Supporting Information for

Solution self-assembly of polycarbonate block copolymers containing crystalline side chain

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EXPERIMENTAL SECTION

Materials and Characterizations.

Materials. 1-Dodecanethiol, potassium phosphate tribasic, carbon disulfide, 1-(4-Chlorophenyl) ethanol, sodium chloride，anhydrous $MgSO_4$, Trimethylolpropane (TMP), octadecanoic acid, 4-dimethylaminopyridine (DMAP), dichloromethane were purchased from ALADDIN and used as received. 3-(3-Dimethylaminopropyl)-1-ethylcarbodiimide hydrochloride (EDCI), propyl chloroformate, triethylamine, 1,8-Diazabicyclo [5.4.0] undecane-7-ene (DBU), ethyl acetate, petroleum ether were purchased from Damas-beta and used as received. Acetone was used as received without further purification. Analytical thin layer chromatography (TLC) was carried on silica gel plates produced by Yantai chemical industry and Column chromatography was using silica gel in 200-300 mesh. Toluene was distilled twice under vacuum over calcium hydride before use. Tetrahydrofuran was distilled twice under vacuum over anhydrous magnesium sulfate before use. *N*, *N*-dimethylacrylamide (DMA) and 1,4-dioxane were purified by passing through a column of basic alumina before use. 2,2'-Azobis(2-methylpropionitrile) (AIBN) was recrystallized twice from methanol and stored in the dark at 4 °C. Other reagents were was filtered twice through a 0.22 μm organic solvent-resistant filter before use.

Sample Synthesis

Synthesis of Chain Transfer Agent (CTA).

1-Dodecanethiol (3.06 ml, 12.8 mmol), potassium phosphate tribasic (3.0 g, 14.0 mmol) and carbon disulfide (2.3 ml, 40.0 mmol) were dissolved in 2-propanone (50 ml)

and placed in a 100 ml reaction flask. After stirring for 2 hours, 1-(4-Chlorophenyl) ethanol (2 g, 12.8 mmol) was added in the reaction mixture. After stirring for 3 days, the reaction mixture was separated. After evaporation of the solvent under reduced pressure, the reaction mixture was dissolved in a minimal volume of dichloromethane and the solution was washed with saturated sodium chloride (NaCl) solution three times. The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. The crude was finally purified by column chromatography (ethyl acetate/petroleum ether 1:4 v/v) and 4.2 g of pure product was obtained. Yield: 78.62 %.

Synthesis of 2,2-bis(hydroxymethyl)butyl stearate (MC18C).

Trimethylolpropane (TMP) (8.76 g, 64 mmol), octadecanoic acid (3.83 g, 12.8 mmol), 4-dimethylaminopyridine (DMAP) (0.16 g, 1.28 mmol) and 3-(3-Dimethylaminopropyl)-1-ethylcarbodiimide hydrochloride (EDCI) (3.76g, 19.2 mmol) were dissolved in dichloromethane (140 ml) and placed in a 200 ml reaction flask. The reaction was stopped after 24 hours. After evaporation of the solvent under reduced pressure, the mixture was resuspended in ethyl acetate to precipitate hydrated EDC salts and the excess of triol. The reaction mixture was finally purified by column chromatography (ethyl acetate/petroleum ether 1:4 v/v) and 2.77 g of pure product was obtained. Yield: 54.01 %.

Synthesis of (5-ethyl-2-oxo-1,3-dioxan-5-yl) Methyl Stearate (TMC18C).

In a flame dried flask under an argon atmosphere were introduced 1.56 g (3.9 mmol) of MC18C molecule and 40 ml of dry tetrahydrofuran. The mixture was stirred

for dissolution of the solids and an ice bath was then set. 1.12 mL (11.7 mmol) of propyl chloroformate were subsequently injected in the flask, followed by 1.64 mL (11.7 mmol) of triethylamine (NEt_3). The mixture was stirred for 24 hours at room temperature. Tetrahydrofuran was evaporated under reduced pressure and the residue was resuspended in dichloromethane. After washing the organic solution twice with brine and drying over anhydrous $MgSO_4$, the solvent was then removed. The white residue was then purified by column chromatography (ethyl acetate/petroleum ether 1:4 v/v) and 1.41 g of pure (5-ethyl-2-oxo-1,3-dioxan-5-yl) methyl stearate were obtained. Yield: 84.83 %.

Synthesis of Poly((5-ethyl-2-oxo-1,3-dioxan-5-yl) Methyl Stearate) (PTMC18C).

In a glove box filled with nitrogen, (5-ethyl-2-oxo-1,3-dioxan-5-yl) methyl stearate (TMC18C) (400 mg, 0.94 mmol), CTA (chain transfer agent) (9.35 mg, 0.023 mmol), 1,8-Diazabicyclo [5.4.0] undecane-7-ene (DBU) (3.57 mg, 0.023 mmol) and toluene solution (2 mL) were mixed in a 10 mL ampoule. The mixture was then stirred at 80 ℃ for 72 h. After three precipitations in ice-cold methanol, the product was collected by centrifugation and then dried under vacuum. The composition was calculated from ^{1}H NMR by analysis of the specific peaks belonging to PTMC18C, yielding $PTMC18C_{38}$. Yield: 57.31 %.

Synthesis of PTMC18C-*b*-PDMA Block Copolymers.

In a typical experiment, $PTMC18C_{38}$ (100 mg, 0.0057 mmol), DMA (68.16 mg, 0.69 mmol) and AIBN (0.82 mg, 0.005 mmol) were dissolved in 1,4-Dioxane (2 mL) and placed in an ampoule. The solution was then subjected to three freeze-pump-thaw

cycles and was heated at 80 °C for 24 h. The reaction was subsequently quenched by immersion of the ampoule in liquid nitrogen and the block polymer was precipitated thrice in ice-cold ethoxyethane before being dried under vacuum. The degree of polymerization of each block was calculated using the corresponding ^{1}H NMR spectra by analysis of the specific peaks belonging to PTMC18C and PDMA, yielding PTMC18C$_{38}$-*b*-PDMA$_{157}$ as a white solid. Yield: 68.33 %.

