

Supporting Information

Thin film phase behavior of bottlebrush/linear polymer blends

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Nuclear Magnetic Resonance (NMR) Spectroscopy: Figure S1 compares ^1H NMR spectra of PS bottlebrush polymers acquired before and after removal of the chain transfer agent (CTA) through aminolysis in the presence of triphenylphosphine. The hydrogen at the position of 3.25 ppm (H_a), corresponding to the one the dodecyl chain near thiol group, disappears after removal of CTA end-groups. An absorbance peak at 380 nm also disappears after removal of the CTA.

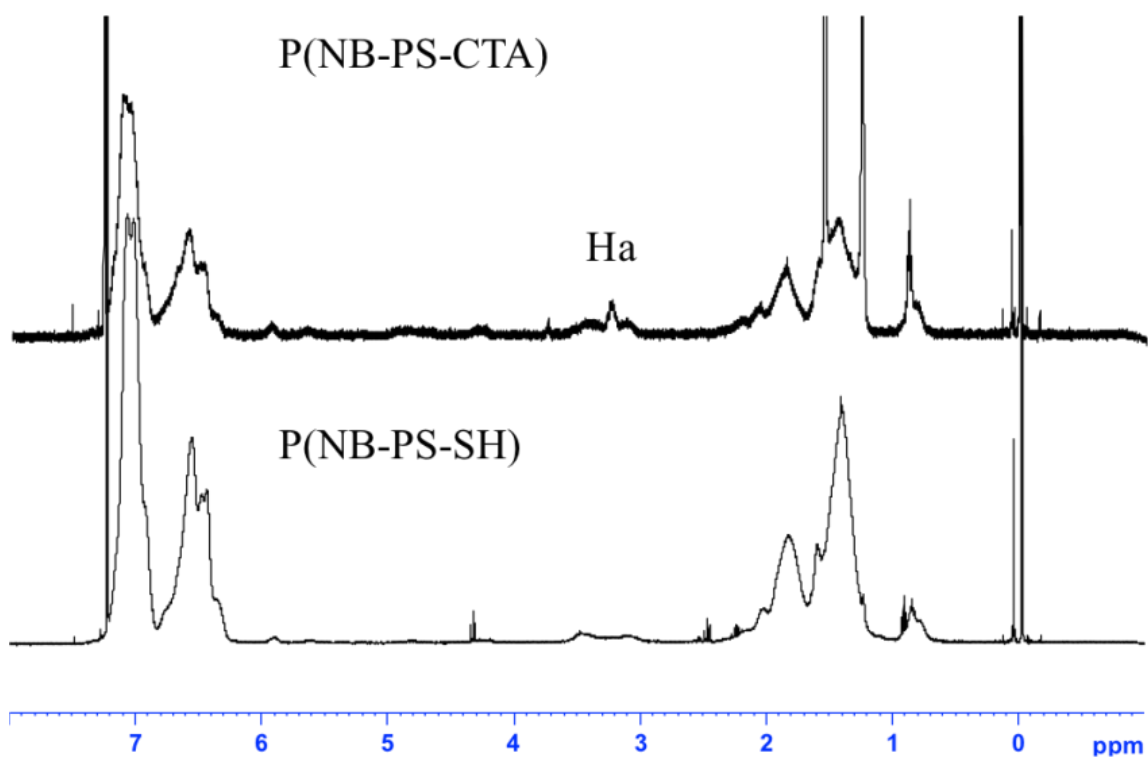


Figure S1: ^1H NMR spectra of PS bottlebrush with CTA side-chain endgroups (P(NB-PS-CTA) , top); and PS bottlebrush with thiol side-chain endgroups (P(NB-PS-SH)), bottom) in CDCl_3 with the concentration of 20mg/ml.

Gel Permeation Chromatography (GPC)

