Discrete Block Copolymers with Diverse Architectures:

Resolving Complex Spherical Phases with One Monomer Resolution

Yanxiao Sun,[1†] Rui Tan,[1†] Zhuang Ma,[1] Zhanhui Gan,[1] Gang Li,[1] Dongdong Zhou,[1] Yu Shao,[3] Wen-Bin Zhang,[3] Rui Zhang,[1] and Xue-Hui Dong [1, 2]*

[1]South China Advanced Institute of Soft Matter Science and Technology, School of Molecular Science and Engineering, South China University of Technology, Guangzhou 510640, China

[2]State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China

[3]Key Laboratory of Polymer Chemistry & Physics of Ministry of Education, Center for Soft Matter Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

[†] These authors contribute equally

*Corresponding author: xdong@scut.edu.cn

1. Materials.

The following chemicals were used as received: *D*-camphorsulfonic acid (TCI, 98%), benzyl alcohol (BnOH, TCI, 99%), *tert*-butyldimethylsilyl chloride (TBDMSCl, TCI, 98%), imidazole (TCI, 98%), Pd/C (Aldrich, 10 wt%), boron trifluoride etherate (TCI, 98%), *N,N'*-diisopropylcarbodiimide (DIC, Aldrich, 99%), hexamethylcyclotrisiloxane (Adamas, 98%), meso-lactide (TCI, 85%), chlorodimethylsilane (TCI, 95%), dimethylphenylsilane (TCI, 97%), 3-buten-1-ol (TCI, 98%), Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Karstedt catalyst, Aldrich, ~2% Pt), tris(pentafluorophenyl)borane ($B(C_6F_5)_3$, TCI, 98%), 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid (TCI, 95%), allylacetic acid (Acros, 99%), DOWEX 50WX8 (Acros, 100-200 mesh, ion-exchange resin), anhydrous pyridine, 1 M phosphate buffer (pH = 7). 4-(Dimethylamino)-pyridinium-4-toluenesulfonate (DPTS) was synthesized according to the literature[1]. Other anhydrous solvents, including toluene, dimethylformamide (DMF), dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), were obtained with an INERT Pure Solv System (Inert Corporation, USA).

2. Characterizations

Nuclear Magnetic Resonance (NMR). All ^{1}H NMR spectra were acquired in $CDCl_3$ using a Bruker 500 MHz NMR spectrometer. The spectra were referenced to the residual solvent peak in $CDCl_3$ at *δ* 7.26 ppm.

Size exclusion chromatography (SEC). SEC analyses were measured at 40 °C on a Tosoh HLC-8320 instrument equipped with three TSKgel columns (SuperH2000, SuperH3000, and SuperH4000 in series), a double flow type RI detector, and a UV-8320 UV detector, using THF as eluent. The flow-rate was 0.6 mL/min. Data acquisition was performed using EcoSEC software, and molecular weights and molecular weight distributions were calibrated with polystyrene standards (Polymer Laboratories).
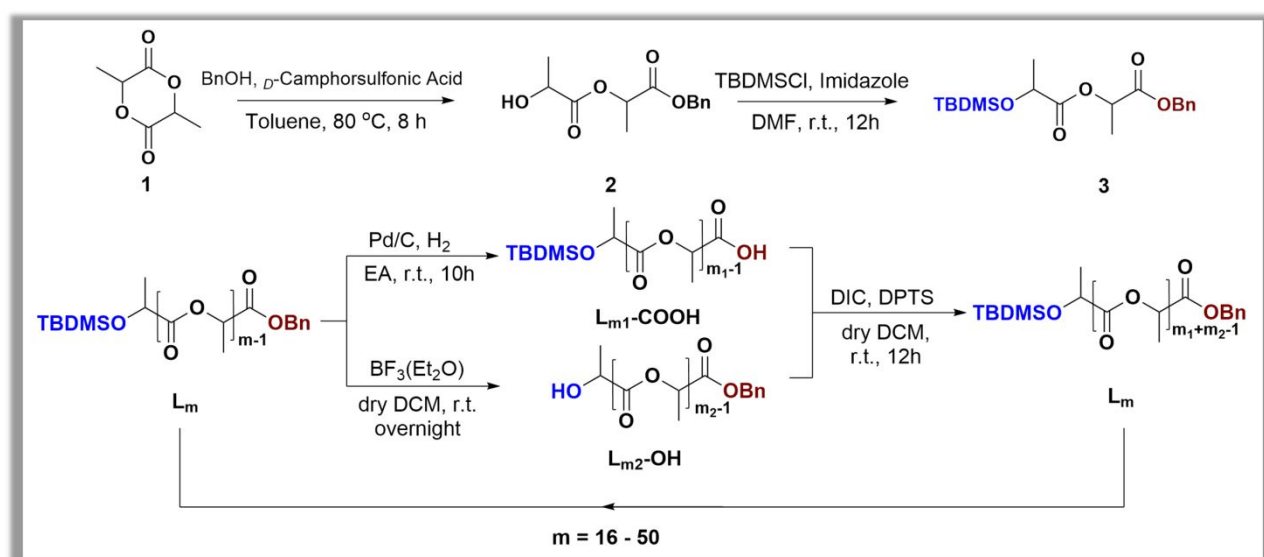
Matrix-assisted laser desorption/ionization time-of-flight (MALDI-ToF). MALDI-ToF mass spectroscopy (MS) were acquired on an UltrafleXtreme MALDI-ToF mass spectrometer (Bruker Daltonics) equipped with a 1 kHz smart beam-II laser. Trans-2-[3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Sigma-Aldrich, >98%) was used as the matrix and prepared in $CHCl_3$ at a concentration of 20 mg/mL. The cationizing agent sodium trifluoroacetate was prepared in ethanol at a concentration of 10 mg/mL. The matrix and cationizing salt solutions were mixed in a ratio of 10/1 (v/v). All samples were dissolved in $CHCl_3$ at a concentration of 10 mg/mL. After sample preparation and solvent evaporation, the target plate was inserted into the MALDI-ToF mass spectrometer. The attenuation of the laser was adjusted to minimize undesired polymer fragmentation and maximize the sensitivity.

Small angle X-ray scattering (SAXS). SAXS experiments were performed on Shanghai Synchrotron Radiation (SSRF), beamline BL16B1. The incident X-ray photon energy was 10 keV; the wavelength of the X-ray was 0.124 nm; the photo

flux was 1×10^{11} phs/s. The beam size is around 0.4×0.5 mm^2. Scattered X-rays were captured on a 2-dimensional Pilatus detector. The instrument was calibrated with diffraction patterns from silver behenate. Different annealing protocols have been applied. In general, samples were heated to 80 °C for 10 minutes on a Linkam hotstage (LTS420), and then annealed at 25 °C for different periods of time (1 day or 35 days). These samples (25 °C for 1 day) were also further annealed at elevated temperature (40 °C) for additional time (one more day).

3. Syntheses

3.1 Discrete *o*LA

Scheme S1. Synthesis of discrete *o*LA (**L$_m$**) *via* an iterative exponential growth route.

L$_2$-OH (**2**): Meso-lactide (**1**, 50.00 g, 0.34 mol) and benzyl alcohol (BnOH, 44.10 g, 0.41 mol, 1.2 eq) were dissolved in 150 mL of dry toluene. Then *D*-camphorsulfonic acid (CSA, 2.00 g, 0.01 mol, 0.03 eq) was added to the mixture. The mixture was stirred at 80 °C for 8 h under nitrogen atmosphere. The reaction was quenched by adding another toluene (80 mL) and washing with NaHCO$_3$ aqueous solution (3×100 mL) and brine (1×100 mL). The organic phase was collected and dried with anhydrous MgSO$_4$. The solvent was removed, and the crude product was purified by automated column chromatography with PE/EA (gradient 90/10 to 80/20) giving the pure product L$_2$-OH as a colorless oil (68.00 g, 80% yield). ^{1}H-NMR (500 MHz, CDCl$_3$, ppm, δ): 7.40-7.30 (m, 5H, Ar-H), 5.23 (1H, -OCH(CH$_3$)CO-), 5.21 (1H, ArCH$_2$O-), 5.15 (1H, ArCH$_2$O-), 4.34 (1H, HOCH(CH$_3$)CO-), 2.67 (1H, HOCH-), 1.54 (3H, -OCH(CH$_3$)CO-), 1.44 (3H, HOCH(CH$_3$)CO-).

