Supporting Information

Implicit Side-Chain Model and Experimental Characterization of Bottlebrush Block Copolymer Solution Assembly

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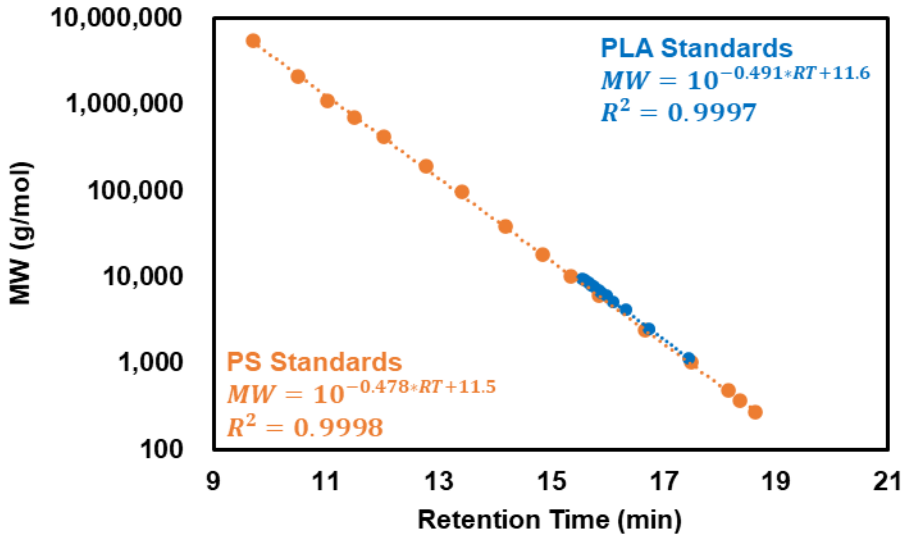
Materials and characterization methods

All reactions were performed in an argon-filled glovebox (O_2 < 2 ppm, H_2O < 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. [$(H_2IMes)(3\text{-Br-py})_2(Cl)_2Ru$=CHPh], G3 was synthesized according to literature.[10] exo-5-Norbornene-2-carboxylic acid and exo-5-Norbornene-2-methanol was synthesized according to literature.[11]

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AVANCE III 500 MHz spectrometer. Spectra are reported in ppm and referenced to the residual solvent signal: $CDCl_3$ (^{1}H 7.26 ppm, ^{13}C 77.16 ppm).

Conventional Size Exclusion Chromatography (SEC) was performed using a Tosoh Ecosec 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 GMH_{HR}-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 2.1 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).



Size Exclusion Chromatography (SEC) was performed using a Tosoh Ecosec 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.[1–3] We provide the key characterization here, and direct readers to prior publications for more details and characterization of the methodology.

Characterization data

Table S1: Characterization data for macromonomers.

Chemistry	$M_{n,theory}$ (g/mol)[a]	$M_{n,GPC}$ (g/mol)[b]	M_w/M_n[b]
PS	4,700	4,500	1.03
PLA	4,100	4,200	1.05

[a] Calculated by $M_n^{theory} = \frac{moles\ of\ styrene}{moles\ of\ secBuLi}$ or by $M_n^{theory} = \frac{2 * moles\ of\ lactide}{moles\ of Nor-OH} (expected\ conv.)$; Expected conv. can be calculated from the kinetic data from literature.[9] [b]Calculated from conventional GPC calibration respect to PS standards or PLA standards.

Table S2: Characterization data for PS-PLA diblock bottlebrush (PS: 4.5 kg/mol; PLA: 4.2 kg/mol, 50 wt% PS).

Targeted N_{bb}	M_n[a] (kg/mol)	M_w/M_n[a]	wt %[b]				Block length PS:PLA	$M_{w,LS}$[c] (kg/mol)
			Diblock BB	Block 1	PLA arm	PS arm		
400	592	1.05	94	5	>1	1	194:222	1780

[a]Calculated from conventional GPC calibration respect to PS standards [b]See SI section of reference[3] for calculation details. [c]Determined from triple detect GPC