The synthetic process of the other block copolymers such as PTMC18C$_{38}$-*b*-PDMA$_{385}$ was similar to PTMC18C$_{38}$-*b*-PDMA$_{157}$. Detailed molecular characterizations were summarized in **Table S1**.

Self-Assembly of BCPs in Selective Solvents.

Solution self-assembly of BCPs in selective solvents was subjected to a heating-cooling-aging process. In a typical experiment, with PTMC18C$_{38}$-*b*-PDMA$_{157}$ as an example, PTMC18C$_{38}$-*b*-PDMA$_{157}$ (5 mg) was added to 1 mL of MeOH (5.0 mg mL^{-1}) in a 5 mL vial. The sample was heated at 65 °C for 3 h without stirring. Then the solution was slowly cooled to room temperature (25 °C) with cooling time scale of about 100 min (0.4 °C/min) and aged at room temperature for 3 or 5 days. Small aliquots were obtained from the solution to study the final self-assembled nanostructures.

Characterization Techniques.

Nuclear Magnetic Resonance (NMR). ^{1}H NMR spectra (400 MHz) of polymers were recorded at 40 °C on a BRUKER AVANCE AV400MHz using $CDCl_3$ as solvent.

Size-Exclusion Chromatography (SEC). SEC analysis was performed on a

Waters system fitted with an RI detector and equipped with a PLGel 3 μm (50 × 7.5 mm) guard column and two PLGel 5 μm (300 × 7.5 mm) mixed-D columns using THF as the eluent at a flow rate of 1.0 mL min−1. SEC data were calculated against PMMA standards and analyzed using Cirrus v3.3 software.

Differential Scanning Calorimetry (DSC). DSC analysis was carried out under N_2 gas at a scan rate of 10 °C min^{-1} with Q2000 model devices from TA Instruments.

Small Angle X-ray Scattering (SAXS). The SAXS measurement of the powder of the solid BCP samples was performed on the BL16B1 beamline at Shanghai Synchrotron Radiation Facility (SSRF) with an X-ray wavelength of 1.24 Å and sample to detector distance of 2 m. The detector distance was calibrated using a silver behenate standard sample.

Wide Angel X-ray Diffraction (WAXD). WAXD analysis was performed using an X-ray powder diffractometer purchased from Bruker AXS Ltd using Cu Kα (λ = 0.154 nm) radiation with a 2θ range of 3–60°.

Dynamic light scatter (DLS). The particle size of PTMC18C_{38}-*b*-PDMA_{157} platelets in MeOH at different temperature, and particle size distributions as a function of aging time were measured by dynamic light scattering (DLS) using a Horiba Zetasizer apparatus (LB-550 V) equipped with a 5.0 mW laser diode operating at λ = 650 nm at 25 °C. The apparent hydrodynamic radius (R_h) at different heating temperatures was immediately obtained from the Zetasizer Software (ZS) appendant to the DLS measurement by automatic analysis of the intensity correlation function.

Transmission Electron Microscope (TEM). Samples for TEM analysis were

prepared by drop casting 30 μL of micellar solution onto a carbon-coated copper grid placed on filter paper. Samples were all stained with 1 wt% uranyl acetate in methanol. Imaging of samples was performed using a JEM-1400 flash transmission electron microscope operating at 90 kV.

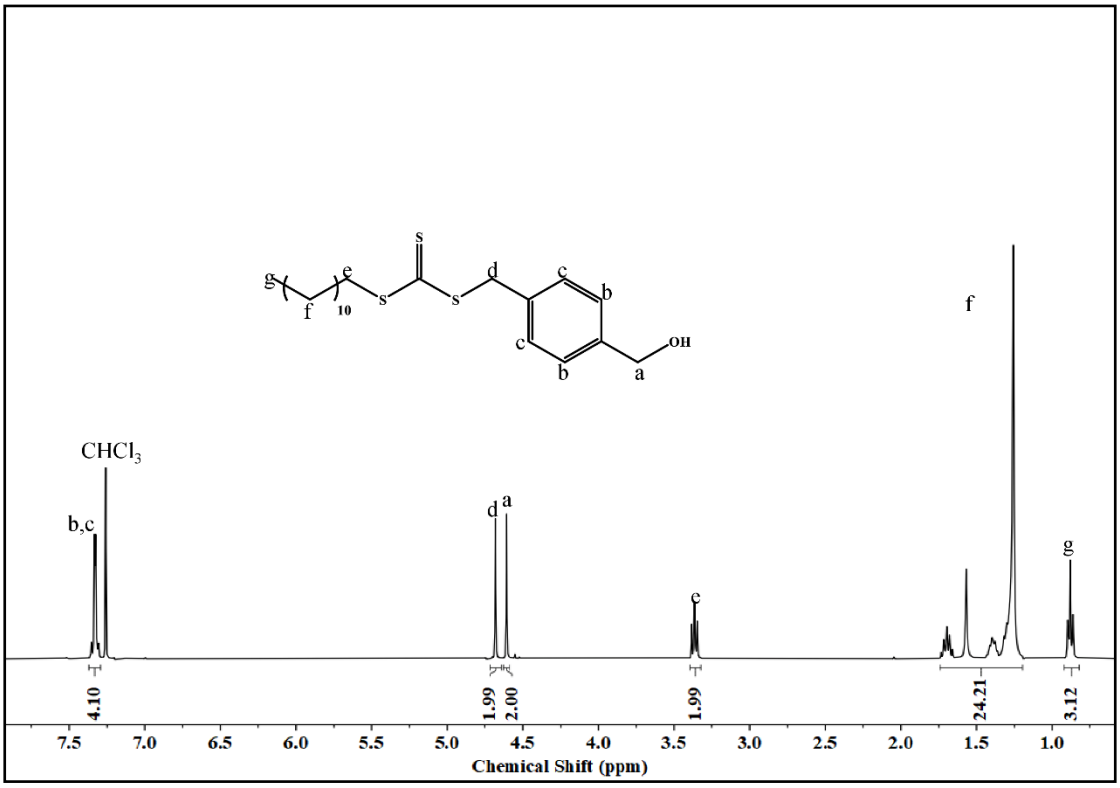

Figure S1. ^{1}H NMR spectrum of CTA in $CDCl_3$ solution.

