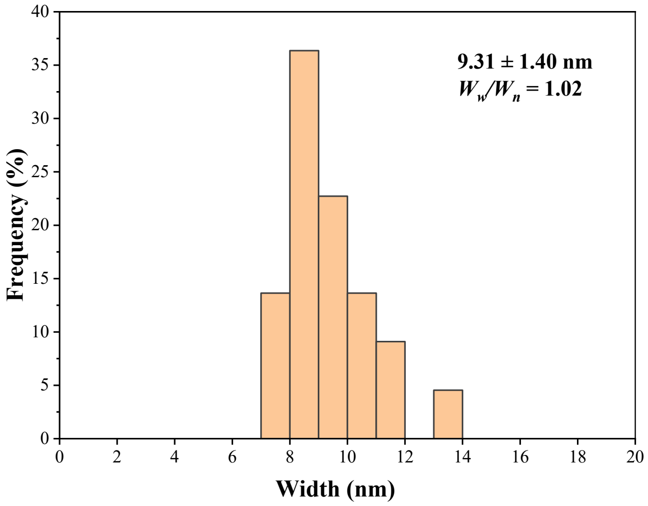


Figure S8. Histogram showing the fiber width distribution of the BCP5. For BCP5, cylindrical micelles were scarce; statistical analysis was therefore restricted to well-defined, individual fibers with unambiguous termini, precluding reliable determination of length dispersity.

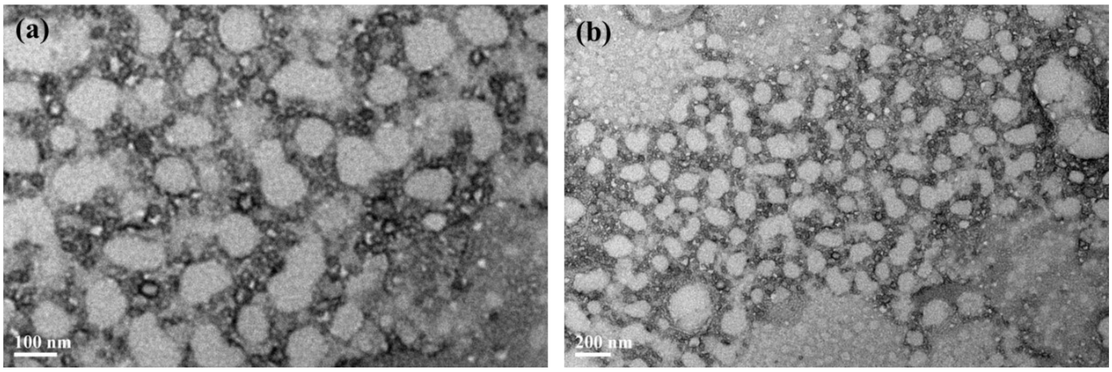


Figure S9. TEM images of the micelles of triblock copolymers BCP6 dispersed in THF/water (0.1 mg $mL^{-1}$).

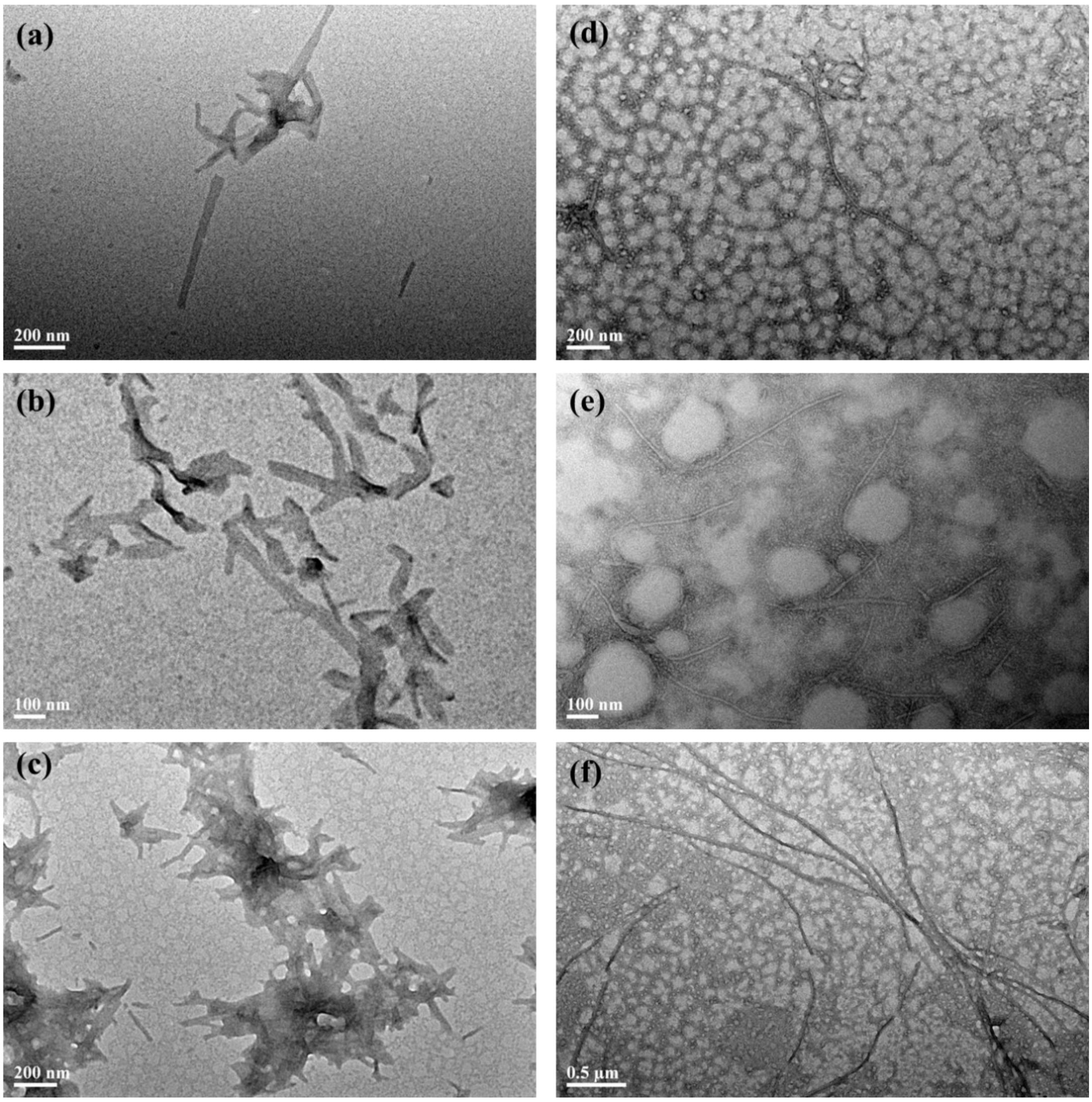


Figure S10. TEM images of micelles assembled under acidic (pH = 4), neutral (pH = 7) and basic (pH = 10) conditions: (a) BCP2, pH = 4; (b) BCP2, pH = 7; (c) BCP2, pH = 10; (d) BCP4, pH = 4, (e) BCP4, pH = 7, (f) BCP4, pH = 10. The assembly pH was adjusted using aqueous NaOH or HCl, while a neutral reference was prepared using aqueous NaCl solution.

## References

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