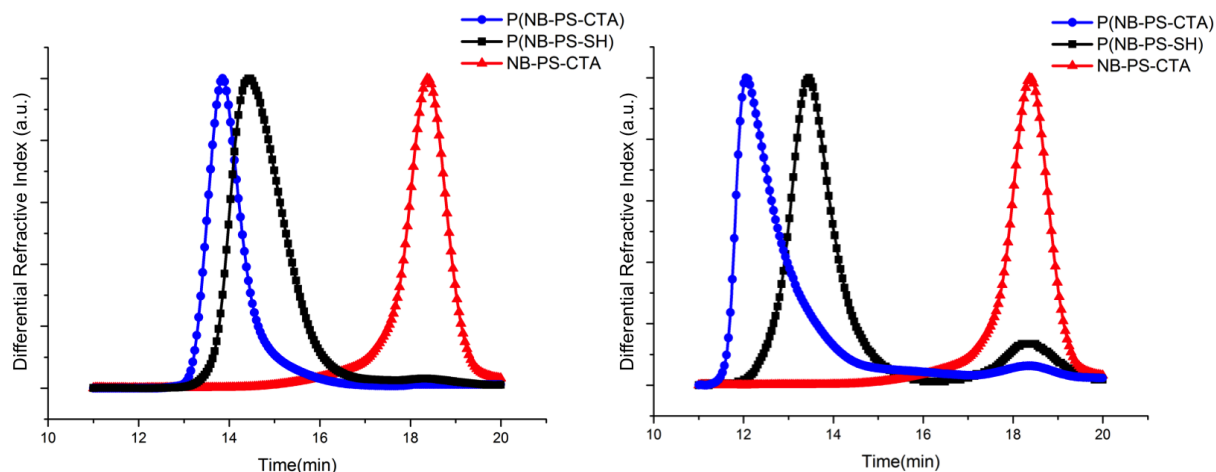


Figure S2: Size-exclusion chromatography analysis of PS bottlebrush and macromonomers used for PS bottlebrush batch 1 (left) and batch 2 (right). Both plots show the PS macromonomer (NB-PS-CTA, red triangles), the PS bottlebrush with CTA side-chain endgroups (P(NB-PS-CTA), blue circles), and the final PS bottlebrush with thiol-terminated side-chains (P(NB-PS-SH), black squares). A decrease in molecular weight is observed after CTA removal reflecting a decrease in the overall molecular weight of the block copolymer.

Miscibility of linear PS/linear dPS by Flory-Huggins Theory: The χ parameter for blends of PS and dPS is:¹

$$\chi = 0.2T(\text{K})^{-1} - 2.9 \times 10^{-4}$$

This is valid for the temperature range of approximately 140-230 °C, and at 165 °C, $\chi \approx 1.7 \times 10^{-4}$.

The critical solution temperature (T_c) for these blends can be estimated with Flory-Huggins theory:²

$$\chi_c = \frac{1}{2} \left(\frac{1}{N_{PS}^{1/2}} + \frac{1}{N_{dPS}^{1/2}} \right)^2 = 0.2T_c(\text{K})^{-1} - 2.9 \times 10^{-4}$$

Table S1 summarizes T_c for blends of linear PS and linear dPS, where we define a linear PS molecule with the equivalent molecular weight to a bottlebrush. Such blends are completely miscible. (Note that we extrapolate χ to temperatures where the model is no longer valid; this is merely to illustrate that the annealing temperature of 165 °C is well above the critical point.)

Table S1: Critical temperature predicted by Flory-Huggins theory for analogous linear PS/linear dPS blends.

$N_{dPS} = N_m$	$N_{PS} = N_b N_{sc}$	χ_c	T_c (°C)
19	12,159	2.8×10^{-2}	-266
96	12,159	6.2×10^{-3}	-242
490	12,159	1.8×10^{-3}	-160
1,201	12,159	7.8×10^{-4}	-75
2,500	12,159	4.2×10^{-4}	8

Atomic Force Microscopy: Atomic force microscopy images were collected with a MultiMode 3 (Veeco) in Tapping Mode using silicon probes with a spring constant of approximately 40 N/m. Typical parameters for data acquisition were 1.7 Hz scan frequency, $10\ \mu\text{m} \times 10\ \mu\text{m}$ scan area, and 512×512 image resolution. The surfaces are very flat with no evidence of phase separation.