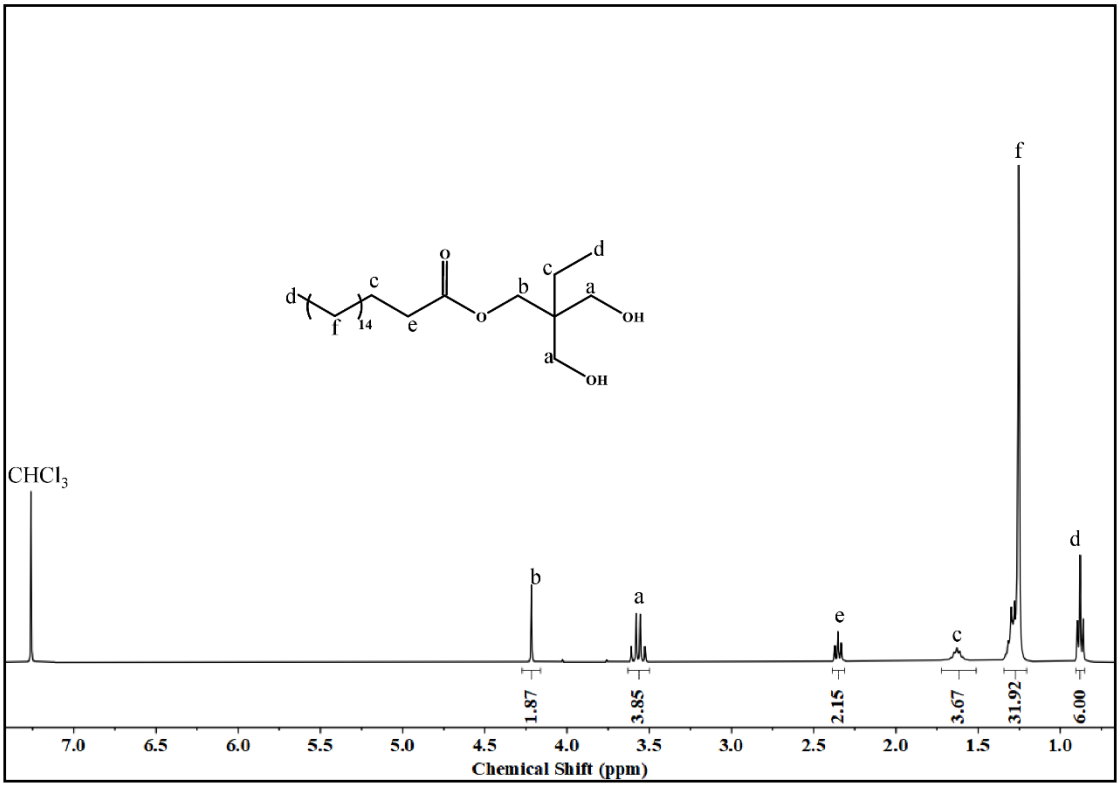

Figure S2. ^{1}H NMR spectrum of MC18C in $CDCl_3$ solution.

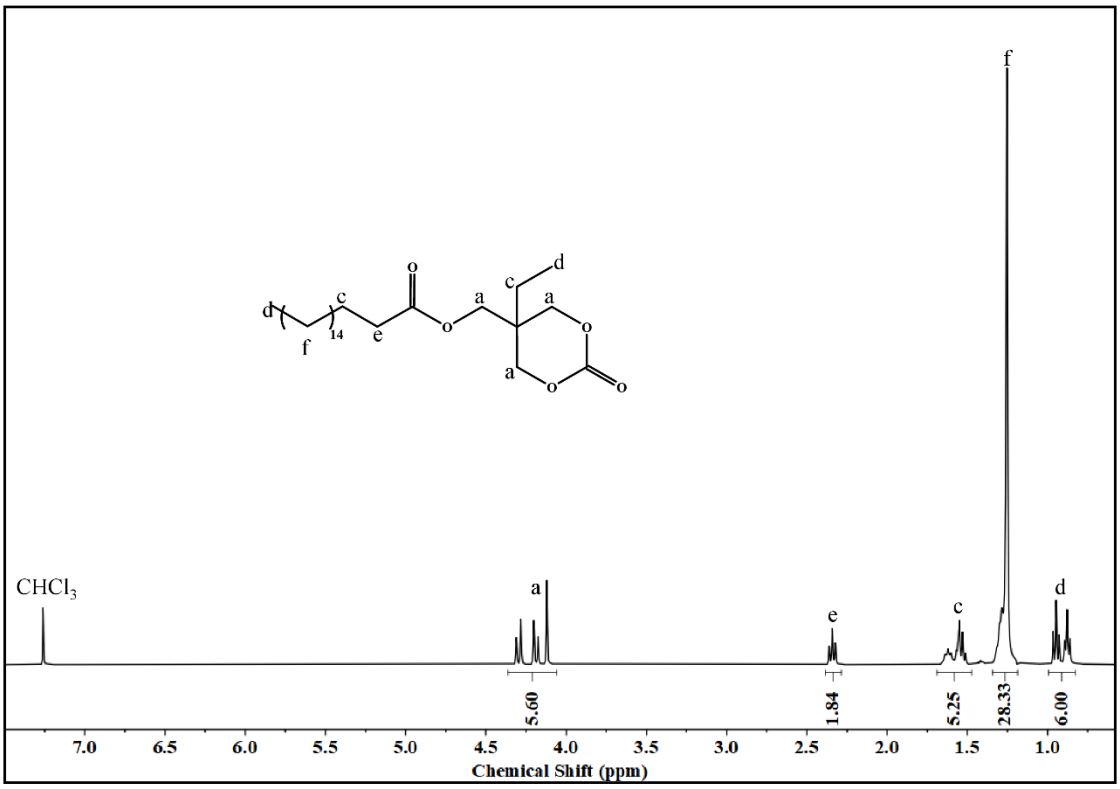

Figure S3. ^{1}H NMR spectrum of TMC18C in $CDCl_3$ solution.

