

Supporting Information

Order-to-Disorder Transitions in Lamellar Melt Self-Assembled Core-Shell Bottlebrush Polymers

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Experimental Section

Materials. All solvents and reagents were purchased from Sigma-Aldrich Chemical Co. (Milwaukee, WI) and used as received unless otherwise noted. ϵ -Decalactone (>99%) was distilled from CaH_2 under reduced pressure and passed through activated Brockman Type I basic alumina in an argon glovebox. Anhydrous, anaerobic tetrahydrofuran (THF) and toluene were collected from a Vacuum Atmospheres, Inc. solvent purification system and individually degassed by three freeze-thaw cycles using $\text{N}_2(l)$. Tin(II) 2-ethylhexanoate (92.5-100%) was triply distilled under reduced pressure and stored in an argon glovebox. *rac*-lactide (99%) was recrystallized once from ethyl acetate and dried *in vacuo* prior to storage in a glove box. Grubbs' 3rd generation bis(pyridine) Ru-catalyst (**G3**) was prepared from Grubbs' 2nd generation catalyst by treatment with pyridine, according to a literature procedure.¹ No unusual safety hazards were encountered in this research except where noted below.

¹H NMR Spectroscopy. ¹H NMR spectra were acquired at 22 °C in CDCl_3 using a Bruker Avance 400 MHz spectrometer equipped with a Smartprobe using a 25 s pulse repetition delay. All spectra were referenced relative to the residual protiated solvent peak of CDCl_3 (δ 7.26 ppm). Molar masses for the **LDL** triblock macromonomers were calculated by quantitative integration of the polymer chain methine protons relative to the terminal methine protons. Representative ¹H NMR spectra for a poly(ϵ -decalactone) and a corresponding **LDL** triblock are given in Figures S1 and S2, respectively.

Size Exclusion Chromatography (SEC). SEC analyses were performed at 22 °C on a Viscotek GPCMax VE 2001 system equipped with three Agilent Technologies PLGel Mixed-B columns (350 mm x 7.5 mm) and a Viscotek VE 3580 refractive index detector, using BHT-stabilized tetrahydrofuran (THF) with a solvent flow rate of 1 mL/min. SEC with multi-angle

laser light scattering (SEC-MALLS) measurements were performed in THF at 25 °C using an Agilent 1260 Infinity liquid chromatography system equipped with three Tosoh Styragel HR columns and a Wyatt DAWN Heleos II 18-angle laser light scattering detector, as well as a Wyatt OPTILAB T-rEX refractive index detector. For each sample, SEC-MALLS analysis assumed 100% mass recovery in order to calculate the refractive index increment (dn/dc) of the sample for absolute molar mass determination.

Small-angle X-Ray Scattering (SAXS). SAXS samples were prepared by solvent casting solutions comprising 40 mg of a given sample in toluene (0.7 mL) into alodined aluminum DSC pans on a temperature-regulated hotplate set to $T = 90\text{--}110$ °C. Samples were subsequently annealed under high vacuum at 130 °C for 2 h to effect solvent removal, prior to sealing the DSC pans with hermetic lids. SAXS analyses at the Sector 12-ID-B beamline of the Advanced Photon Source (Argonne, IL) employed an incident beam energy of either 14.0 keV ($\lambda = 0.886$ Å) with a 3.617 m sample-to-detector distance. Two-dimensional synchrotron SAXS patterns were recorded on a Pilatus 2M detector with 1475×1679 pixel resolution (25.4 cm \times 28.9 cm area). The sample-to-detector distance was calibrated using a silver behenate standard ($d = 58.38$ Å), which allowed calibration of the scattering wavevector q -scale in all obtained data. Temperature-dependent SAXS measurements used a Linkam DSC hot-stage, on which samples were equilibrated for at least 5 min at each temperature prior to data collection; typical exposure times of ~ 0.1 s yielded high quality data with no detectable sample damage. **Safety Note:** Synchrotron SAXS analyses pose significant safety hazards, and thus institutional radiation safety protocols were strictly followed to minimize exposure to ionizing radiation.