L$_2$ (**3**): L$_2$-OH (36.00 g, 0.14 mol) was dissolved in 200 mL of dry toluene. *tert*-Butyldimethylsilyl chloride (TBDMSCl, 43.10 g, 0.28 mol, 2 eq) and imidazole (38.10 g, 0.56 mol, 4 eq) were added to the solution under nitrogen atmosphere.

The mixture was stirred at room temperature overnight. The reaction was quenched by adding $NaHCO_3$ aqueous solution (200 mL). The mixture was extracted with hexane (3 × 150 mL), followed by drying with $MgSO_4$. The organic phase was collected and dried with anhydrous $MgSO_4$. The solvent was removed and the crude product was purified by automated column chromatography with PE/EA (gradient 95/5 to 90/10) giving the pure product of L_2 as a colorless oil (46 g, 80% yield). ^{1}H-NMR (500 MHz, $CDCl_3$, ppm, δ): 7.39-7.29 (5H, Ar-$\underline{H}$), 5.20-5.12 (3H, -OC$\underline{H}$(CH$_3$)CO-, ArC$\underline{H}_2$O-), 4.34 (1H, TBDMS-OC$\underline{H}$(CH$_3$)$_2$)-), 1.51 (3H, -OCH(C$\underline{H}_3$)CO-), 1.41 (3H, TBDMS-OCH(C$\underline{H}_3$)CO-), 0.90 (9H, (C$\underline{H}_3$)$_3$C-Si(CH$_3$)$_2$-), 0.10 (3H, (CH$_3$)$_3$C-Si(C$\underline{H}_3$)$_2$-), 0.08 (3H, (CH$_3$)$_3$C-Si(C$\underline{H}_3$)$_2$-).
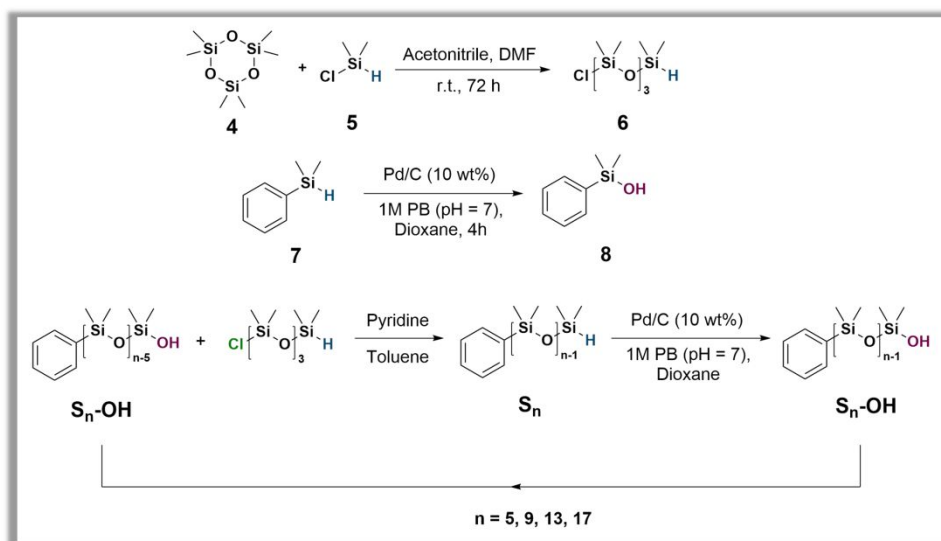
General method for synthesizing L_m-COOH: Take L_8-COOH as an example. L_8 (35.38 g, 0.04 mol) was dissolved in 70 mL of ethyl acetate. Pd/C (10 wt% on carbon, 0.47 g, 0.40 mmol, 0.01 eq) was added into the mixture. The mixture was stirred at a hydrogen atmosphere for 10 hours. The mixture was filtered with celite to remove the insoluble parts. The solvent was removed, giving the product L_8-COOH (30.13 g, 96% yield) as a colorless oil in good purity. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm, δ): 5.22-5.08 (7H, -OC$\underline{H}$(CH$_3$)CO-), 4.39 (1H, TBDMS-C$\underline{H}$(CH$_3$)CO-), 1.59-1.49 (21H, -OCH(C$\underline{H}_3$)CO-), 1.44 (3H, TBDMS-CH(C$\underline{H}_3$)CO-), 0.89 (9H, (C$\underline{H}_3$)$_3$C-Si(CH$_3$)$_2$-), 0.10 (3H, (CH$_3$)$_3$C-Si(C$\underline{H}_3$)$_2$-), 0.08 (3H, (CH$_3$)$_3$C-Si(C$\underline{H}_3$)$_2$-).

General method for synthesizing L_m-OH: Take L_8-OH as an example. L_8 (35.15 g, 0.04 mol) was dissolved in 70 mL of dry CH_2Cl_2 under a nitrogen atmosphere. Then BF_3-etherate (27 mL, 0.22 mol, 5 eq) was added into the mixture slowly in 30 min at 0 °C. After that, the mixture was stirred overnight at room temperature. The reaction was quenched by pouring into a saturated aqueous solution of $NaHCO_3$ (100 mL). The resulting organic phase was washed with water (3 × 150 mL) and dried with anhydrous $MgSO_4$. The solvent was removed, and the crude product was purified by automated column chromatography (gradient 75/25 to 66/34), giving the pure product L_8-OH (27.72 g, 92% yield) as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm, δ): 7.39-7.28 (5H, Ar-$\underline{H}$), 5.28-5.09 (9H, -OC$\underline{H}$(CH$_3$)CO-, ArC$\underline{H}_2$O-), 4.33 (1H, HOC$\underline{H}$(CH$_3$)CO-), 1.76 (1H, $\underline{H}$OCH(CH$_3$)CO-), 1.62-1.43 (24H, -OCH(C$\underline{H}_3$)CO-).

General method for synthesizing L_m: Take L_{16} as an example. L_8-COOH (30.13 g, 0.04 mol, 1.05 eq), L_8-OH (27.72 g, 0.04 mol, 1.0 eq), and DPTS (2.27 g, 0.01 mol, 0.25 eq) were dissolved in 120 mL of dry CH_2Cl_2 under a nitrogen atmosphere. The mixture was cooled to 0 °C and DIC (18 mL, 0.12 mol, 3 eq) was added slowly into the mixture in 30 min. The mixture was then stirred at room temperature for another 12 h. The reaction was quenched by washing with water (3×100 mL). The organic phase was collected and dried with anhydrous $MgSO_4$. The solvent was removed in vacuum and the crude product was purified by automated column chromatography with PE/EA (gradient 80/20 to 75/25), giving the pure product L_{16} (47.89 g, 86% yield) as a colorless viscus liquid. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm, δ): 7.39-7.28 (5H, Ar-$\underline{H}$), 5.25-5.06 (17H, -OC$\underline{H}$(CH$_3$)CO-, ArC$\underline{H}_2$O-), 4.35 (1H, TBDMS-C$\underline{H}$(CH$_3$)CO-), 1.60-1.43 (45H, -OCH(C$\underline{H}_3$)CO-), 1.41 (3H, TBDMS-CH(C$\underline{H}_3$)CO-), 0.9 (9H, (C$\underline{H}_3$)$_3$C-Si(CH$_3$)$_2$-), 0.08 (3H, (CH$_3$)$_3$C-Si(C$\underline{H}_3$)$_2$-), 0.06

(3H, (CH$_3$)$_3$C-Si(C$\underline{\text{H}}$$_3$)$_2$-).

3.2 Discrete *o*DMS

Scheme S2. Syntheses of discrete *o*DMS (**S***$_n$*) *via* a step growth route.