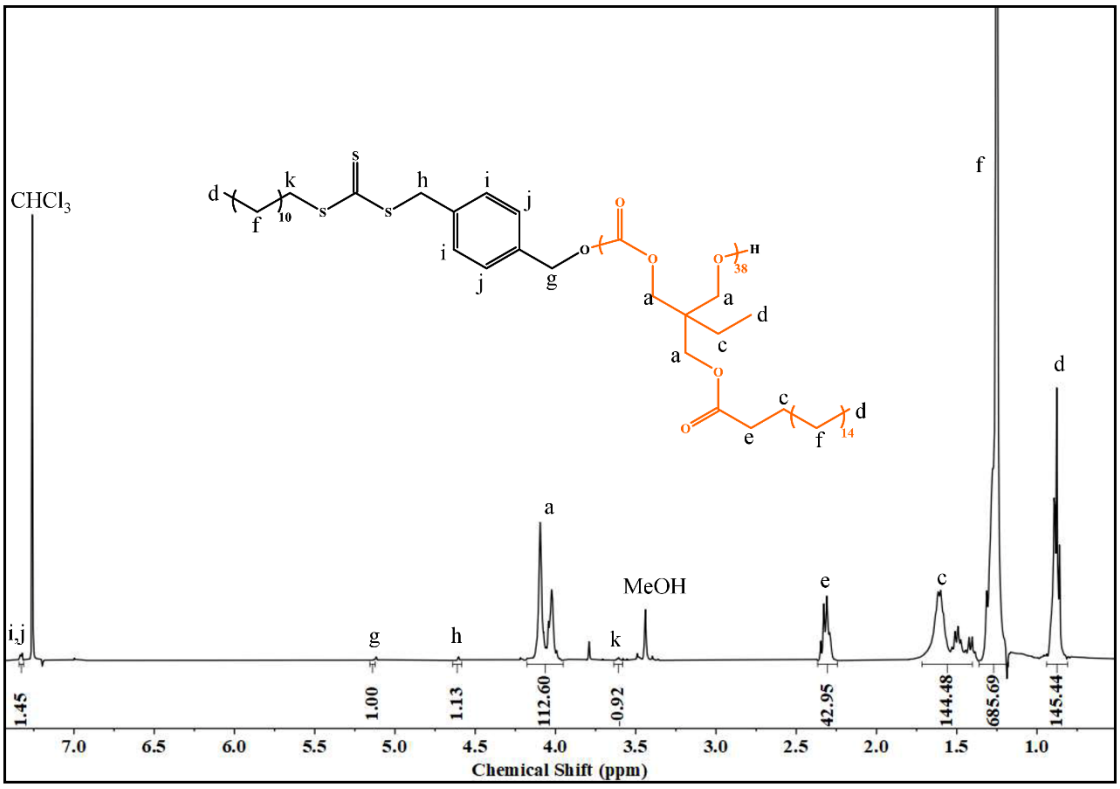

Figure S4. ^{1}H NMR spectrum of $PTMC18C_{38}$ in $CDCl_3$ solution.

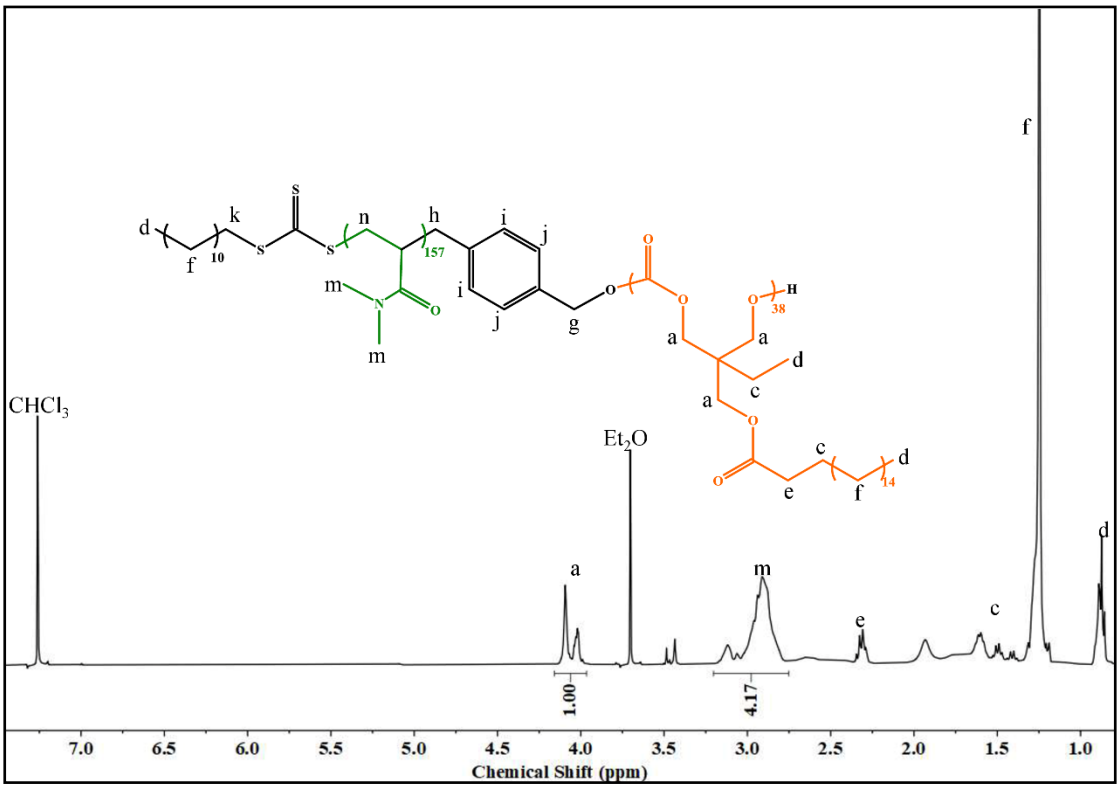

Figure S5. ^{1}H NMR spectrum of PTMC18C$_{38}$-*b*-PDMA$_{157}$ in $CDCl_3$ solution.