Samples for lab source SAXS analyses were solvent cast from a solution comprising 40 mg polymer in 0.7 mL toluene onto a glass slide at 90 °C. The resulting polymer films were isolated

and placed into home-made aluminum sample holders with Kapton windows, annealed *in vacuo* at 130 °C for 2 h, and sealed for analysis. Lab source SAXS measurements were made using a SAXSLAB Ganesha300XL instrument in the University of Minnesota College of Science & Engineering Characterization Facility. Cu K_α X-rays ($\lambda = 1.54 \text{ \AA}$) generated by a Xenocs Geni3DX source were collimated through 2 or 3 sets of “scatterless” 4-bladed slits (JJ X-Ray, A/S) prior to passage through the sample. 2D-SAXS patterns were acquired on a Dectris EIGER 1M detector with 1030×1065 pixels ($75 \text{ }\mu\text{m} \times 75 \text{ }\mu\text{m}$ pixel size) at a sample-to-detector distance of 46.8 cm. Samples were mounted in an evacuated sample environment and equilibrated at the desired temperature on a Linkam hot-stage for ~ 20 min prior to data acquisition using exposure times of ~ 3 -5 min. **Safety Note:** X-ray scattering analyses pose a significant safety hazard, and University of Minnesota radiation safety protocols were followed to mitigate ionizing radiation exposure.

All 2D-SAXS patterns were azimuthally-integrated to obtain one-dimensional scattered intensity $I(q)$ versus scattering wavevector q plots, using the DataSqueeze software package (<http://www.physics.upenn.edu/~heiney/datasqueeze/index.html>). 1D-SAXS intensity profiles were further analyzed using customized Igor Pro procedure files developed by our group.²

Dynamic Mechanical Spectroscopy (DMS). Order-to-disorder transition temperatures (T_{ODT} 's) for **LDL** triblock macromonomers were determined by DMS isochronal temperature ramp tests on a TA Instruments ARES-LS2 strain-controlled rheometer using a heating rate of 3 °C/min. Measurements were conducted using a 25 mm diameter parallel-plate geometry, with $|\gamma| = 1\%$ and $\omega = 1 \text{ rad/s}$.

5-Norbornene-2-*exo*,3-*exo*-dimethanol Inimer Synthesis. *cis*-5-Norbornene-*exo*-2,3-dicarboxylic anhydride was purified by column chromatography using 1:2:6 ethyl

acetate:acetone:hexanes as the eluent to remove the *endo* isomer impurity. The resulting product was coarsely dried by rotary evaporation to afford a white solid, which was exhaustively dried on a high vacuum line prior to reduction of the anhydride with LiAlH_4 in a manner similar to that reported by Hanson and co-workers.³ **Safety Note:** *The following protocol uses LiAlH_4 , which is an extremely water-reactive solid. Particular care must be exercised in the highly exothermic addition of anhydrous THF to the dry, solid LiAlH_4 as described below to prevent potentially dangerous decomposition reactions.*

LiAlH_4 (1.4 g, 36.9 mmol) was added to an oven-dried 500 mL three-necked flask charged with a Teflon-coated magnetic stir bar, after which the flask was evacuated and refilled with $\text{N}_2(\text{g})$ three times to render the atmosphere inert and oxygen-free. The flask was cooled to 0 °C in a water/ice bath, prior to adding THF (10 mL) dropwise to the solid LiAlH_4 via an addition funnel. The purified *cis*-5-Norbornene-*exo,exo*-2,3-dicarboxylic anhydride (3.02 g, 18.4 mmol) was dissolved in THF (25 mL) and added dropwise via an addition funnel to the stirring LiAlH_4 /THF mixture at 0 °C. This reaction mixture was allowed to warm to 22 °C gradually, while stirring overnight. This reduction reaction was quenched by first cooling the flask to 0 °C, followed by dropwise addition of deionized H_2O (5 mL). The reaction mixture was then vacuum filtered through a Celite pad to remove the solids and the filtrate was dried over $\text{MgSO}_4(\text{s})$. Removal of the THF solvent via rotary evaporation afforded a colorless, viscous oil. The oil was further purified by neutral silica gel column chromatography using 1:3 ethyl acetate:hexanes as the eluent, followed by solvent removal *in vacuo*.