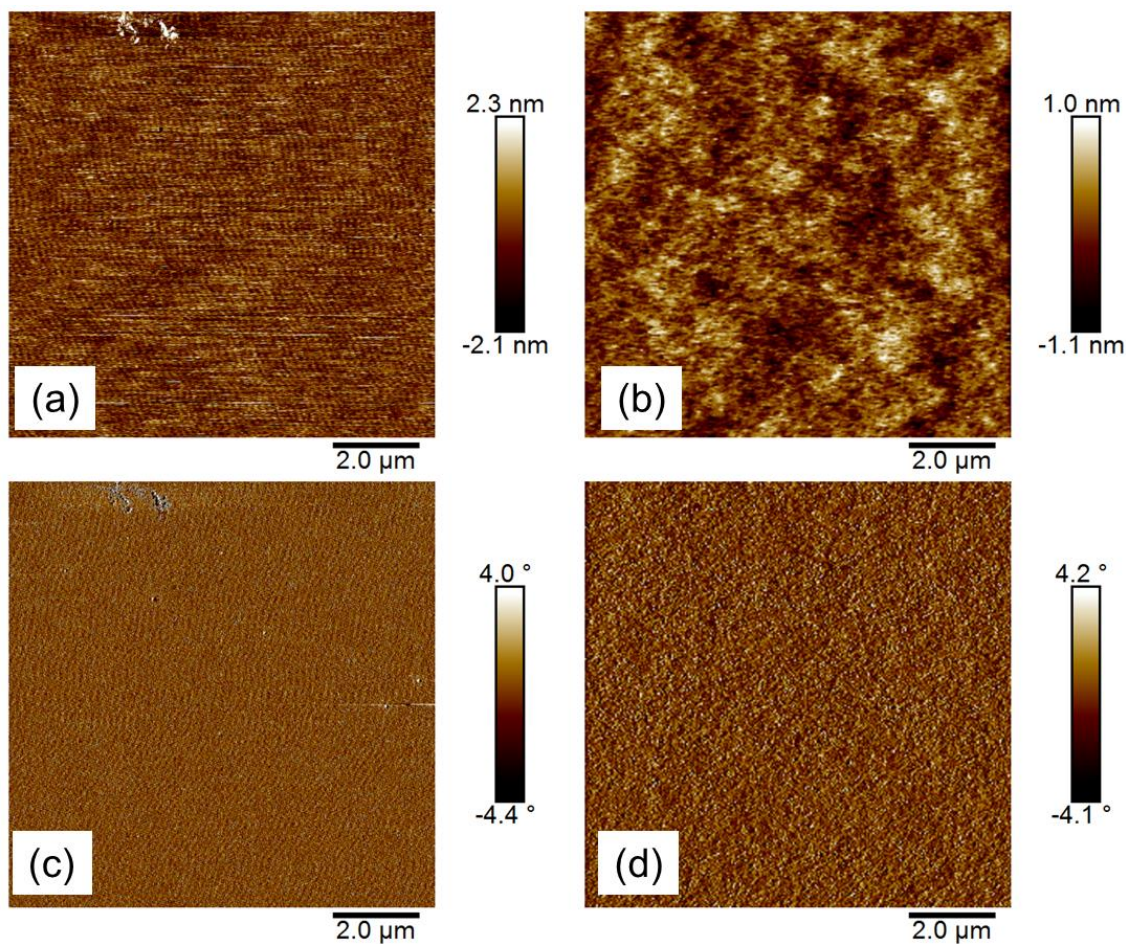


Figure S3: Atomic force microscopy measurements of blend films (10 wt% bottlebrush polymer). (a,c) Height and phase measurements of film's surface, $N_m = 19$; (b,d) Height and phase measurements of film's surface, $N_m = 2500$.

Optical Microscopy: Optical microscopy images of as-cast and annealed 150 nm films were acquired using a Nikon LV150 reflected light microscope. Images were acquired at a magnification of 2.5X (Figure S4) and 100X (Figure S5). The surfaces exhibit some variation in thickness over very large length scales (ca. 1 mm), but are optically flat over tens of micrometers.

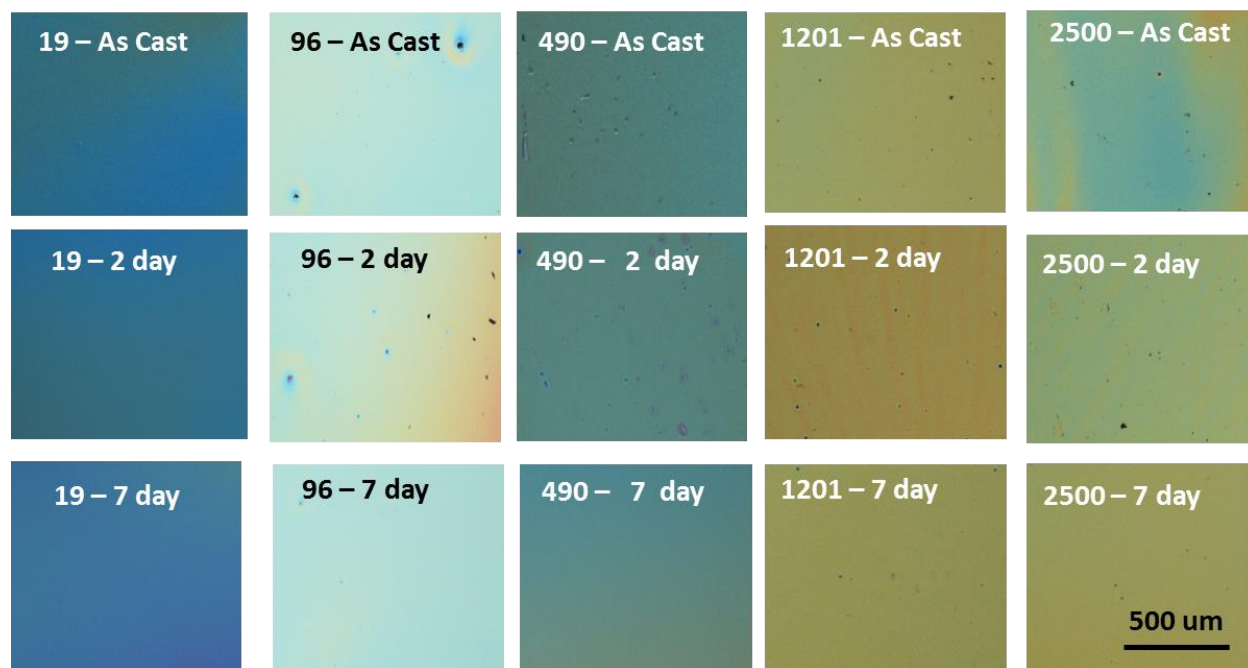


Figure S4: Optical microscopy measurements (2.5X) of blend films (10 wt% bottlebrush polymer, $N_{sc} = 61$). The matrix degree of polymerization N_m is noted on each micrograph, along with the annealing time at 165 °C.