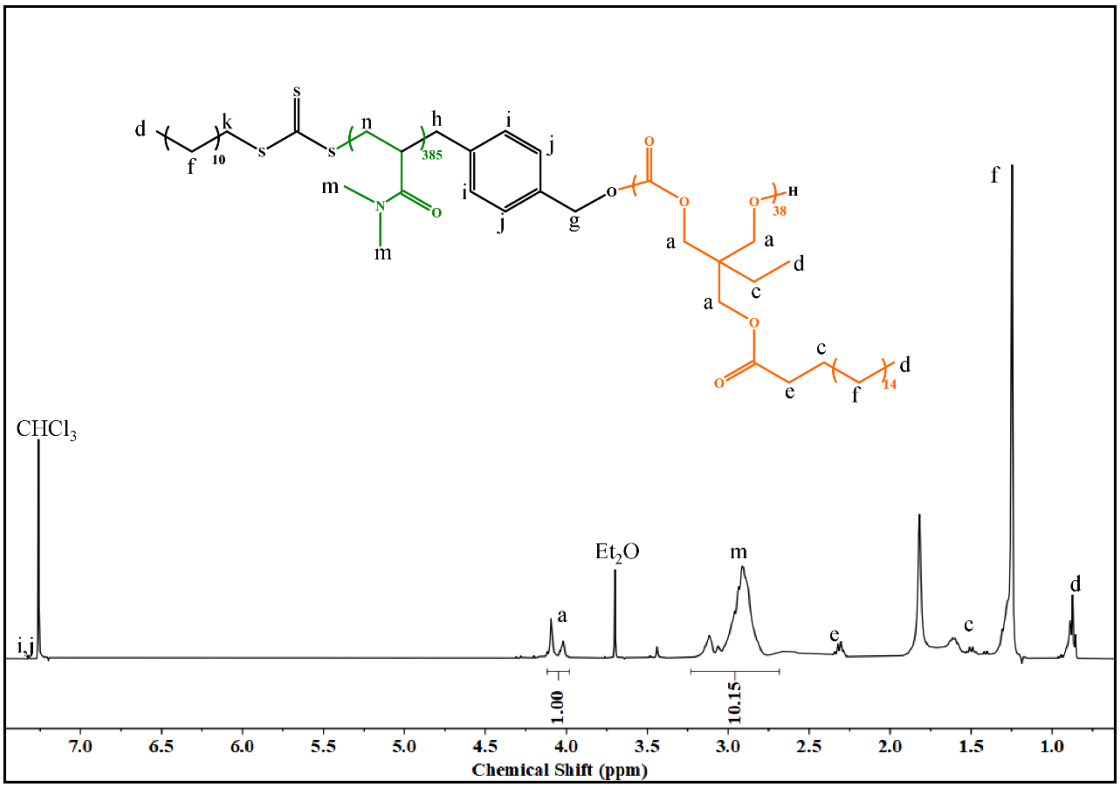

Figure S6. ^{1}H NMR spectrum of PTMC18C$_{38}$-*b*-PDMA$_{385}$ in $CDCl_3$ solution.

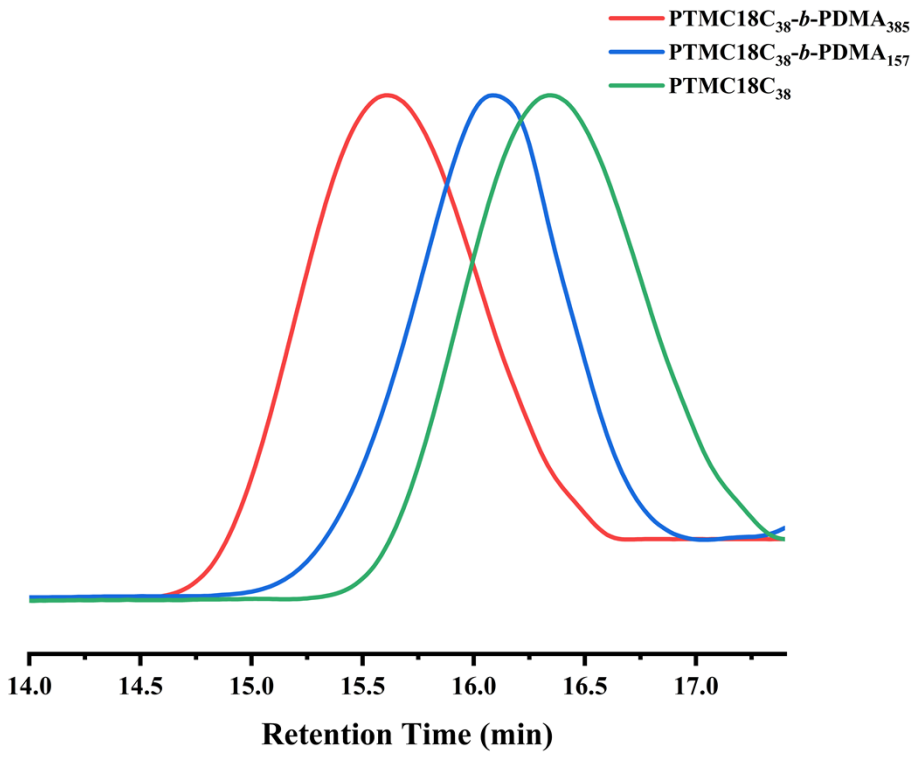

Figure S7. SEC traces of PTMC18C_{38} homopolymer and its corresponding block copolymers with different PDMA block length (refractive index detector, THF as eluent, 50 °C, PMMA standards).

Table S1. Molecular Characterization Data of Synthesized Polymers.