Cl-Si$_4$-H (**6**): In a glove box, hexamethylcyclotrisiloxane (**4**, 80.00 g, 0.36 mol), chlorodimethylsilane (**5,** 37.40 g, 0.40 mol), and acetonitrile (20 mL) were added into a 500 mL round-bottom flask. Then DMF (1 mL) was added into the mixture. The mixture was stirred at room temperature for 72 hours. Pure compound **6** was obtained by vacuum distillation (fraction at 35-40 °C) as a colorless oil (65.98 g, 58% yield). ^{1}H NMR (500 MHz, CDCl$_3$, ppm, δ): 4.70 (1H, -Si$\underline{\text{H}}$), 0.45 (6H, ClSi(C$\underline{\text{H}}$$_3$)$_2$-), 0.20 (6H, HSi(C$\underline{\text{H}}$$_3$)$_2$-), 0.13 ppm (6H, -C$\underline{\text{H}}$$_3$), 0.09 (6H, -C$\underline{\text{H}}$$_3$).
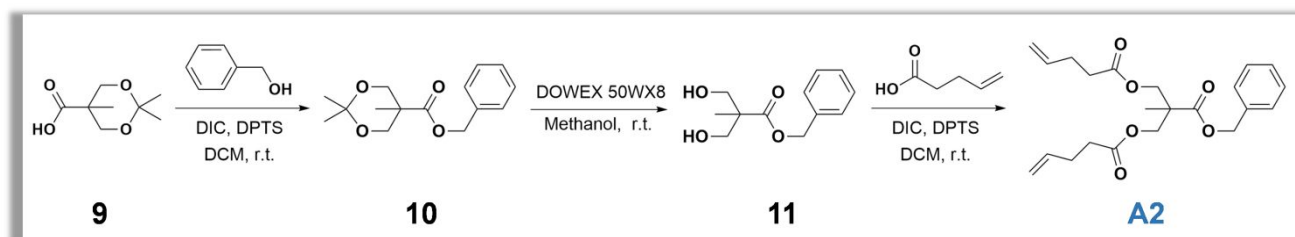
General methods for synthesizing S$_n$-OH: Take S$_5$-OH as an example. Pd/C (0.27 g, 10% on carbon, 0.005 eq of Pd) was suspended in a mixture of 1M phosphate buffer (PB, 25 mL, pH = 7) and dioxane (100 mL). A solution of S$_5$ (22.40 g, 0.05 mol) in dioxane (20 ml) was then added dropwise into the mixture at 0 °C. The mixture was stirred at room temperature overnight. The reaction was quenched by filtration to remove Pd/C. The filtrate was extracted with toluene (3 × 100 mL). The combined organic phase was washed with water (3 × 150 mL) and dried with anhydrous MgSO$_4$. Toluene was removed, giving the product S$_5$-OH as a colorless oil (20.70 g, 89% yield) in good purity. ^{1}H NMR (500 MHz, CDCl$_3$, ppm, δ): 7.59-7.34 (5H, Ar-$\underline{\text{H}}$), 0.33 (6H, ArSi(C$\underline{\text{H}}$$_3$)$_2$O-), 0.14 (6H, HOSi(C$\underline{\text{H}}$$_3$)$_2$-), 0.12-0.05 (18H, -C$\underline{\text{H}}$$_3$).

General methods for synthesizing S$_n$: Take S$_{17}$ as an example. Compound **6** (3.16 g, 0.01 mol) was dissolved in 50 mL of dry toluene under nitrogen atmosphere. Pyridine (1 mL) and a solution of S$_{13}$-OH (10.40 g, 0.01 mol) in toluene (10 mL) was added dropwise to the mixture at 0 °C. After that, the mixture was stirred at room temperature overnight. The reaction was quenched by washing with water (3 × 30 mL). The organic phase was dried with anhydrous MgSO$_4$.

Toluene was removed and the obtained crude product was purified by automated column chromatography with hexane (100 %), giving pure product S_{17} as a colorless oil (8.71 g, 66% yield). ^{1}H NMR (500 MHz, CDCl$_3$, ppm, δ): 7.59-7.32 (5H, Ar-H), 4.70 (1H, -Si$\underline{H}$), 0.34 (6H, ArSi(C$\underline{H}_3$)$_2$O-), 0.19 (6H, HSi(C$\underline{H}_3$)$_2$-), 0.10-0.05 (90H, -C$\underline{H}_3$).

3.3 Molecular adaptors

1. *Adaptor* **A2**.

Scheme S3. Syntheses of adaptor **A2**.

Compound 10. 2,2,5-Trimethyl-1,3-dioxane-5-carboxylic acid (**9**, 1.07 g, 6.14 mmol), BnOH (0.63 g, 5.84 mmol, 0.95 eq), and DPTS (0.69 g, 3.10 mmol, 0.5 eq) were dissolved in 20 mL of dry CH$_2$Cl$_2$ under nitrogen atmosphere. DIC (5 mL, 0.03 mol, 5eq) was added dropwise to the mixture at 0 °C. Then the mixture was stirred at room temperature for another 12 h. The reaction was quenched by filtration to remove the white precipitate and washed with water (3×10 mL). The organic phase was separated and dried with anhydrous MgSO$_4$. CH$_2$Cl$_2$ was removed and the obtained crude product was purified by automated column chromatography with PE/EA (gradient 90/10), giving pure product Compound **10** (1.43 g, 88% yield). ^{1}H NMR (CDCl$_3$, 500 MHz, ppm, δ): 7.35 (5H, Ar-H), 5.20 (2H, ArC$\underline{H}_2$-), 4.21 (2H, -CC$\underline{H}_2$O-), 3.68 (2H, -CC$\underline{H}_2$O-), 1.38 (6H, -OC(C$\underline{H}_3$)$_2$), 1.20 (3H, -C$\underline{H}_3$).

Compound 11. Compound **10** (1.43 g, 5.41 mmol) was dissolved in 10 mL of MeOH. One spatula of DOWEX50WX8 was added into the mixture. The mixture was stirred at room temperature for 6 hours. The reaction was quenched by filtration to remove the ion-exchange resin. Methanol was removed and the obtained crude product was purified by automated column chromatography with PE/EA (gradient 90/10), giving the product Compound **11** (1.15g, 95% yield) in good purity. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm, δ): 7.36 (5H, Ar-$\underline{H}$), 5.21 (2H, ArC$\underline{H}_2$-), 3.92 (2H, -CC$\underline{H}_2$O-), 3.75 (2H, -CC$\underline{H}_2$O-), 2.85 (2H, -O$\underline{H}$), 1.08 (3H, -C$\underline{H}_3$).

Adaptor **A2**. Compound **11** (1.15 g, 5.13 mmol), allylacetic acid (1.13 g, 11.29 mmol, 2.2 eq), and DPTS (0.57g, 2.56 mmol, 0.5 eq) were dissolved in 20 mL of dry CH$_2$Cl$_2$ under nitrogen atmosphere. Then DIC (4 mL, 0.02 mol, 5eq) was added dropwise to the solution at 0 °C. The mixture was stirred at room temperature for 12 h. The reaction was quenched by filtration to remove the white precipitate and washed with water (3 × 20 mL). The organic phase was separated and

dried with anhydrous MgSO$_4$. CH$_2$Cl$_2$ was removed and the obtained crude product was purified by automated column chromatography with PE/EA (gradient 85/15), giving pure product adaptor **A2** (1.63 g, 82% yield). ^{1}H NMR (CDCl$_3$, 500 MHz, ppm, δ): 7.33 (5H, Ar-H̲), 5.72-5.82 (2H, CH$_2$=CH̲CH$_2$-), 5.20 (2H, ArCH̲$_2$-), 4.97-5.05 (4H, CH̲$_2$=CH-), 4.24 (4H, -CCH̲$_2$O-), 2.28-2.37 (8H, CH$_2$=CHCH̲$_2$-, CH$_2$=CHCH$_2$CH̲$_2$-), 1.26 (3H, -CH̲$_3$).

2. *Adaptor* **A4**.

Scheme S4. Synthesis of adaptor **A4**.

Compound 12. Compound **9** (8.55 g, 49.11 mmol, 2.2 eq), compound **11** (5.00 g, 22.31 mmol), and DPTS (3.25 g, 11.15 mmol, 0.5 eq) were dissolved in 10 mL of dry CH$_2$Cl$_2$ under nitrogen atmosphere. DIC (8.60 mL, 55.78 mol, 2.5 eq) was added dropwise to the mixture at 0 °C. Then the mixture was stirred at room temperature for another 12 h. The reaction was quenched by filtration to remove the white precipitate and washed with water (3×10 mL). The organic phase was separated and dried with anhydrous MgSO$_4$. CH$_2$Cl$_2$ was removed in vacuum and the obtained crude product was purified by automated column chromatography with PE/EA (gradient 80/20 to 50/50), giving pure product Compound **12** (10.77 g, 90% yield). ^{1}H NMR (CDCl$_3$, 500 MHz, ppm, δ): 7.34 (5H, Ar-H̲), 5.16 (2H, ArCH̲$_2$-), 4.33 (4H, -CCH̲$_2$OOC-), 4.10 (4H, -CCH̲$_2$O-), 3.58 (4H, -CCH̲$_2$O-), 1.40 (6H, -OC(CH̲$_3$)$_2$), 1.34 (6H, -OC(CH̲$_3$)$_2$), 1.30 (3H, -CCH̲$_3$CH$_2$OOCCH$_3$), 1.09 (6H, - CCH̲$_3$CH$_2$O).