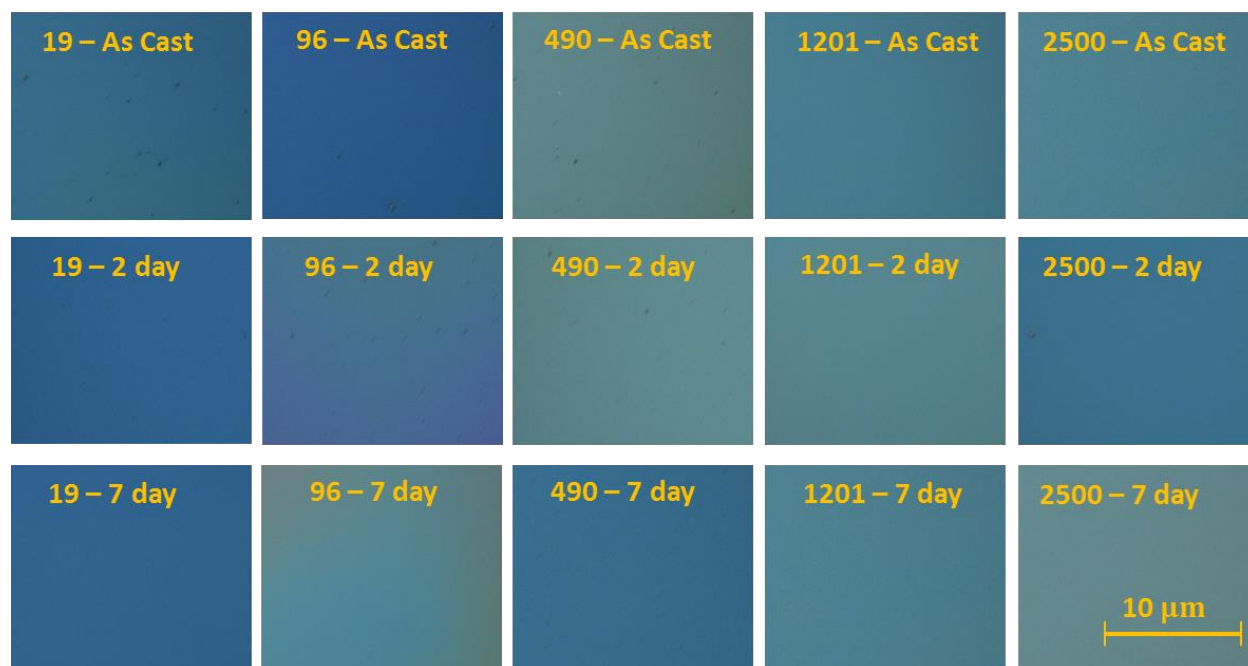


Figure S5: Optical microscopy measurements (100X) of blend films (10 wt% bottlebrush polymer, $N_{sc} = 61$). The matrix degree of polymerization N_m is noted on each micrograph, along with the annealing time at 165 °C.

SIMS Data for 200 nm Films: Figure S6 reports the SIMS data for 200 nm films with fits to the composition profile described in the manuscript. The interfacial excesses are reported in Figure 3 of the manuscript.

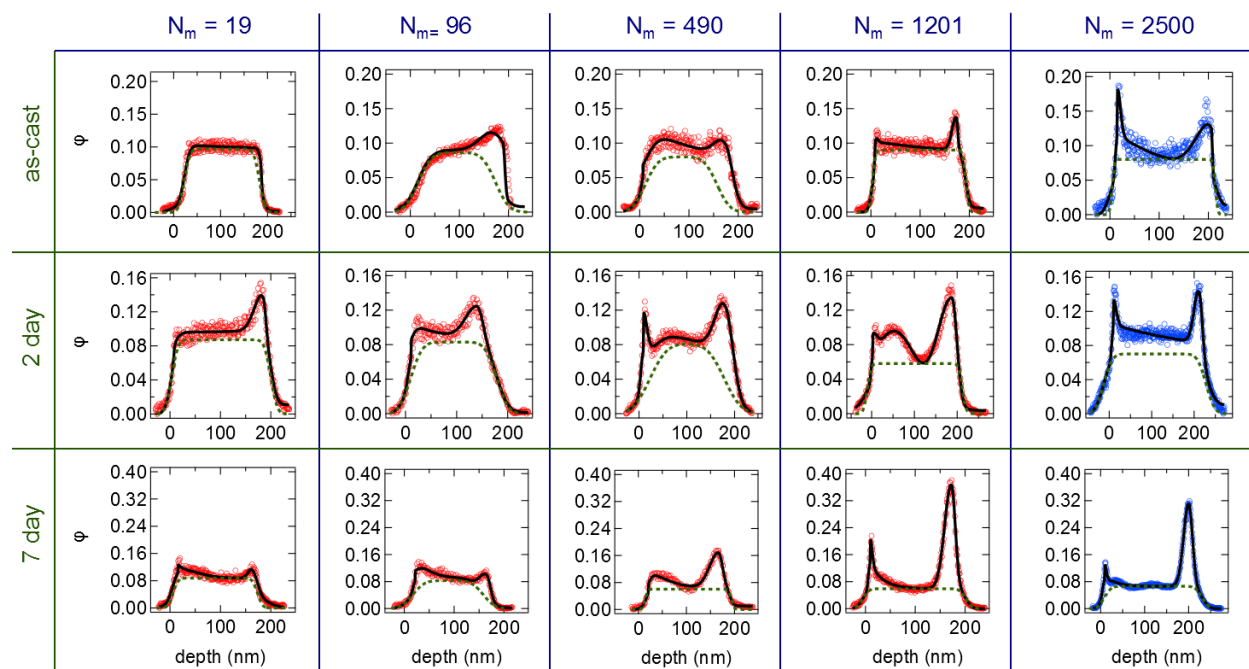


Figure S6: Concentration of bottlebrush polymer (ϕ) as a function of depth into the film (position 0 denotes the air interface, and 200 nm is the substrate interface). Each column is a different matrix chain length N_m , while each row is a different annealing time (165 °C). Open symbols denote the SIMS data (red is $N_b = 193$, and blue is $N_b = 90$). Solid black lines/grey dashed lines are fits to the model described in the discussion.