Polymer Composition [b]	$Đ_M$ (M_w/M_n) [a]	M_n (kDa) [b]
PTMC18C_{38}	1.19	17.5
PTMC18C_{38}-*b*-PDMA$_{157}$	1.17	33.0
PTMC18C_{38}-*b*-PDMA$_{385}$	1.14	55.6

[a] $Đ_M$ were measured by SEC using THF as eluent.

[b] Number-average molecular weights and polymer compositions were measured from ^{1}H NMR spectra.

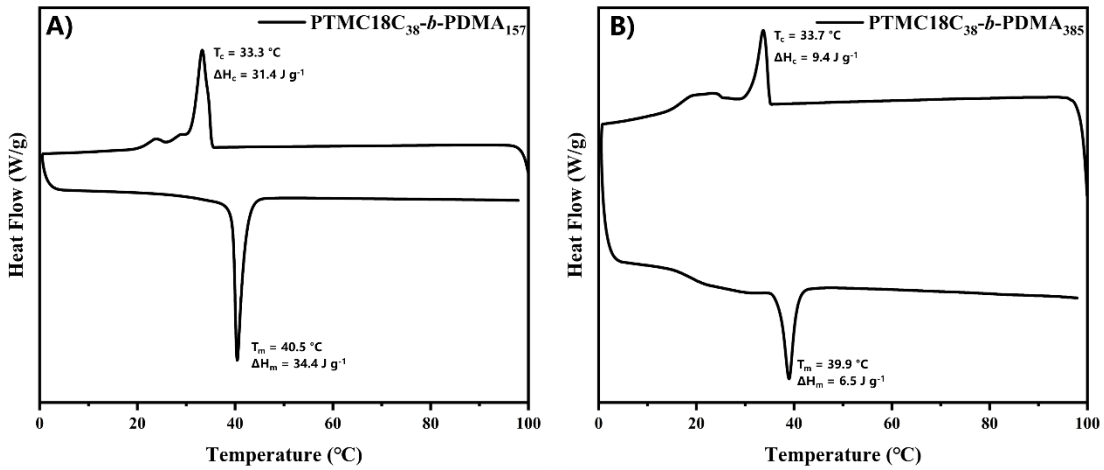

Figure S8. DSC cooling and second heating curves of (A) PTMC18C_{38}-*b*-PDMA_{157}, (B) PTMC18C_{38}-*b*-PDMA_{385}. The samples were first heating to 100 °C and annealing for 5 min to remove thermal history, and then cooling to 0 °C and further heating to 100 to record the cooling and second heating scans. Both the cooling and heating scans were 10 °C/min.

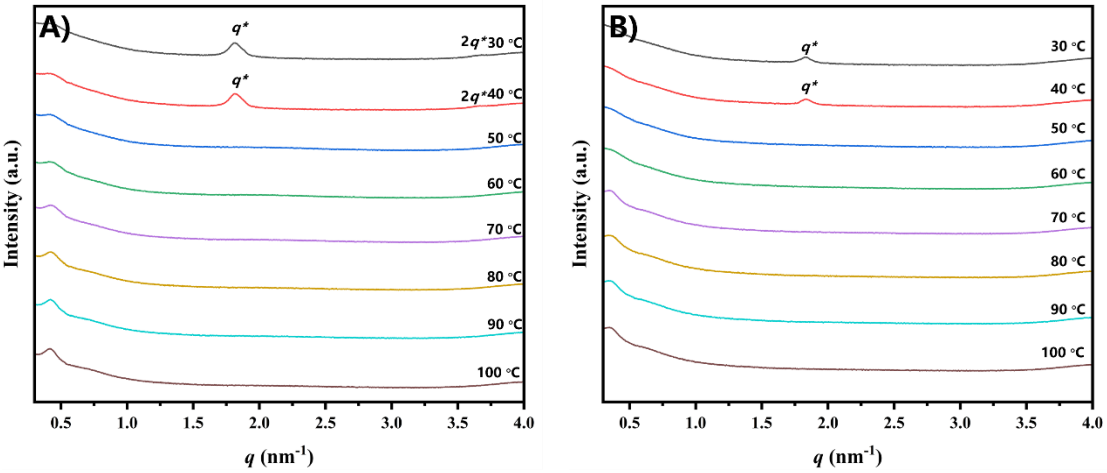

Figure S9. Temperature-dependent SAXS profiles of (A) PTMC18C_{38}-*b*-PDMA$_{157}$, (B) PTMC18C_{38}-*b*-PDMA$_{385}$ at different temperatures upon a heating process. Noting that the heating rate is 10 °C/min.

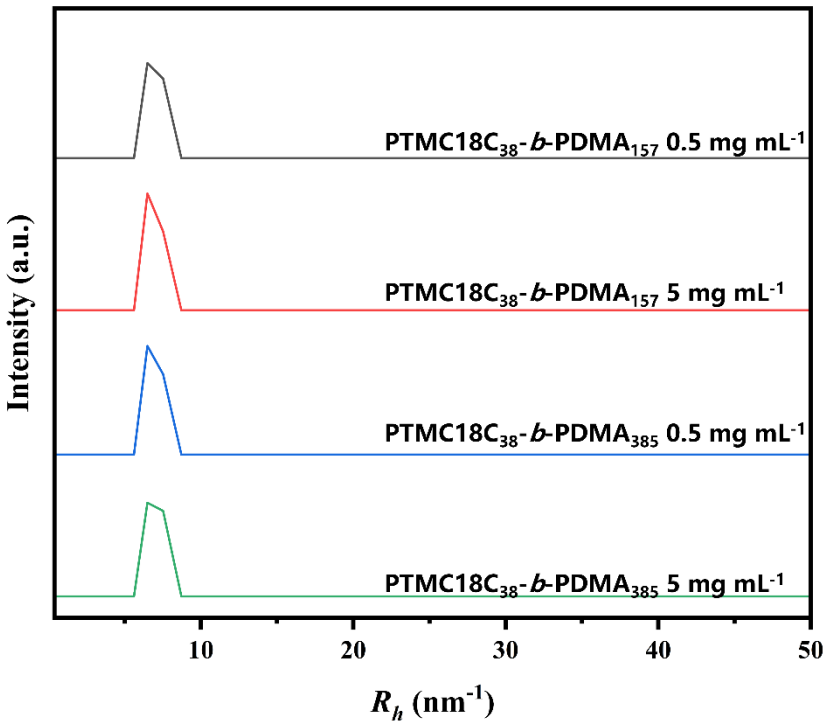

Figure S10. DLS profiles of PTMC18C$_{38}$-*b*-PDMA$_{157}$ and PTMC18C$_{38}$-*b*-PDMA$_{385}$ methanol solution at 65 °C.

