Supporting Information for:

Concentration-Driven Self-Assembly of PS-b-PLA Bottlebrush Diblock Copolymers in Solution

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1. Extended Materials and Characterization Methods

![Scheme of the synthesis of PS-b-PLA diblock bottlebrushes via sequential addition ROMP of PS and PLA macromonomers.](image)

**Figure S1.** Scheme of the synthesis of PS-b-PLA diblock bottlebrushes via sequential addition ROMP of PS and PLA macromonomers.

All reactions were performed in an argon-filled glovebox (O\(_2\) < 2 ppm, H\(_2\)O < 0.5 ppm) at room temperature using oven-dried glassware. THF, toluene, and DCM was dried using a commercial solvent purification system. rac-Lactide {Aldrich}, sec-butyllithium solution {1.3 M in cyclohexane/hexane (92/8), ACROS Organics} and ethylene oxide solution (2.5-3.3 M in THF, Aldrich) was used as received. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) {Aldrich} was distilled over CaH\(_2\) and storage under argon at -20 °C. Styrene was pass through neutral alumina plug and stored under argon at -20 °C. \[(H_2IMes)(3-Br-py)_2(Cl)_2Ru=CHPh\] G3 was synthesized according to literature.\(^1\) exo-5-Norborene-2-carboxylic acid and exo-5-Norborene-2-methanol was synthesized according to literature.\(^2\)

Conventional Size Exclusion Chromatography (SEC) was performed using a Tosoh Ecowsec HLC-8320GPC at 40 °C with THF (HPLC grade) as the eluent. This SEC is equipped with both a refractive index and UV detector (detector set to 266 nm). The SEC is fitted with a guard column (6.0 mm ID x 4.0 cm x 5 μm), and two analytical columns (7.8 mm ID x 30 cm x 5 μm; TSKgel GMHHR-H). The reference flow rate is 0.5 mL min\(^{-1}\) while the analytical column is at 1.0 mL·min\(^{-1}\). Polystyrene standards (16 points ranging from 200 Mw to 5.5 million Mw) were used as the general calibration. An additional calibration was created for specifically for linear polylactic acid and only used for linear polylactic acid (12 points ranging from 500 Mw to 10,000 Mw).
**Figure S2.** Conventional size exclusion chromatography calibration curves with polystyrene and polylactic acid standards.

Size Exclusion Chromatography (SEC) was performed using a Tosoh Ecosc HLC-8320GPC at 40 °C with THF (HPLC grade) as the eluent. This SEC is equipped with a refractive index, UV detector, and LenS3 Multi-Angle Light Scattering Detector. The SEC is fitted with a guard column (6.0 mm ID x 4.0 cm x 5 μm), and two analytical columns (7.8 mm ID x 30 cm x 13 μm; TSKgel Alpha-M). The reference flow rate is 0.3 mL min⁻¹ while the analytical column is at 0.6 mL·min⁻¹. The detectors were calibrated with a narrow polystyrene standard (Mw= 99,000 Da). Polymer solutions were prepared at a known concentration (ca. 1 mg/mL) and an injection volume of 20 μL was used. dn/dc values for the bottlebrush polymers were obtained for each injection by assuming 100% mass elution of the bottlebrush from the columns (the injection mass was adjusted according to the known wt% from conventional SEC).

**Synthesis procedures**

The synthesis methodology used in this manuscript to produce the diblock bottlebrush polymer has been reported in several prior publications with extensive characterization and detailed procedures.⁴ We provide the key characterization here, and direct readers to prior publications for more details and characterization of the methodology. NMR characterization of identical materials, but a different synthesis batch has been previously reported⁴.

**Characterization data**

**Table S1:** Characterization data for PS macromonomers.

| Sample   | $M_n$theory (g/mol)ᵃ | $M_n,GPC$ (g/mol)ᵇ | $M_w/M_n$ᵇ |
|----------|----------------------|--------------------|-------------|
| PS-long  | 4,700                | 4,500              | 1.03        |

ᵃCalculated by $M_n^{theory} = \frac{\text{moles of styrene}}{\text{moles of secBuLi}}$  
bCalculated with respect to PS standards This sample was used in another publication⁶ and the data is repeated here.

**Table S2:** Characterization data for PLA macromonomers.

| Sample   | $M_n$theory (g/mol)ᵃ | $M_n,GPC$ᵇ (g/mol) | $M_w/M_n$ᵇ |
|----------|----------------------|--------------------|-------------|
| PLA-long | 4,100                | 4,200              | 1.05        |

ᵃCalculated by $M_n^{theory} = \frac{2 \times \text{moles of lactide}}{\text{moles of Nor -- OH}} (\text{expected conv.})$  
bCalculated with respect to PLA standards This sample was used in another publication⁶ and the data is repeated here.
Table S3: Characterization data for PS-PLA diblock bottlebrushes

| N_{bb} | M_{n,\text{theory}} (kg/mol)^a | M_n^b (kg/mol) | M_w/M_n^b | wt %^c | Block Length (DP) | M_{w,\text{LS}}^d (kg/mol) |
|--------|-------------------------------|----------------|-------------|--------|------------------|-----------------------------|
|        |                               |                |             | Diblock BB | Block 1 | PLA Brush | PS Brush |                  |                  |
| 100    | 435                           | 130            | 1.05        | 94      | 5    | >1     | 1        | 49:55              | 421              |
| 255    | 1110                          | 356            | 1.04        | 94      | 5    | >1     | 1        | 124:141            | 1050             |
| 400^e  | 1740                          | 592            | 1.05        | 94      | 5    | >1     | 1        | 194:222            | 1780             |

|       |                               |                |             |         |                  | |