Synthesis of NB-dPS-CTA macromonomers. NB-dPS-CTA was prepared *via* reversible-addition fragmentation chain transfer (RAFT) polymerization. For the synthesis of NB-dPS6K-CTA, *d*₈-styrene (10.0 g, 89.13 mmol), NB-CTA (194.1 mg, 0.349 mmol), and AIBN (5.7 mg, 3.47×10⁻² mmol) were mixed in a 100 mL RBF, and the solution was purged by bubbling nitrogen through the solution for 30 minutes. The polymerization was initiated by raising the temperature to 65 °C. After 9 h, the reaction flask was removed from the heat and the polymer was recovered by precipitation in methanol. (1.54 g, 71 % yield, based on the conversion of styrene.) The GPC spectrum is presented in Figure S7.

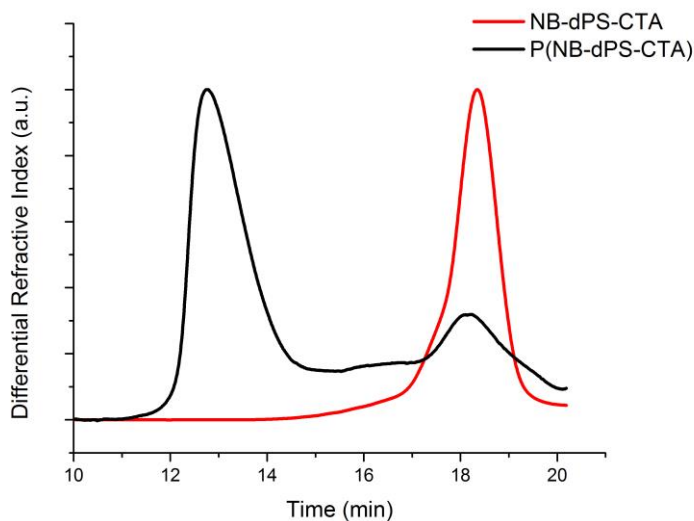


Figure S7: GPC spectra of dPS macromonomer (NB-dPS-CTA, red line) and dPS bottlebrush (P(NB-dPS-CTA), black line).

P(NB-dPS6K-CTA): Bottlebrush polymers were prepared by ROMP using a procedure similar to that for protonated PS bottlebrushes. The macromonomers were added to a dry, 10 mL round bottom flask charged with a stir bar. The flask was then degassed with three pump-purge cycles, and the desired amount of degassed, anhydrous dichloromethane (total macromonomer concentration was 0.02-0.05 M) was added. (H₂IMes)(pyr)₂(Cl)₂RuCHPh was dissolved in degassed, anhydrous dichloromethane in a separate flask. The catalyst solution was transferred to the reaction flask containing macromonomers *via*

cannula to initiate the polymerization and stirred at room temperature for at least 1 hour. The reaction was quenched by addition of ethyl vinyl ether after completion. The product was collected by precipitation in methanol dried under vacuum. (95% yield, based on the conversion of NB-PS-CTA). The GPC spectrum is presented in Figure S7.

SIMS Data for dPS bottlebrush/PS matrix: The objective of these experiments was to determine if isotopic labeling or type of functional group at the end of side-chains play a role in the bottlebrush segregation profiles. After 2 days of thermal annealing at 165°C, we observe that dPS bottlebrushes segregate more strongly than PS bottlebrushes at the free surface, which is expected based on (1) the slightly lower surface energy of dPS compared with PS, and (2) the presence of low surface energy CTA groups at the chain ends. The surface and substrate excesses after annealing are $z^* = 3.3$ nm and 4.0 nm, respectively. (For comparison, the corresponding surface excess for PS bottlebrush/dPS matrix was approximately 1.5 nm after 2 or 7 days of annealing, while the substrate excess was 3-6 nm depending on the annealing time.) The dPS bottlebrushes have shorter backbone lengths than either PS bottlebrush, and the difference in size/aspect ratio might play a role in the observed phase behavior.