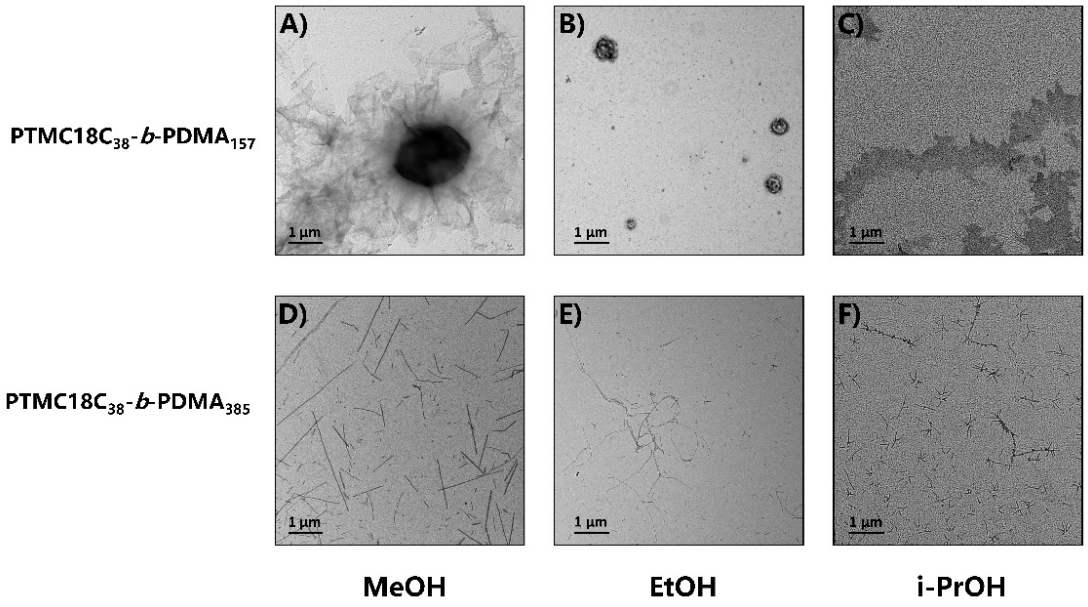

Figure S11. Representative TEM images of different micellar morphologies obtained via solution self-assembly of (A-C) PTMC18C_{38}-*b*-$PDMA_{157}$ and (D-F) PTMC18C_{38}-*b*-$PDMA_{385}$ in (A, D) MeOH, (B, E) EtOH, (C, F) i-PrOH at their respective boiling points for 3 h prior to cooling to room temperature (25 °C) and aging for 3 days. The polymer concentration during self-assembly was fixed as 5.0 mg mL^{-1}. All the TEM samples were stained with uranyl acetate (1 wt%).

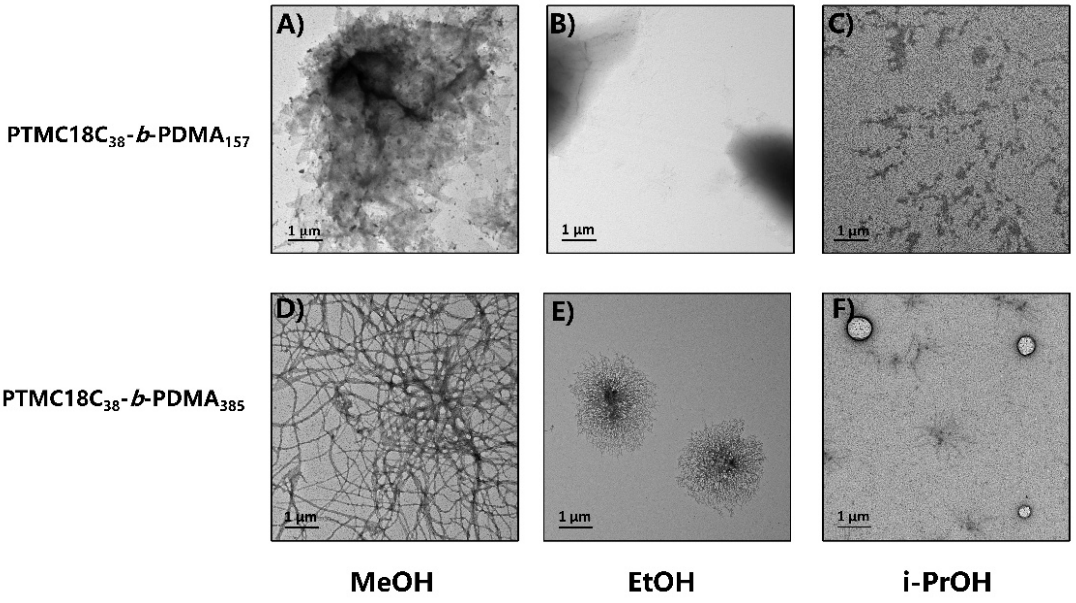

Figure S12. Representative TEM images of different micellar morphologies obtained via solution self-assembly of (A-C) PTMC18C_{38}-*b*-$PDMA_{157}$ and (D-F) PTMC18C_{38}-*b*-$PDMA_{385}$ in (A, D) MeOH, (B, E) EtOH, (C, F) i-PrOH at their respective boiling points for 3 h prior to cooling to room temperature (25 °C) and aging for 3 days. The polymer concentration during self-assembly was fixed as 0.5 mg mL^{-1}. All the TEM samples were stained with uranyl acetate (1 wt%).