Facile product isolation in higher yields with improved purities was achieved using a Fieser work-up to quench the reaction and to isolate the desired norbornene dimethanol. Under this strategy, the reaction was quenched after 12 h with deionized $d\text{H}_2\text{O}$ (1:1 w/v LiAlH_4 :DI water).

The reaction was subsequently treated with 15 wt% aqueous NaOH (1:1 v/v dH₂O:NaOH(aq)), and then dH₂O (3:1 v/v dH₂O:NaOH(aq)). After stirring for 15 min, anhydrous MgSO₄(s) was added to dry the reaction product prior to filtration through a plug of Celite. Solvent removal from the resulting filtrate yielded the desired norbornene dimethanol, which was purified by column chromatography under the aforementioned conditions. Yield 1.72 g (57%). ¹H NMR (400 MHz; CDCl₃): δ (ppm) 6.17 (CH=, *t*, 2 H), 3.73 (CH₂OH, *m*, 4 H), 2.51 (CH-CH₂-CH, *m*, 2 H), 1.81 (CH-CH₂OH, *m*, 2 H) 1.39–1.21(CH₂ bridge, *m*, 2 H).

Representative Synthesis of LDL (147, 0.52) Triblock Polymer. This synthesis protocol was adapted from Martello *et al.*⁴ In an argon glovebox, Sn(Oct)₂ (71.2 mg, 176 μmol) was dissolved in dry toluene (1.00 mL) as a stock solution. Norbornene dimethanol (87.3 mg, 566 μmol), ε-decalactone (2.49 g, 14.6 mmol), and Sn(Oct)₂ stock (83 μL of stock solution) were added to an oven-dried 50 mL pressure tube charged with a Teflon-coated magnetic stir bar. The tube was sealed, removed from the glovebox and stirred in an oil bath at 170 °C for 2.5 h prior to cooling. The pressure tube was then returned to the glovebox, and a reaction aliquot of the poly (ε-decalactone) was removed for ¹H NMR and SEC analyses. Anhydrous toluene (5.7 mL) and *rac*-lactide (3.12 g, 21.7 mmol) were then added to the pressure tube, which was resealed and brought out of the glovebox. Lactide polymerization was achieved by heating to 110 °C for 4 h in a temperature-regulated oil bath. The solution was then cooled, diluted with toluene, and precipitated three times in cold methanol prior to freeze-drying the isolated solids from benzene. ¹H NMR (400 MHz; CDCl₃): δ(ppm) 6.16 (CH= initiator, *s*, 1.86 H), 5.04-5.29 (-CH(CH₃)-O-, *m*, 90 H), 4.85 (-CH(C₄H₉)-O-, *quin*, 29 H), 4.35 (CH(CH₃)-OH end group, *m*, 1.90 H) 4.25-3.95(-CH₂-O- initiator, *m*, 4.69 H), 2.26 (-O-C=O-CH₂-, *m*, 57 H), 1.70-1.43 (-CH(CH₃)-O- and

-O-C=OCH₂CH₂CH₂CH₂CH(CH₂CH₂CH₂CH₂)-O-, *m*, 461 H), 1.41 – 1.16 (-O-C=OCH₂CH₂CH₂CH₂CH(CH₂CH₂CH₂CH₃)-O-, *m*, 179 H), 0.88 (-CH₃, *m*, 88 H).

Representative Synthesis of csLDL (147, 0.52)-11 Core-shell Bottlebrush Polymer. In an argon glovebox, **G3** (21.2 mg, 29.2 μmol) was dissolved in toluene (1.47 g) to make a stock solution. In a second vial, **LDL**(147, 0.52) (3.14 g) was dissolved in toluene (15.68 g) to make a polymer stock solution with [**LDL**] = 0.015 M. Using a syringe, **LDL** stock solution (9.63 g) was transferred into an oven-dried 25-mL scintillation vial equipped with a Teflon-coated magnetic stir bar. The polymerization was initiated by injecting the desired amount of **G3** stock solution (814 μL) into the stirred polymer solution. After 12 h, the vial was removed from the glovebox and the reaction was quenched by the addition of ethyl vinyl ether (~0.25 mL) and stirring for 20 min. The resulting polymer solution was sequentially precipitated three times in cold methanol before freeze-drying the isolated solids from benzene. The resulting **csLDL** (147,0.52) was characterized with SEC-MALLS and SAXS as described above.