^a Calculated as M_{n,\text{theory}} = 0.5 \times N_{BB} \times (M_{n,PS}^{\text{GPC}} + M_{n,PLA}^{\text{GPC}})^b Calculated with respect to PS standards^c See SI section of reference^5 for calculation details. ^d Determined from triple detect GPC ^e This sample was also used in a prior publication^6 and the data is repeated here.
Figure S3. RI-GPC traces for the synthesis of PS-b-PLA long brush sweep. a) PLA and PS macromonomer (Both of these SEC traces were used in another publication\textsuperscript{6} and the data is repeated here.). b) First block, PS-bottlebrush (no data was obtained for PS-BB-200). c) PS-b-PLA bottlebrush (the $N_{bb}=400$ SEC traces were used in another publication\textsuperscript{6} and the data is repeated here).
2. Volume Fraction Calculations

2.1 Block Volume Fraction

The volume fraction of PS ($\phi_{PS} = 0.53$) was calculated using equation SI-1, where molecular weights ($M_{n,PS-NB}$, $M_{n,PLA-NB}$) are the values measured by GPC [Table S1, S2], block degree of polymerization ($DP_{PS-NB}$, $DP_{PLA-NB}$) are the corrected values taken from Table S3, and block densities ($\rho_{PS-NB}$, $\rho_{PLA-NB}$), are approximated as the bulk density of poly(styrene) ($1.04 \frac{g}{cm^3}$ ref$^8$) and poly(lactic acid) ($1.25 \frac{g}{cm^3}$ ref$^9$).

$$\phi_{PS} = \frac{(M_{n,PS-NB} * DP_{PS-NB}/\rho_{PS-NB})}{(M_{n,PS-NB} * DP_{PS-NB}/\rho_{PS-NB}) + (M_{n,PLA-NB} * DP_{PLA-NB}/\rho_{PLA-NB})}$$ [SI-1]

This calculation results in values of $\phi_{PS} = 0.533$, 0.530, and 0.528 for polymers N100, N255, and N400, respectively.

2.2 Polymer Volume Fraction in Solution

The total volume fraction of polymer ($\Phi_p$) in solution was calculated using equation SI-2, where $C$ represents the prepared solution concentration, and $\rho_{poly}$ represents the average density of the polymer, accounting for the measured mass of each block.

$$\Phi_p = \frac{\left[ \frac{mg_{poly}}{mL_{solvent}} \right]}{\rho_{poly} \left[ \frac{g_{poly}}{mg_{poly}} \right]} \times 0.001 \left[ \frac{g_{poly}}{mL_{poly}} \right]$$ [SI-2]

Calculated polymer volume fractions were consistent to two significant figures between each polymer series.
3. Scattering Contrast Calculations

Scattering length densities for each component ($\tilde{\rho}_i$) were calculated at an X-ray energy of 13.3 keV using the built-in calculator in SASVIEW (http://www.sasview.org/) as $7.992 \times 10^{-6}$ Å$^{-2}$, $9.499 \times 10^{-6}$ Å$^{-2}$, and $11.186 \times 10^{-6}$ Å$^{-2}$ for toluene, poly(styrene), and poly(lactic acid), respectively.

The mean scattering length density of the mixture was calculated as per equation [SI-3], using $\phi_{PS} = 0.53$, and $\Phi_P$ as defined in SI §2. The scattering contrast for each component is then computed as the absolute value of the difference between component and mean scattering length density.

$$\rho_{mean} = \Phi_P \times \tilde{\rho}_{PS} + (\Phi_P - \phi_{PS}) \times \tilde{\rho}_{PLA} + (1 - \Phi_P) \times \tilde{\rho}_{toluene}$$  [SI-3]

The component and mean scattering length density and contrast are plotted in Figure S4, where vertical lines in the lower plot correspond to experimentally measured polymer volume fractions.

**Figure S4.** Calculated component and mean scattering length density and component contrast as a function of polymer volume fraction ($\Phi_P$) in solution.
4. 1D Scattering Data

Figure S5. Background-subtracted 1D scattering data (not normalized by concentration).
Figure S6. Correlation length calculated from the center position of the high-q S(q) peak, determined by fitting as a Voigt profile. Vertical error bars are propagated from the uncertainty of the fit.
Figure S7. Reproduction of Figure 4b. with superimposed scaling coefficients for lamellar domain spacing versus concentration. Scaling coefficient (m) is fit to $d \sim \Phi_p^m$. Red lines and text refer to literature reports of scaling in linear block copolymers from experiment (Lodge et al., 2003\textsuperscript{10}) and theory (Whitmore et al., 1990\textsuperscript{11}). Similar values were also found experimentally in the low-concentration regime ($m \approx 1/3$) by Shibayama et al. (1983).\textsuperscript{12}
7. Supplemental References

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