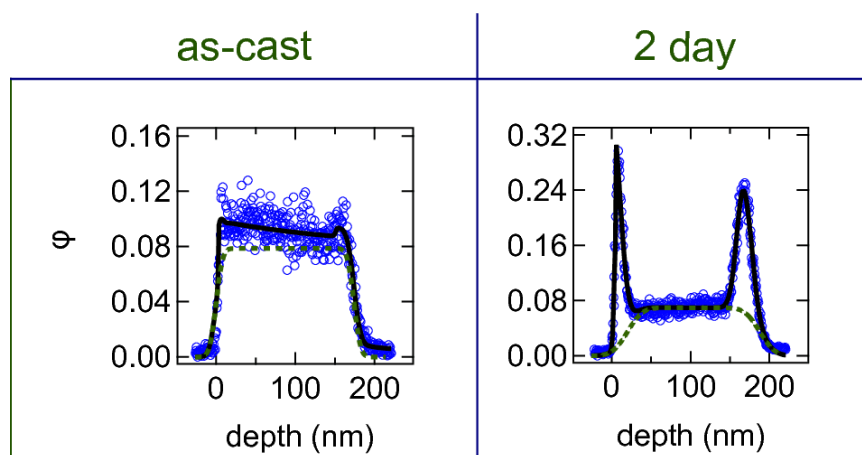
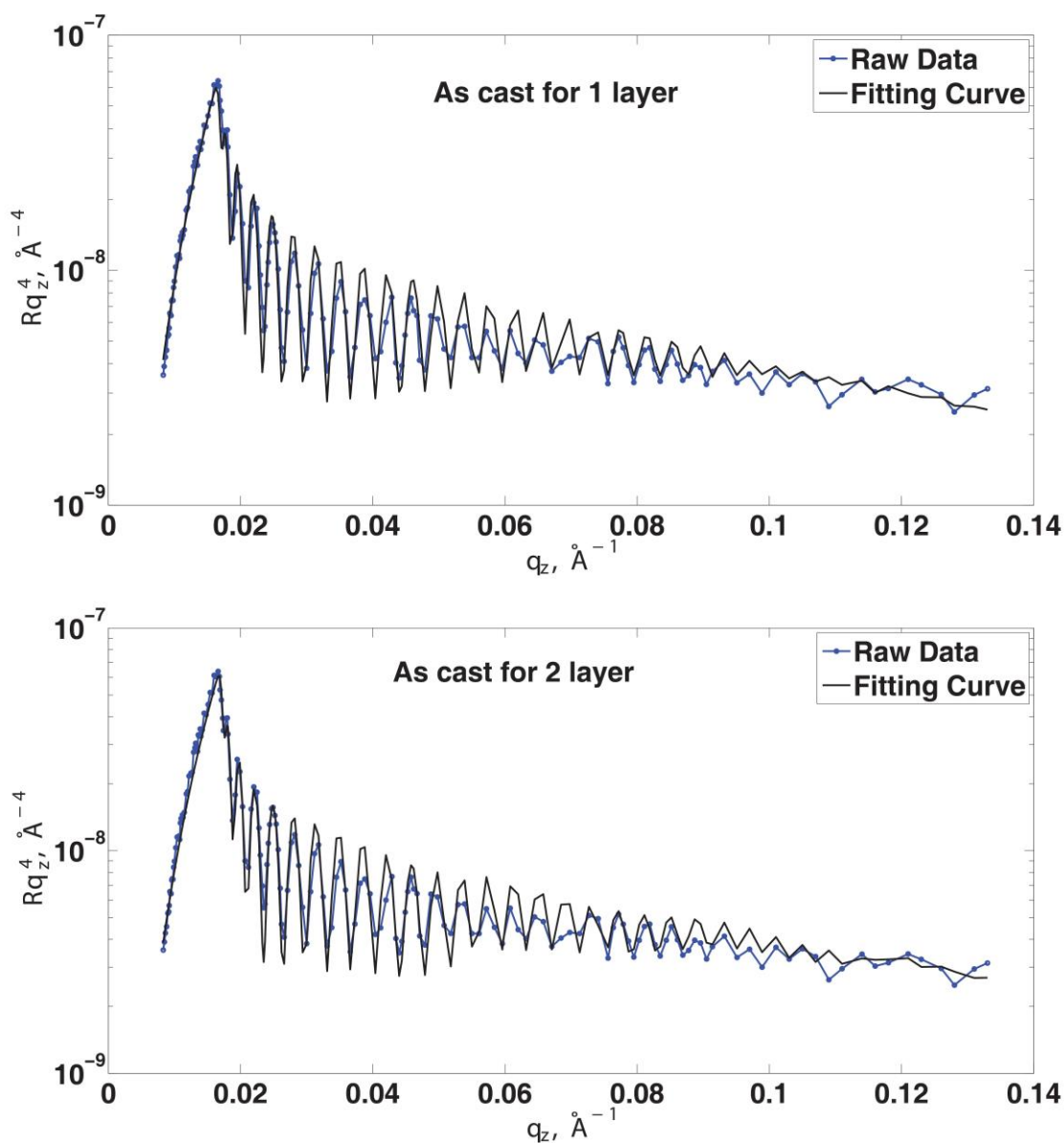