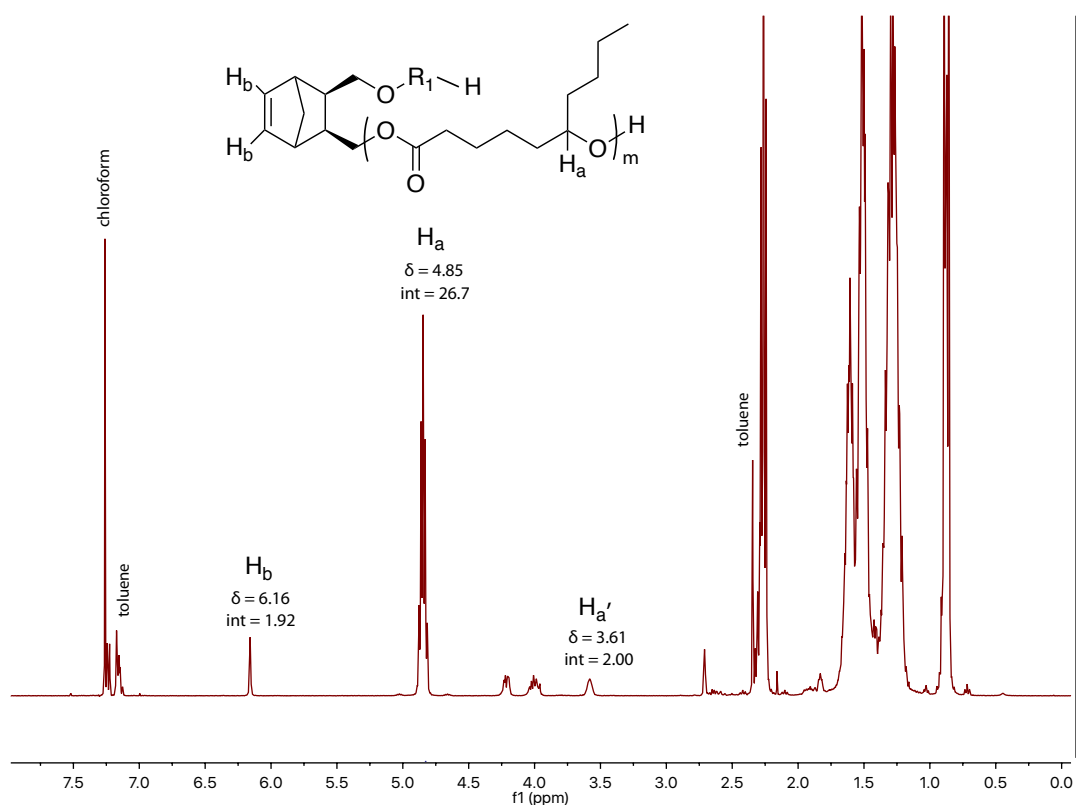


Figure S1. ^1H NMR spectrum of poly(ϵ -decalactone) homopolymer (**D**) in CDCl_3 at 22°C used for molecular weight ($M_{n,D}$) determination by end group analysis. The polymer methine (H_a) peak was integrated with respect to the terminal methine ($\text{H}_{a'}$) proton to determine the degree of polymerization. In the chemical structure given, R_1 refers to the second poly(ϵ -decalactone) chain pendant of the norbornene dimethanol.