Adaptor **A4**. Compound **12** (5.00 g, 9.32 mmol) was dissolved in 10 mL of MeOH. Two spatulas of DOWEX50WX8 was added into the mixture. The mixture was stirred at room temperature for 6 hours. The reaction was quenched by filtration to remove the ion-exchange resin. Methanol was removed in vacuum and the crude product was purified by automated column chromatography with CH$_2$Cl$_2$/CH$_3$OH (gradient 100/0 to 90/10), giving the product adaptor **A4** (3.40 g, 80% yield) in good purity. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm, δ): 7.35 (5H, Ar-H̲), 5.18 (2H, ArCH̲$_2$-), 4.45 (2H, -CCH̲$_2$OOC-), 4.29 (2H, -CCH̲$_2$OOC-), 3.77-3.82 (4H, -CCH̲$_2$O-), 3.63-3.70 (4H, -CCH̲$_2$O-), 3.07-3.14 (4H, -OH̲), 1.32 (3H, -CCH̲$_3$CH$_2$OOCCH$_3$), 0.98 (6H, - CCH̲$_3$CH$_2$OH).
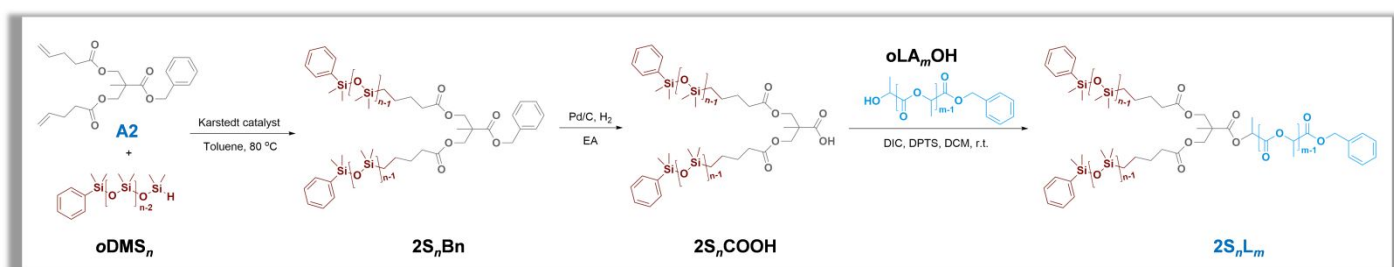
3.4 Linear-linear discrete block copolymer S_nL_m

Scheme S5. Syntheses of linear-linear discrete block copolymers S_nL_m.

General methods for synthesizing L_m-Alkene: Take L_{16}-*Alkene* as an example. L_{16}-COOH (0.93 g, 0.72 mmol), 3-buten-1-ol (0.06 g, 0.87 mmol, 1.2 eq), and DPTS (0.04 g, 0.18 mmol, 0.25 eq) was dissolved in 5 mL of dry DCM under nitrogen atmosphere. DIC (0.3 mL, 2.17 mmol, 3 eq) was then added dropwise into the mixture at 0 °C. The mixture was stirred at room temperature for anther 12 h. The reaction was quenched by filtration to remove the precipitate and washed with water (3 × 5 mL). The organic phase was separated and dried with anhydrous MgSO$_4$. DCM was removed, and the crude product was purified by automated column chromatography with PE/EA (gradient 75/25) giving pure product L_{16}-*Alkene* (0.86 g, 89% yield) as a colorless viscous liquid. ^{1}H NMR (500 MHz, CDCl$_3$, ppm, δ): 5.82-5.69 (1H, CH$_2$=C$\underline{H}$-), 5.26-5.04 (17H, C$\underline{H}_2$=CH-, -OC$\underline{H}$(CH$_3$)CO-), 4.40 (1H, TBDMS-C$\underline{H}$(CH$_3$)CO-), 4.28-4.12 (2H, -OC$\underline{H}_2$CH$_2$-), 2.40 (2H, -OCH$_2$C$\underline{H}_2$-), 1.58-1.24 (45H, -OCH(C$\underline{H}_3$)CO-), 1.18 (3H, TBDMS-CH(C$\underline{H}_3$)CO-), 0.9 (9H, (C$\underline{H}_3$)$_3$C-Si(CH$_3$)$_2$-), 0.10-0.06 (6H, (CH$_3$)$_3$C-Si(C$\underline{H}_3$)$_2$-).

General method for synthesizing of $S_{17}L_m$: Take $S_{17}L_{16}$ as an example. In a glove box, L_{16}-*Alkene* (0.86 g, 0.64 mmol) and S_{17} (1.02 g, 0.77 mmol, 1.2 eq) were dissolved in 10 mL of dry toluene. A drop of Karstedt Catalyst was then added into the mixture. The mixture was stirred at 80 °C for 12 hours. Toluene was removed, and the obtained crude product was purified by automated column chromatography with PE/EA (gradient 80/20 to 75/25), giving pure product $S_{17}L_{16}$ (1.58 g, 78% yield) as a thick oil. ^{1}H NMR (500 MHz, CDCl$_3$, ppm, δ): 7.58-7.32 (5H, Ar-$\underline{H}$), 5.26-5.04 (15H, -OC$\underline{H}$(CH$_3$)CO-), 4.40 (1H, TBDMS-C$\underline{H}$(CH$_3$)CO-), 4.18-4.09 (2H, -OC$\underline{H}_2$CH$_2$-), 1.64-1.51 (49H, -OCH(C$\underline{H}_3$)CO-, -OCH$_2$C$\underline{H}_2$-, -C$\underline{H}_2$CH$_2$Si(CH$_3$)$_2$-), 1.27 (3H, TBDMS-CH(C$\underline{H}_3$)CO-), 0.9 (9H, (C$\underline{H}_3$)$_3$C-Si(CH$_3$)$_2$-), 0.55 (2H, -C$\underline{H}_2$Si(CH$_3$)$_2$-), 0.34 (6H, ArSi(C$\underline{H}_3$)$_2$O-), 0.10-0.01 (102H, -C$\underline{H}_3$).

3.5 Linear-branched discrete block copolymer $2S_nL_m$

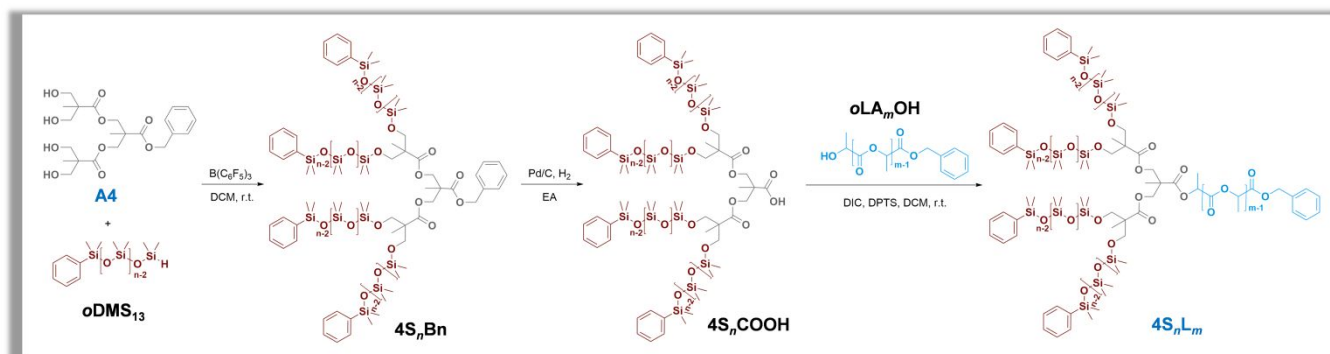**Scheme S6**. Syntheses of linear-branched discrete block copolymer $2S_nL_m$.