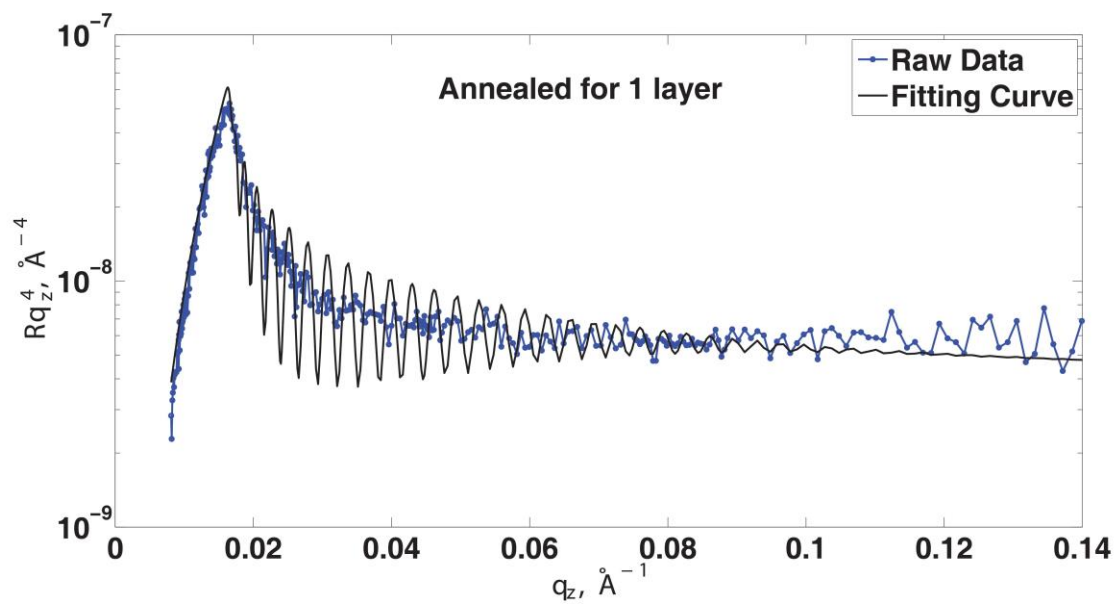
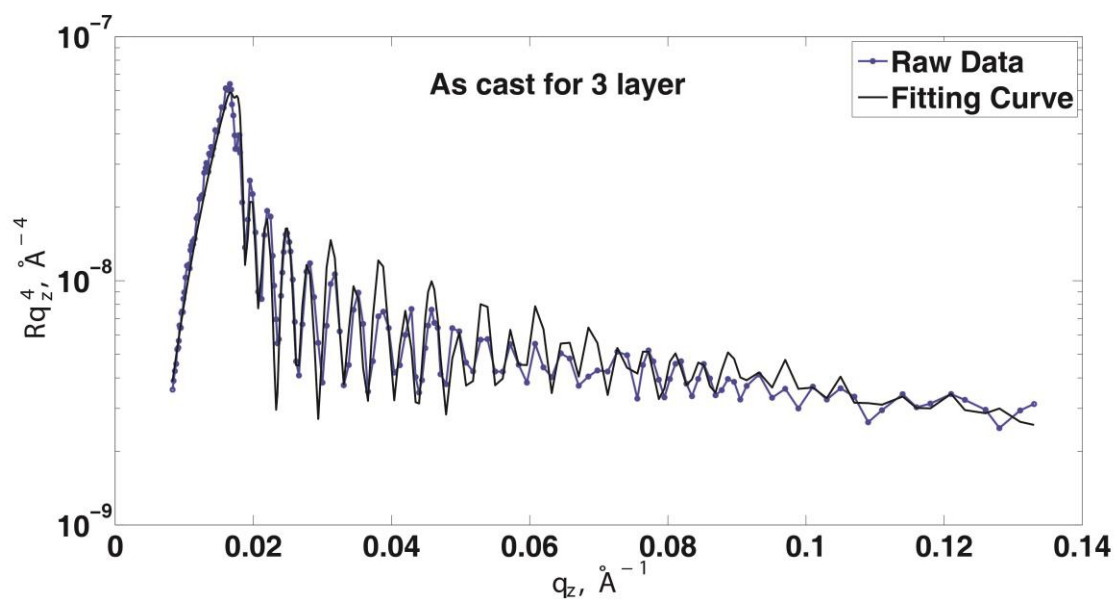
Figure S8: SIMS data of dPS bottlebrushes with hydrogenated linear PS. The dPS bottlebrush has side chain lengths of $N_{sc} = 52$ ($\bar{D} = 1.23$) and backbone length of $N_b = 49$ ($\bar{D} = 1.28$). The linear PS matrix has $N_m = 2476$ ($\bar{D} = 1.05$).

Neutron Reflectometry (NR): Measurements were made using the Liquids Reflectometer (LR) of the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory with the source to sample distance of 13.6 m, sample to detector distance of 1.5 m, wavelength range 2.5Å -17.5Å, bandwidth 3.5 Å, q range 0.006 Å⁻¹ to 0.192 Å⁻¹ and minimum reflectivity 1×10^{-7} . Data were collected at six different angles with incident-beam slits set to maintain a constant wave vector resolution of $\delta Q/Q = 0.05$, which allows the data obtained different angles to be stitched together into a single reflectivity curve. Approximately 1 ml of polymer solution (chloroform, 20 mg/ml, 10 wt% bottlebrush) was dropped onto freshly cleaned round Si wafer (diameter: 1 inch) and spun cast at a rate of 1500 RPM for 1 min. Samples were annealed at 165 °C for 16 hrs under vacuum. Data were collected for each sample before and after annealing.

The aim of NR experiments is to determine the distribution of bottlebrush throughout the thickness of the film. Three NR models were implemented with the Parratt recursions: (i) A single layer film characterized by a uniform concentration of bottlebrush; (ii) A bilayer film that allows for bottlebrush excess at one interface; and (iii) A trilayer film that accounts for excess at both interfaces. The neutron scattering length density (SLD) was determined using the equation $SLD = b/v$, where b is the monomer scattering length (sum of scattering lengths of constituent atomic nuclei) and v is the monomer volume. The calculated reflectivity curves were optimized for goodness-of-fit using nonlinear regression. Total film thickness and surface roughness were the only adjustable parameters for Model (i). Total film thickness, surface roughness, and amount of bottlebrush excess were adjustable parameters for Models (ii) and (iii), subject to the constraint that the total amount of bottlebrush in the film was 10 wt%.