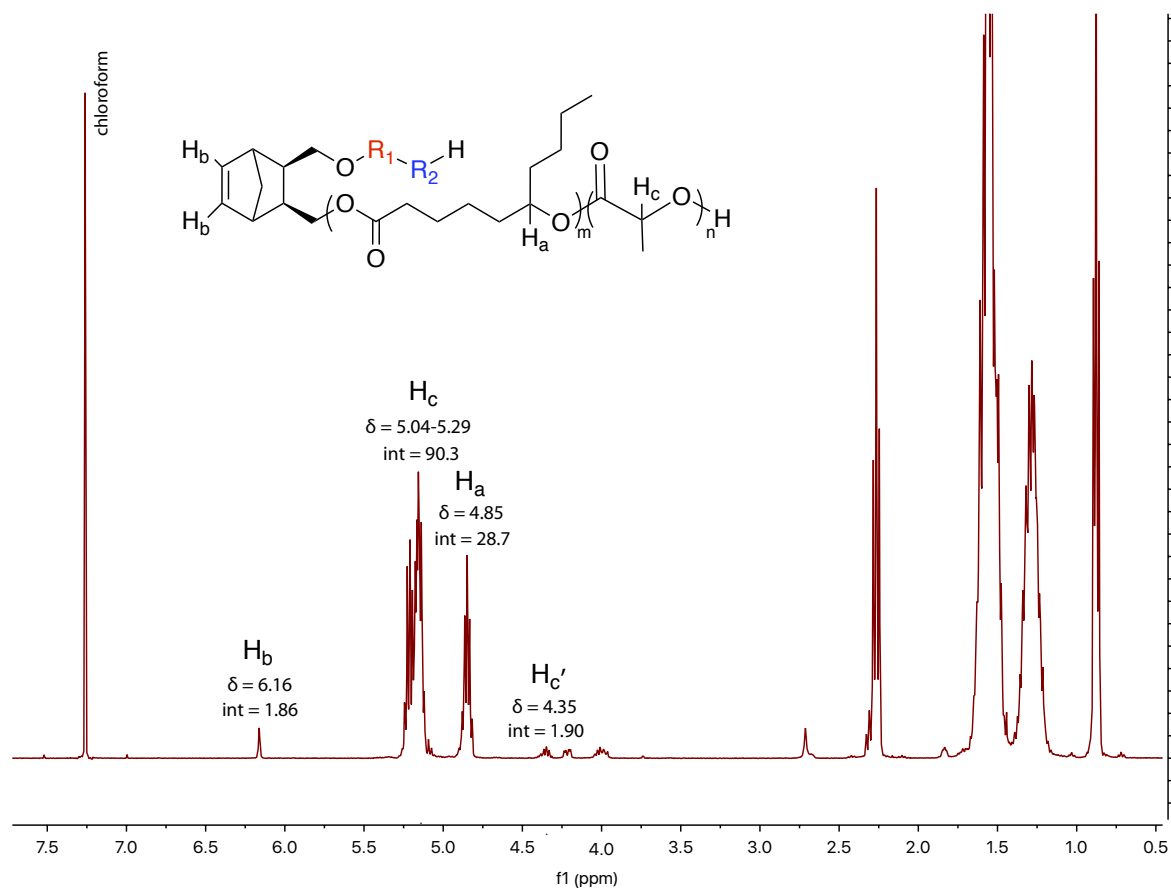


Figure S2. ^1H NMR spectrum of poly(lactide-*block*- ϵ -decalactone-*block*-lactide) triblock (**LDL**) macromonomer in CDCl_3 at 22 $^\circ\text{C}$, which was used for ^1H NMR end group analysis determination of $M_{n,\text{LDL}}$. The integrated peak intensities for resonances corresponding to H_a and H_c were used to determine M_n for the poly(lactide) blocks.

Table S1. Molecular Characteristics of LDL Triblock Polymers

Sample ^a	$M_{n,D}$ (kg/mol) ^b	$M_{n,L}$ (kg/mol) ^b	\bar{D}_D ^c	\bar{D}_{LDL} ^c	N_{arm} ^a	f_L ^a
LDL (116, 0.52)	3.9	2.6	1.17	1.20	116	0.52
LDL (147, 0.52)	4.9	3.4	1.23	1.23	147	0.52
LDL (178, 0.52)	5.8	4.1	1.18	1.23	178	0.52
LDL (186, 0.51)	6.3	4.2	1.17	1.19	186	0.51
LDL (227, 0.51)	7.7	5.1	1.17	1.25	227	0.51