General methods for synthesizing 2S_n-Bn: Take $2S_{13}$-*Bn* as an example. In a glove box, adaptor **A2** (0.50 g, 1.29 mmol) and S_{13} (2.91 g, 2.83 mmol, 2.2 eq) were dissolved in 30 mL of dry toluene. One drop of Karstedt Catalyst was then added into the mixture. The mixture was stirred at 80 °C for 12 hours. The obtained crude product was purified by silica gel chromatography with PE as the elution solvent, which was further purified by Recycling Preparative GPC to give pure product $2S_{13}$-*Bn* (1.98 g, 63% yield). ^{1}H NMR (500 MHz, CDCl$_3$, ppm, δ): 7.63-7.28 (15H, Ar-H), 5.16 (2H, ArC$\underline{H}_2$-), 4.23 (4H, -CC$\underline{H}_2$O-), 2.32-2.17 (4H, -C$\underline{H}_2$CO-), 1.66-1.50 (4H, -C$\underline{H}_2$CH$_2$CO-), 1.38-1.21 (7H, -C$\underline{H}_2$CH$_2$Si(CH$_3$)$_2$-, -CC$\underline{H}_3$), 0.58-0.46 (4H, -C$\underline{H}_2$Si(CH$_3$)$_2$-), 0.34 (12H, ArSi(C$\underline{H}_3$)$_2$O-), 0.15-0.01 (144H, -C$\underline{H}_3$).

General methods for synthesizing 2S_n-COOH: Take $2S_{13}$-*COOH* as an example. $2S_{13}$-*Bn* (1.98 g, 0.81 mmol) was dissolved in 20 mL of ethyl acetate. Pd/C (10 wt% on carbon, 0.08 g, 0.08 mmol, 0.1 eq) was added into the mixture. The mixture was stirred at a hydrogen atmosphere for 10 hours, and then filtered through celite to remove the insoluble parts. Ethyl acetate was removed in vacuum, giving the product $2S_{13}$-*COOH* (1.85 g, 97% yield) in good purity. ^{1}H NMR (500 MHz, CDCl$_3$, ppm, δ): 7.60-7.32 (10H, Ar-$\underline{H}$), 4.29-4.20 (4H, -CC$\underline{H}_2$O-), 2.42-2.22 (4H, -C$\underline{H}_2$CO-), 1.71-1.55 (4H, -C$\underline{H}_2$CH$_2$CO-), 1.42-1.16 (7H, -C$\underline{H}_2$CH$_2$Si(CH$_3$)$_2$-, -CC$\underline{H}_3$), 0.58-0.50 (4H, -C$\underline{H}_2$Si(CH$_3$)$_2$-), 0.34 (12H, ArSi(C$\underline{H}_3$)$_2$O-), 0.15-0.01 (144H, -C$\underline{H}_3$).

General methods for synthesizing 2S_nL_m: Take $2S_{13}L_{24}$ as an example. $2S_{13}$-*COOH* (0.46 g, 0.20 mmol), L_{24}-OH (0.40 g, 0.22 mmol, 1.1 eq), and DPTS (0.03 g, 0.10 mmol, 0.5 eq) were dissolved in 5 mL of dry CH$_2$Cl$_2$ under nitrogen atmosphere. DIC (0.2 mL, 1.00 mmol, 5eq) was then added dropwise into the mixture at 0 °C, and the mixture was stirred at room temperature for another 12 h under nitrogen atmosphere. The reaction was quenched by washing with water (3 × 5 mL). The organic phase was separated and dried with anhydrous MgSO$_4$. DCM was removed and the

obtained crude product was purified by automated column chromatography with PE/EA (gradient 80/20 to 75/25), giving pure product $2S_{13}L_{24}$ (0.62 g, 76% yield). ^{1}H-NMR (500 MHz, CDCl$_3$, ppm, δ): 7.62-7.30 (15H, Ar-$\underline{H}$), 5.26-5.10 (26H, ArC$\underline{H}_2$-, -OC$\underline{H}$(CH$_3$)CO-), 4.38-4.18 (4H, -CC$\underline{H}_2$O-), 2.35-2.23 (4H, -C$\underline{H}_2$CO-), 1.72-1.41 (76H, -OCH(C$\underline{H}_3$)CO-, -C$\underline{H}_2$CH$_2$CO-), 1.40-1.21 (7H, -C$\underline{H}_2$CH$_2$Si(CH$_3$)$_2$-, -CC$\underline{H}_3$), 0.61-0.48 (4H, -C$\underline{H}_2$Si(CH$_3$)$_2$-), 0.34 (12H, ArSi(C$\underline{H}_3$)$_2$O-), 0.10-0.02 (144H, -C$\underline{H}_3$).

3.6 Linear-branched discrete block copolymer $4S_nL_m$

Scheme S7. Syntheses of linear-branched discrete block copolymer $4S_nL_m$.

$4S_{13}$-Bn: In a glove box, **A4** (0.06 g, 0.13 mmol) and S$_{13}$ (0.50 g, 0.49 mmol, 4.0 eq) were dissolved in 5 mL of dry DCM. A solution of B(C$_6$F$_5$)$_3$ (0.02 g, 0.05 mmol, 0.1 eq) in DCM (2 mL) was then added, and the mixture was stirred vigorously for 15 min. The reaction was quenched by washing with water (3 × 5 mL). The organic phase was separated and dried with anhydrous MgSO$_4$. DCM was removed and the obtained crude product was purified by Recycling Preparative GPC, giving pure product $4S_{13}$-*Bn* (0.36 g, 65 % yield). ^{1}H NMR (500 MHz, CDCl$_3$, ppm, δ): 7.63-7.28 (25H, Ar-H), 5.13 (2H, ArC$\underline{H}_2$-), 4.19-4.32 (4H, -CC$\underline{H}_2$OOC-), 3.66-3.73 (8H, -CC$\underline{H}_2$O-), 1.24 (3H, -CC$\underline{H}_3$CH$_2$OOCCH$_3$), 1.06(6H, - CC$\underline{H}_3$CH$_2$OSi(CH$_3$)$_2$-), 0.34 (12H, ArSi(C$\underline{H}_3$)$_2$O-), 0.05-0.10 (288H, -SiC$\underline{H}_3$).

$4S_{13}$-COOH: $4S_{13}$-Bn (0.25 g, 0.05 mmol) was dissolved in 20 mL of ethyl acetate. Pd/C (10 wt% on carbon, 0.02 g, 0.02 mmol, 0.1 eq) was added into the mixture. The mixture was stirred under hydrogen atmosphere for 10 hours, and then filtered through celite to remove the insoluble parts. Ethyl acetate was removed, giving the product $4S_{13}$-*COOH* (0.24 g, 97% yield) in good purity. ^{1}H NMR (500 MHz, CDCl$_3$, ppm, δ): 4.19-4.32 (4H, -CC$\underline{H}_2$OOC-), 3.66-3.73 (8H, -CC$\underline{H}_2$O-), 1.30 (3H, -CC$\underline{H}_3$CH$_2$OOCCH$_3$), 1.06 (6H, - CC$\underline{H}_3$CH$_2$OSi(CH$_3$)$_2$-), 0.34 (12H, ArSi(C$\underline{H}_3$)$_2$O-), 0.05-0.10 (288H, -SiC$\underline{H}_3$).

General methods for synthesizing $4S_{13}L_m$: Take $4S_{13}L_{16}$ as an example. $4S_{13}$-*COOH* (0.13 g, 0.03 mmol), L$_{16}$-OH (0.04 g, 0.03 mmol, 1.1 eq), and DPTS (0.02 g, 0.06 mmol, 2 eq) were dissolved in 5 mL of dry CH$_2$Cl$_2$ under nitrogen atmosphere. DIC (0.05 mL, 0.3 mmol, 10 eq) was added dropwise into the mixture at 0 °C, and the mixture was then stirred at room temperature for 12 h. The reaction was quenched by washing with water (3 × 5 mL). The organic phase

was separated and dried with anhydrous MgSO$_4$. DCM was removed and the obtained crude product was purified by JAI Recycling Preparative GPC (LaboACE LC-5060) giving pure product 4S$_{13}$L$_{16}$ (0.10 g, 60 % yield). ^{1}H-NMR (500 MHz, CDCl$_3$, ppm, δ): 7.63-7.28 (25H, Ar-H), 5.13-5.23 (18H, ArC$\underline{H}_2$-, -OC$\underline{H}$(CH$_3$)CO-), 4.18-4.38 (4H, -CC$\underline{H}_2$OOC-), 3.68-3.75(8H, -CC$\underline{H}_2$O-), 1.50-1.56 (45H, -OCH(C$\underline{H}_3$)CO-), 1.25 (3H, -CC$\underline{H}_3$CH$_2$OOCCH$_3$), 1.10(6H, -CC$\underline{H}_3$CH$_2$OSi(CH$_3$)$_2$-), 0.34 (12H, ArSi(C$\underline{H}_3$)$_2$O-), 0.05-0.10 (288H, -SiC$\underline{H}_3$).