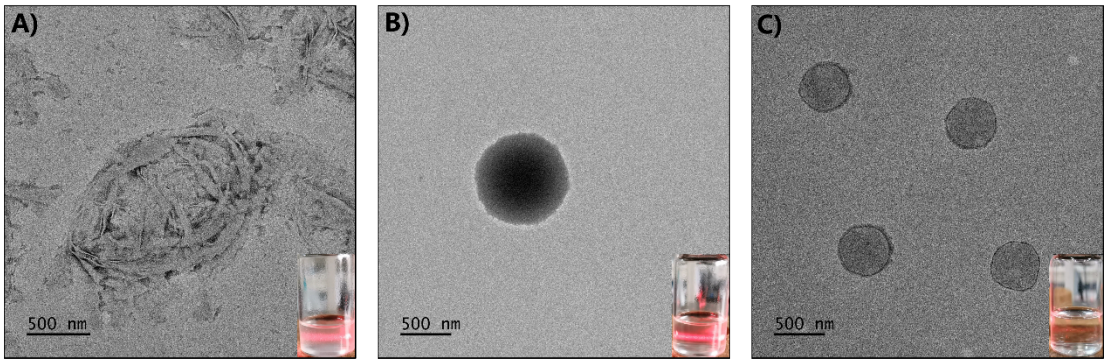

Figure S13. Representative TEM images of self-assembled morphologies of PTMC18C$_{38}$-*b*-PDMA$_{157}$ via solvent exchange method, i.e., dropwise adding (A) MeOH, (B) EtOH and (C) i-PrOH to the BCP solution with a rate of 0.01 mL min^{-1}. All the TEM samples were stained with uranyl acetate (1 wt%). The insets show the Tyndall effect photographs after solvent exchange and then aging at room temperature for 3 days.

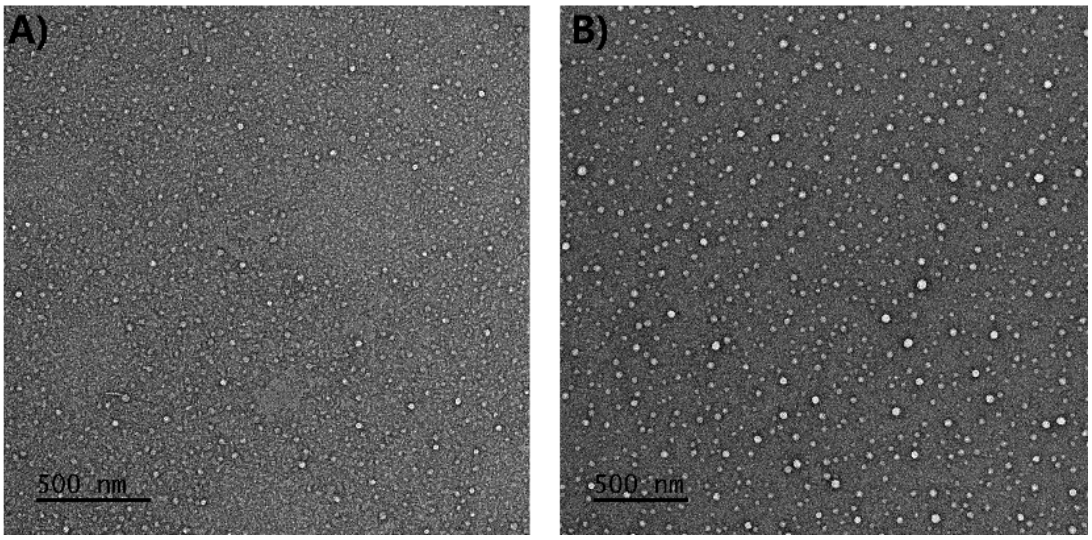

Figure S14. Representative TEM images of self-assembled morphologies of PTMC18C$_{38}$-*b*-PDMA$_{157}$ via solvent exchange method, i.e., dropwise adding i-PrOH to the BCP solution with a rate of (A) 0.01 mL min^{-1}, (B) 1 mL min^{-1} and aging for 0 day. All the TEM samples were stained with uranyl acetate (1 wt%).

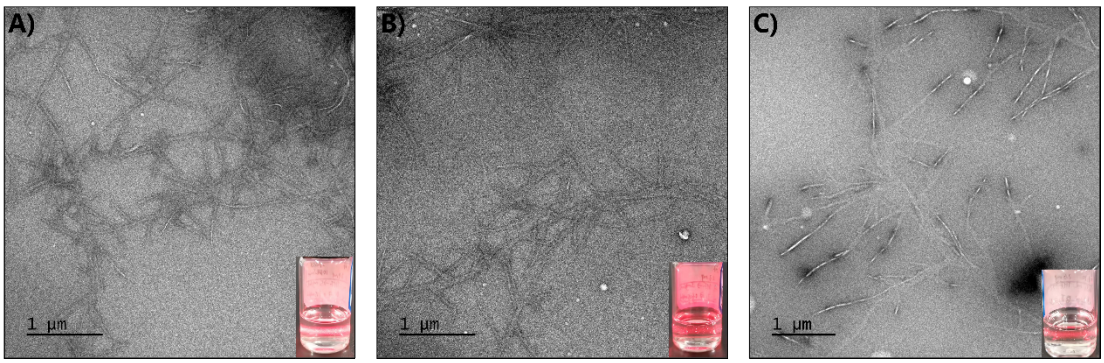

Figure S15. Representative TEM images of self-assembled morphologies of PTMC18C$_{38}$-*b*-PDMA$_{385}$ via solvent exchange method, i.e., dropwise adding (A) MeOH, (B) EtOH and (C) i-PrOH to the BCP solution with a rate of 0.01 mL min^{-1}. All the TEM samples were stained with uranyl acetate (1 wt%). Insets show the Tyndall effect photographs after solvent exchange and then aging at room temperature for 3 days.