^a Samples are identified as **LDL**(N_{arm} , f_L), where N_{arm} is the segment density normalized degree of polymerization for the triblock and f_L is the poly(lactide) volume fraction calculated using the 22 °C densities $\rho_L = 1.24$ g/cm³ and $\rho_D = 0.97$ g/cm³ and a 118 Å³ reference volume. ^b Molar mass calculated from ¹H NMR end group analysis in CDCl₃ at 22 °C using the terminal methine hydrogen. ^c **D** homopolymer segment and **LDL** triblock molar mass dispersities $\bar{D} = (M_w/M_n)$ determined by SEC in THF at 22 °C against poly(styrene) standards.

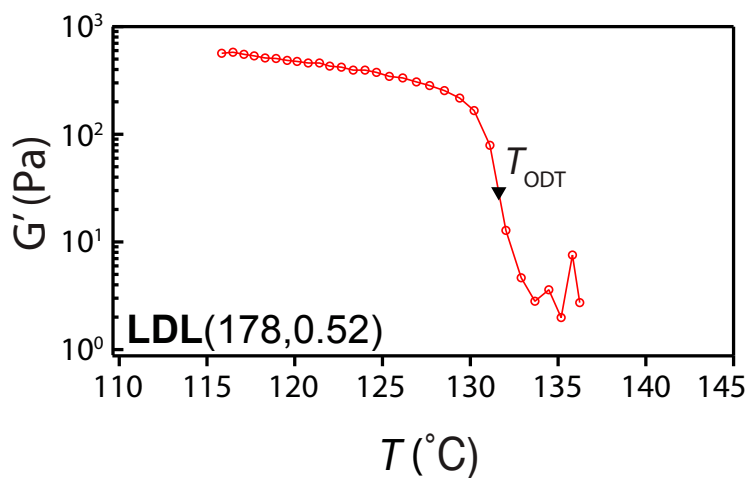


Figure S3. Dynamic elastic storage shear modulus $G'(\omega)$ as a function of temperature (T) for macromonomer **LDL**(178, 0.52), obtained by isochronal dynamic mechanical spectroscopy (DMS) parallel-plate rheometry with $\omega = 1$ rad/s and $|\gamma| = 1\%$. This test employed a temperature ramp rate of 3 °C/min. The midpoint temperature $T_{ODT} = 132$ °C corresponds to the order-to-disorder transition for this sample.⁵⁻⁶

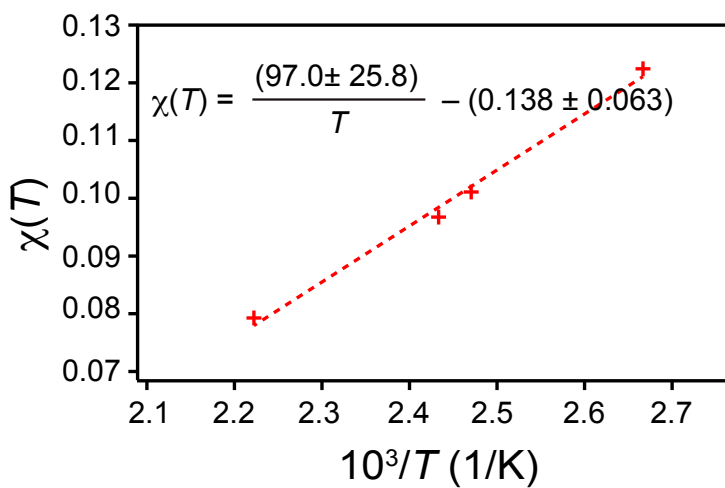


Figure S4. Fit of the temperature-dependent $\chi_{LD}(T) = 17.996/N$ at $T = T_{ODT}$ for the four ordered **LDL** macromonomer samples with $147 \leq N \leq 227$ listed in Table S1. Data were fit to the standard form $\chi(T) = (A/T) + B$ to obtain $A = (97.0 \pm 25.8)$ and $B = -(0.138 \pm 0.063)$.

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