4. Calculations and Discussion

4.1 Volume fraction of oLA block (f_A).

The volume fraction of oLA component (f_A) is determined by Eq. S1:

$$f_A = \frac{M_{LA}/\rho_{LA}}{M_{LA}/\rho_{LA} + M_{DMS}/\rho_{DMS}} \tag{S1}$$

where M_{LA} and M_{DMS} are the molecular weight of oLA and oDMS blocks, while ρ_{LA} and ρ_{DMS} are the density of oLA and oDMS blocks, respectively. According to literature, $\rho_{LA} = 1.25$ g/cm^3, $\rho_{DMS} = 0.95$ g/cm^3.

4.2 Characteristic dimension of the phase (a).

The dimension of the phase (a) refers to lamellar periodicities (for LAM), inter-column distances (for HEX), or lattice parameters (for DG, A15 and σ). It can be calculated from corresponding diffraction peaks accordingly.

$$
\begin{array}{ll}
a = d_1 & \text{for LAM} \\[6pt]
a = \sqrt{6}d_{211} & \text{for DG} \\[6pt]
a = 2d_{10}/\sqrt{3} & \text{for HEX} \\[6pt]
a = \sqrt{2}d_{110} & \text{for A15} \\[6pt]
a = \sqrt{17}d_{410};\ c = 2d_{002} & \text{for σ phase}
\end{array}
\tag{S2}
$$

4.3 Average diameter of spherical motifs of A15 and σ phases (D)

$$\langle D \rangle = \sqrt[3]{\frac{3}{4\pi}}\, a \qquad \text{for A15} \tag{S3}$$

11

$$\langle D \rangle = \sqrt[3]{\frac{V}{5\pi}} \qquad\qquad \text{for } \sigma$$

where a is the cubic lattice parameter of A15, and V is the lattice volume of σ phase ($V = a*a*c$).

4.4 Number of molecules within one spherical motif (N)

$$\langle N \rangle = \frac{\rho a^3}{8m} \times N_A \qquad\qquad \text{for A15}$$

(S4)

$$\langle N \rangle = \frac{\rho V}{30m} \times N_A \qquad\qquad \text{for } \sigma$$

where a is the cubic lattice parameter of A15, V is the lattice volume of σ phase ($V = a*a*c$), m is the molecular weight, and N_A is Avogadro's number.

4.5 Index of peaks in the SAXS pattern of $4S_{13}L_{22}$ (σ phase).

Peak No.	(hkl)	q_{cal} (nm^{-1})	q_{obs} (nm^{-1})	Peak No.	(hkl)	q_{cal} (nm^{-1})	q_{obs} (nm^{-1})
1	110	0.301	--	21	420	0.951	--
2	200	0.425	--	22	411	0.965	0.966
3	101	0.456	--	23	331	0.988	0.989
4	210	0.475	--	24	222	1.006	1.007
5	111	0.503	--	25	421	1.033	--
6	220	0.601	--	26	312	1.050	1.052
7	211	0.623	--	27	430	1.063	--
8	310	0.672	0.672	28	510	1.084	1.084
9	221	0.724	0.726	29	322	1.113	1.115
10	301	0.754	0.754	30	501	1.137	1.137
11	320	0.766	0.766	31	431	1.137	1.137
12	311	0.784	0.784	32	520	1.145	--
13	002	0.807	0.805	33	511	1.156	1.157
14	400	0.850	--	34	402	1.172	--
15	112	0.861	--	35	412	1.191	1.191
16	321	0.866	--	36	440	1.202	--

17	410	0.876	0.876	37	332	1.210	--
18	330	0.902	0.901	38	521	1.214	1.214
19	202	0.912	0.913	39	103	1.228	1.227
20	212	0.936	0.937				

4.6 Index of peaks in the SAXS pattern of $2S_{17}L_{18}$ (A15 phase).

Peak No.	(hkl)	q_{cal} (nm^{-1})	q_{obs} (nm^{-1})	Peak No.	(hkl)	q_{cal} (nm^{-1})	q_{obs} (nm^{-1})
1	110	0.550	0.550	10	400	1.554	1.555
2	200	0.777	0.778	11	410	1.602	1.604
3	210	0.869	0.870	12	411	1.649	1.650
4	211	0.952	0.952	13	330	1.649	1.650
5	220	1.099	1.099	14	420	1.738	1.741
6	310	1.229	1.230	15	421	1.781	1.784
7	222	1.346	1.346	16	332	1.823	1.825
8	320	1.401	1.403	17	422	1.904	1.906
9	321	1.454	1.455				

5. Schemes and Figures

Figure S1. ^{1}H NMR spectra of adaptor **A2** and corresponding intermediates: compound **9** (a), **10** (b), **11** (c), and **A2** (d).

Figure S2. ^{1}H NMR spectra of adaptor **A4** and corresponding intermediates: compound **12** (a) and **A4** (b).

Figure S3. ^{1}H NMR spectra (a), SEC traces (b), and MALDI-ToF MS (c) of oDMS blocks with n = 13 and 17.

Figure S4. Representative ^{1}H NMR spectra of the S_nL_m series and precursors: oDMS$_{17}$ (a), oLA$_{16}$ (b), S$_{17}$L$_{16}$ (c), and S$_{17}$L$_{32}$ (d). Other samples with different oLA chain length have similar spectra with varied integrations.
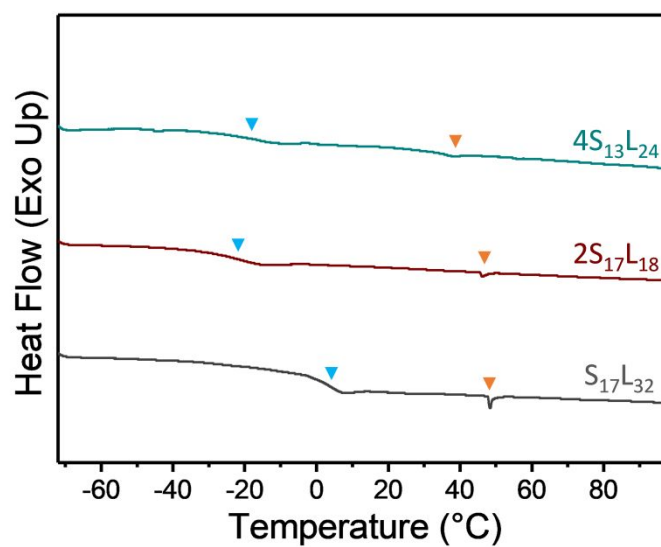
Figure S5. Representative ^{1}H NMR spectra of the $2S_{13}L_m$ series and precursors: $oLA_{16}OH$ (a), $2S_{13}Bn$ (b), $2S_{13}COOH$ (c), $2S_{13}L_{16}$ (d), $2S_{13}L_{32}$ (e), and $2S_{13}L_{40}$ (f). Other samples with different oLA chain length have similar spectra with varied integrations.