Figure S9 shows representative data with best-fit results for PS bottlebrush (10 wt %) blended with 2 kg/mol dPS. Before annealing, clear oscillations in the scattered intensity are observed. The data can be fit to any of the three models (although none of the fits are perfect, as nonlinear regression is too sensitive to the initial guess). After annealing, the oscillations are severely damped due to roughening of the free surface and/or the broad gradients in bottlebrush composition.





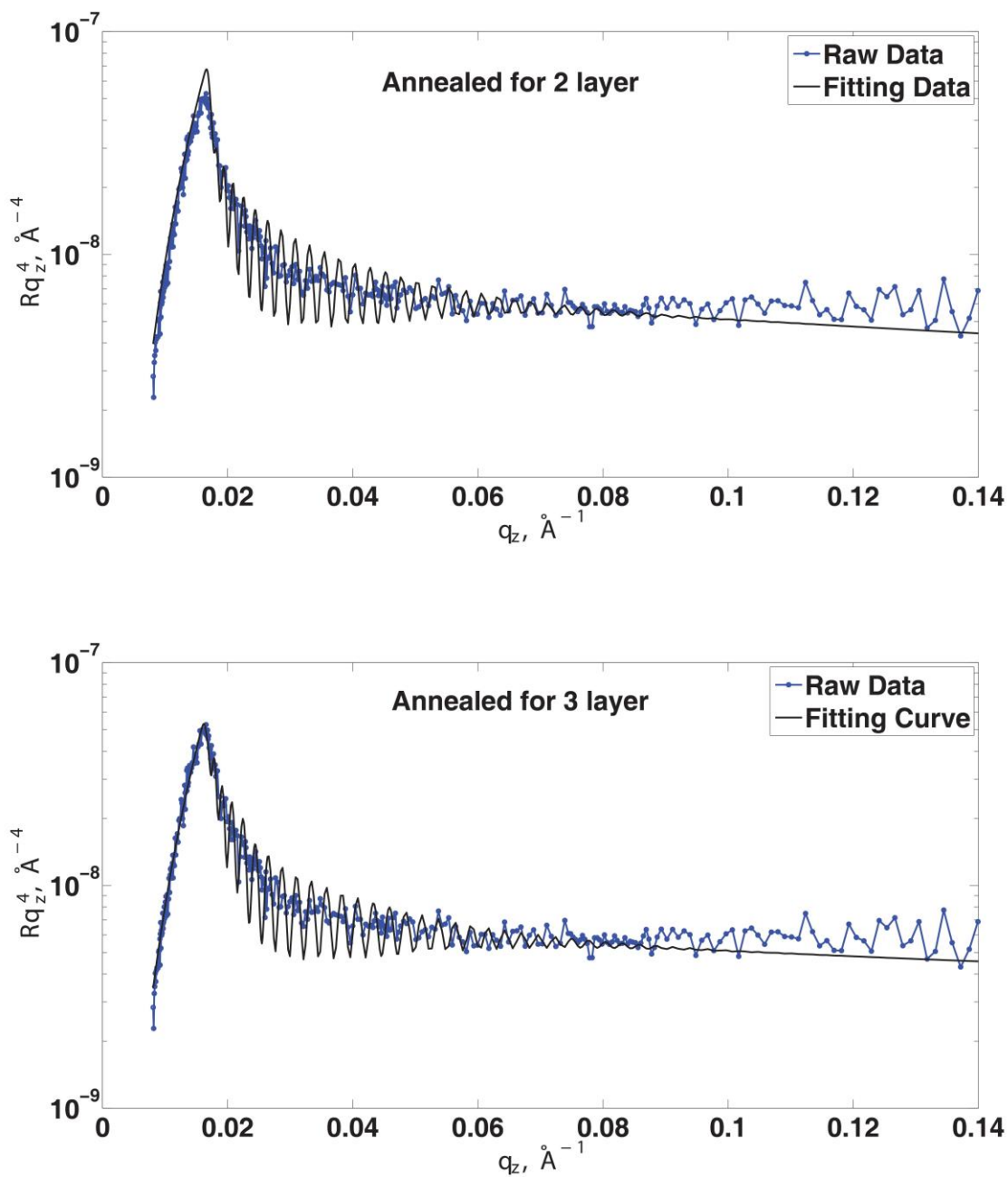


Figure S9: Representative neutron reflectivity spectra of bottlebrush polymer mixed with 2K deuterated linear PS for as cast and thermally annealed films. Data were fit with a 1, 2, or 3-layer model.

References

- (1) Bates, F. S.; Wignall, G. D. Isotope-Induced Quantum-Phase Transitions in the Liquid State. *Phys. Rev. Lett.* **1986**, 57, 1429–1432.
- (2) Eitouni, H. B.; Balsara, N. P. Thermodynamics of Polymer Blends. In *Physical Properties of Polymers Handbook*; Mark, J. E., Ed.; Springer New York, 2007; pp. 339–356.