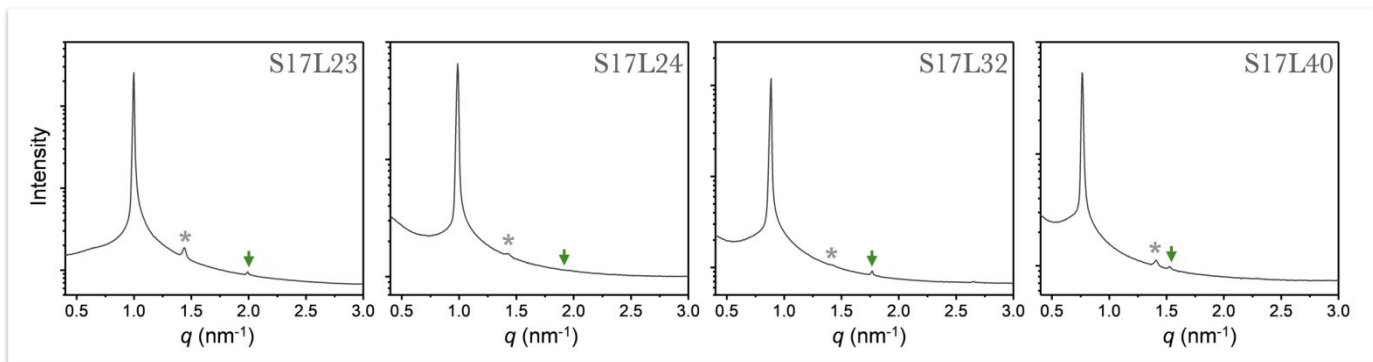**Figure S6.** Representative ¹H NMR spectra of the $2S_{17}L_m$ series and precursors: $oLA_{16}OH$ (a), $2S_{17}Bn$ (b), $2S_{17}COOH$ (c), $2S_{17}L_{14}$ (d), $2S_{17}L_{16}$ (e), and $2S_{17}L_{18}$ (f). Other samples with different oLA chain length have similar spectra with varied integrations.
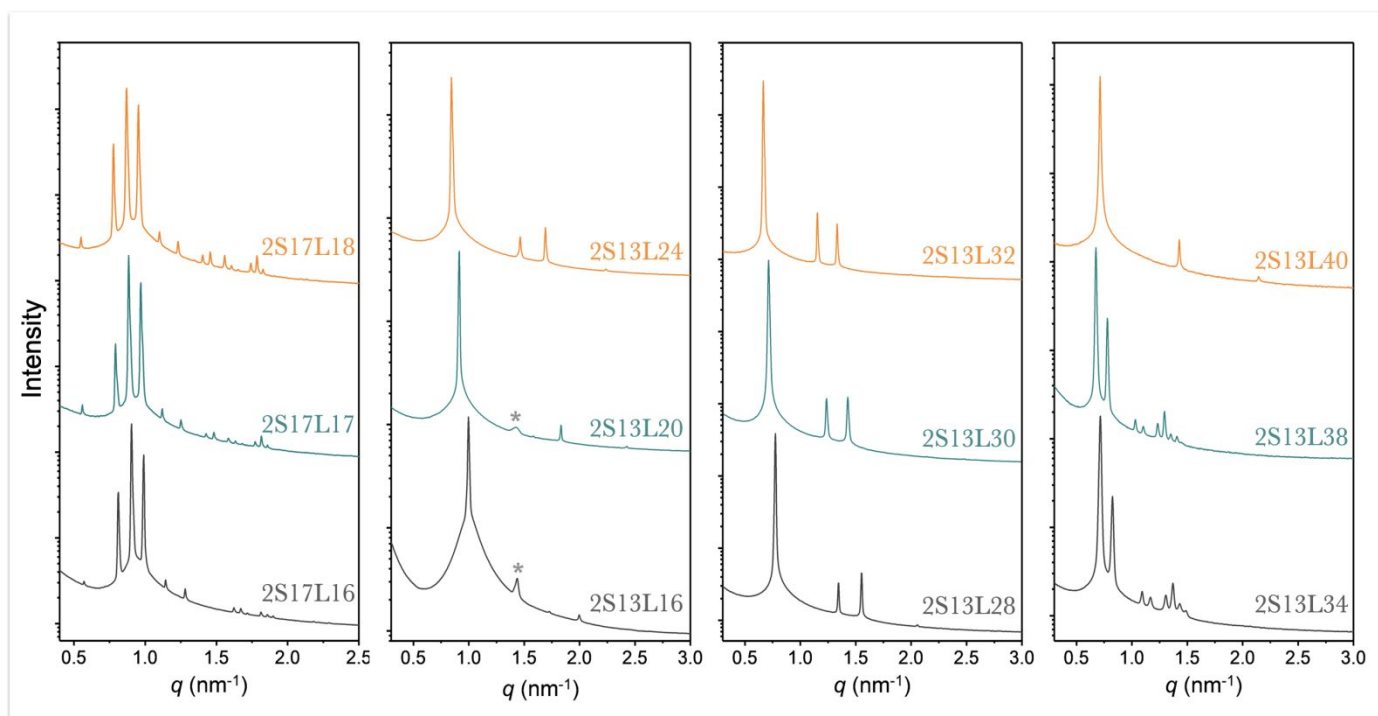
Figure S7. Representative ^{1}H NMR spectra of the $4S_{13}L_m$ series and precursors: $oLA_{16}OH$ (a), $4S_{13}Bn$ (b), $4S_{13}COOH$ (c), $4S_{13}L_{16}$ (d), $4S_{13}L_{32}$ (e), and $4S_{13}L_{50}$ (f). Other samples with different oLA chain length have similar spectra with varied integrations.

Figure S8. Representative ^{13}C NMR spectra: $S_{17}L_{32}$ (a), $2S_{17}L_{18}$ (b), and $4S_{17}L_{46}$ (c). Other samples with different *o*LA chain length have similar spectra.

Figure S9. SEC of discrete block copolymers: $S_{17}L_m$ (a), $2S_{13}L_m$ (b), $2S_{17}L_m$ (c), and $4S_{13}L_m$ (d).

Figure S10. Representative DSC thermograms: $S_{17}L_{32}$ (a), $2S_{17}L_{18}$ (b), and $4S_{17}L_{24}$ (c). Glass transition of oLA block is indicated by blue triangles, and order-to-disorder transition by orange triangles. Heating rate 5 ºC/min.
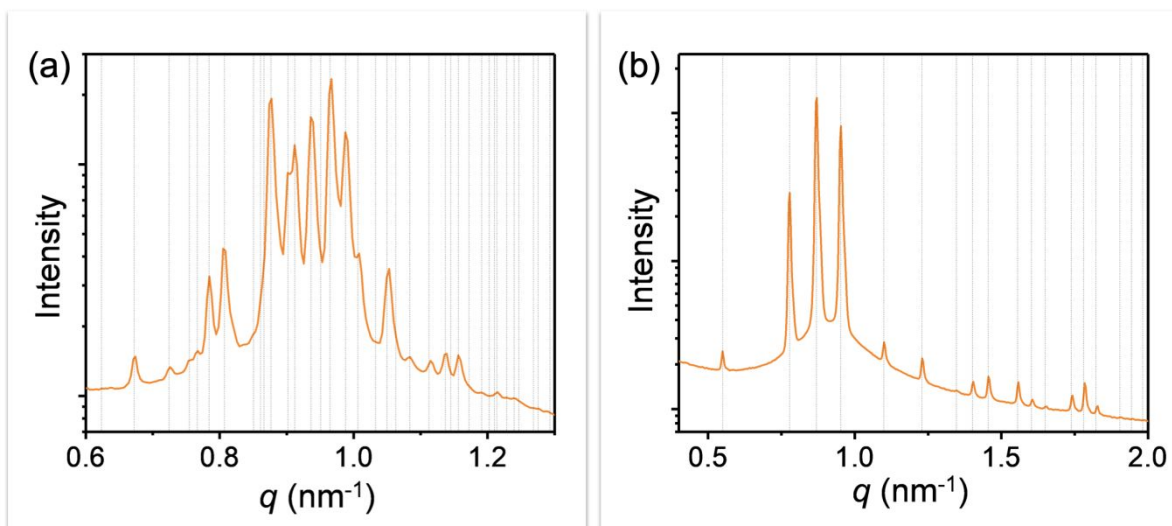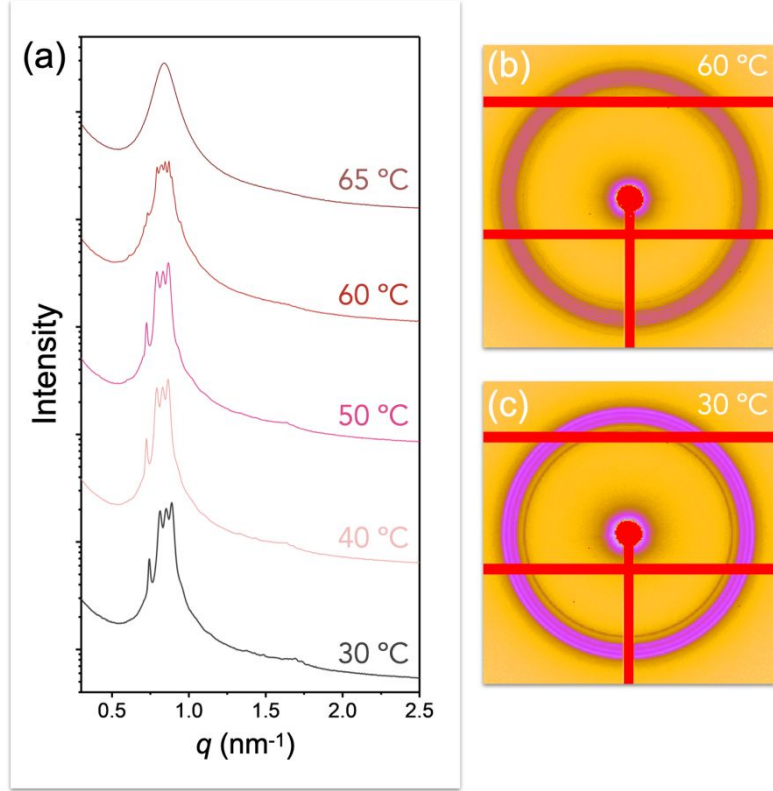
Figure S11. SAXS profiles of S_nL_m series with different compositions at room temperature. Samples were annealed at room temperature for 1 day after heating to 80 ºC for 10 min. Peak at $q = 1.43$ nm^{-1} (*) is scattering from background.
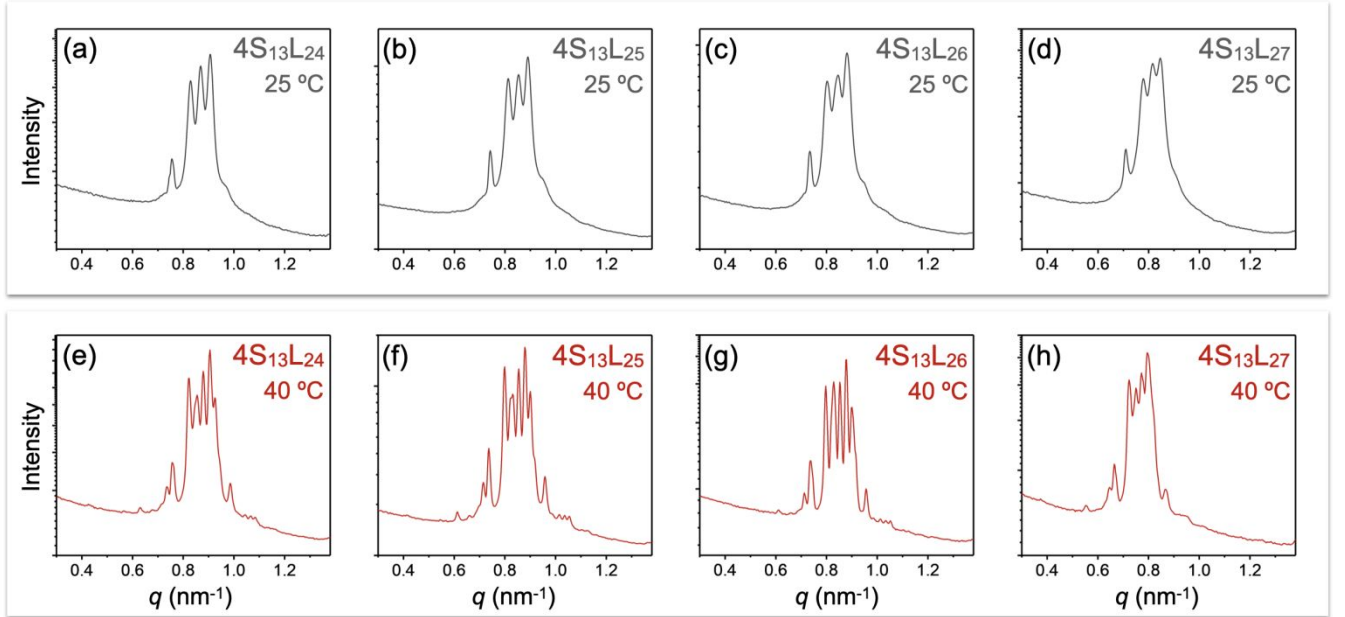

Figure S12. SAXS profiles of $2S_nL_m$ series with different compositions at room temperature. Samples were annealed at room temperature for 1 day after heating to 80 ºC for 10 min. Peak at $q = 1.43$ nm^{-1} (*) is scattering from background.

Figure S13. SAXS profiles of $4S_nL_m$ series with different compositions at room temperature. Samples were annealed at room temperature for 1 day after heating to 80 ºC for 10 min.
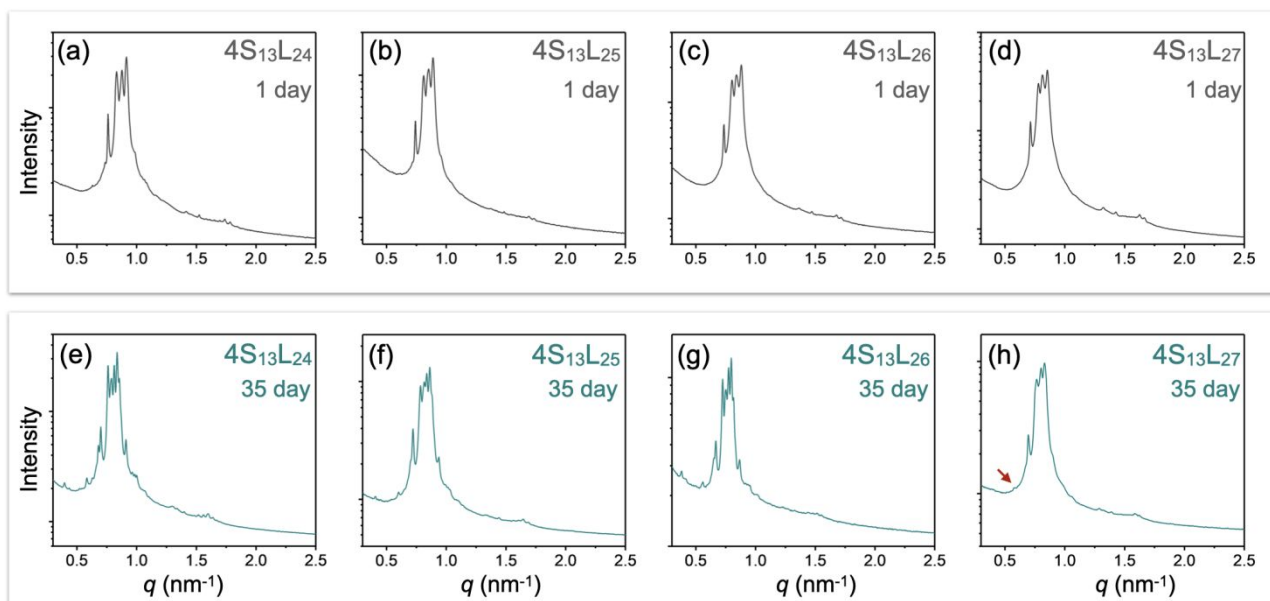

Figure S14. Peak indexing of $4S_{13}L_{22}$ (a, σ phase) and $2S_{17}L_{18}$ (b, A15 phase). Droplines are the allowed reflections based on the calculated lattice parameter.

Figure S15. *In-situ* temperature dependent SAXS profiles of $4S_{13}L_{25}$ (a), and corresponding 2D SAXS patterns at 60 ºC (b, σ phase) and 30 ºC (c, DQC phase). Samples $4S_{13}L_{24}$, $4S_{13}L_{26}$, and $4S_{13}L_{27}$ exhibit similar behaviors.

Figure S16. SAXS profiles of DQC forming samples annealed at 25 (a-d) and 40 ºC (e-h) for 24 hours: $4S_{13}L_{24}$ (a, e), $4S_{13}L_{25}$ (b, f), $4S_{13}L_{26}$ (c, g), and $4S_{13}L_{27}$ (d, h).

Figure S17. SAXS profiles of DQC forming samples annealed at 25 ℃ for 1 day (a-d) and 35 days (e-h): $4S_{13}L_{24}$ (a, e), $4S_{13}L_{25}$ (b, f), $4S_{13}L_{26}$ (c, g), and $4S_{13}L_{27}$ (d, h). The arrow in (h) indicates preliminary sign of transition to σ phase.

6. References

[1] Zhou, J.; Defante, A. P.; Lin, F.; Xu, Y.; Yu, J.; Gao, Y.; Childers, E.; Dhinojwala, A.; Becker, M. L. *Biomacromolecules* **2015**, *16*, 266-274.