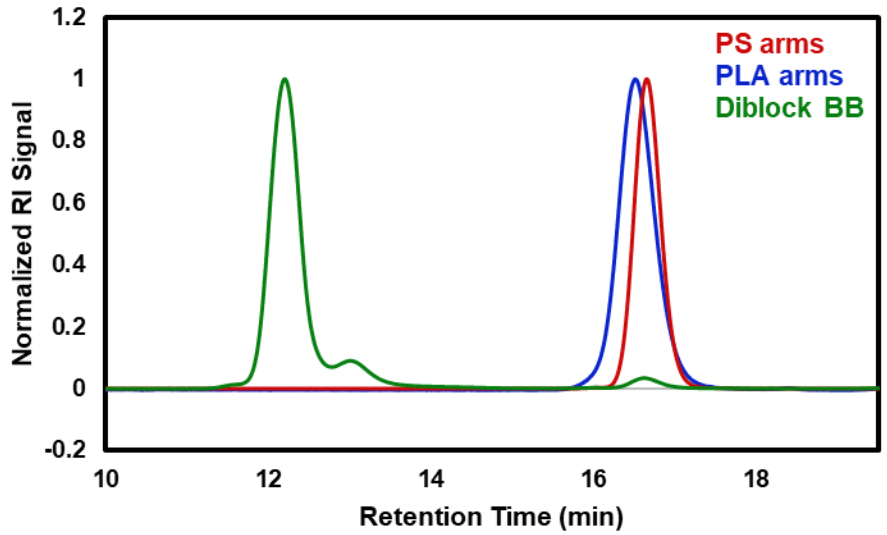


Figure S1: RI-GPC traces for the synthesis of PS-b-PLA diblock bottlebrushes. (The small second hump on the green trace around 13 min is PS-BB cause by catalyst death upon addition of PLA brushes. The small peak at 16.5 min corresponds solely to unfunctionalized PS arms.)

Equilibrium validation in molecular simulations

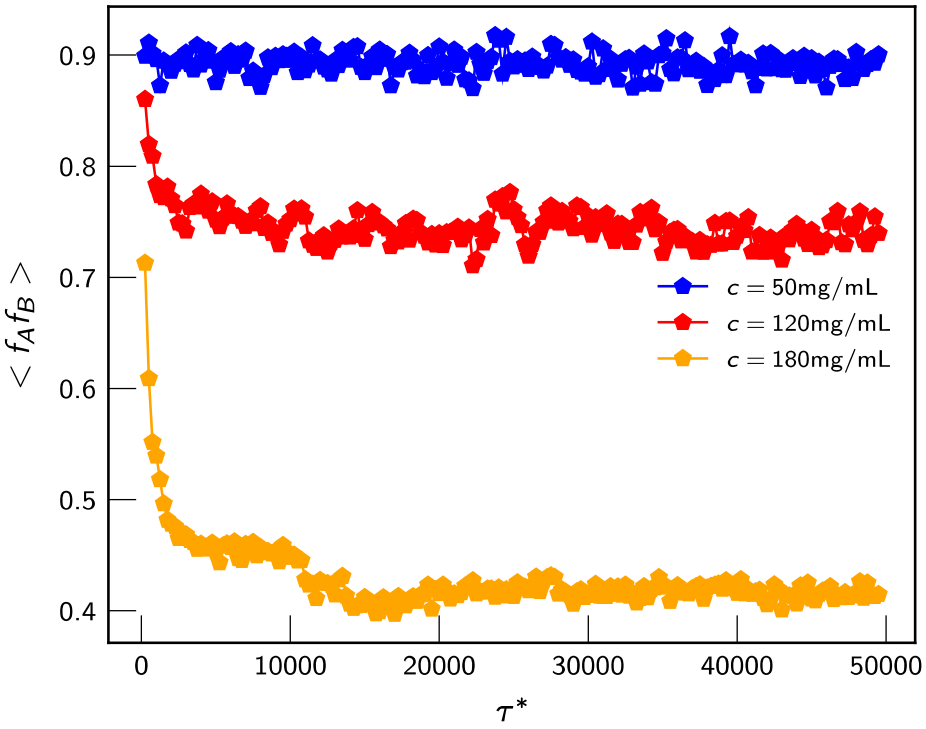


Figure S2: Degree of mixing as a function of simulation time. Here three simulations are chosen, where the bottlebrush has symmetric architecture and a cubic box is used. The degree of mixing reaches a stable state after sufficiently long time in all cases, indicating this quantity is useful for probing equilibrium.

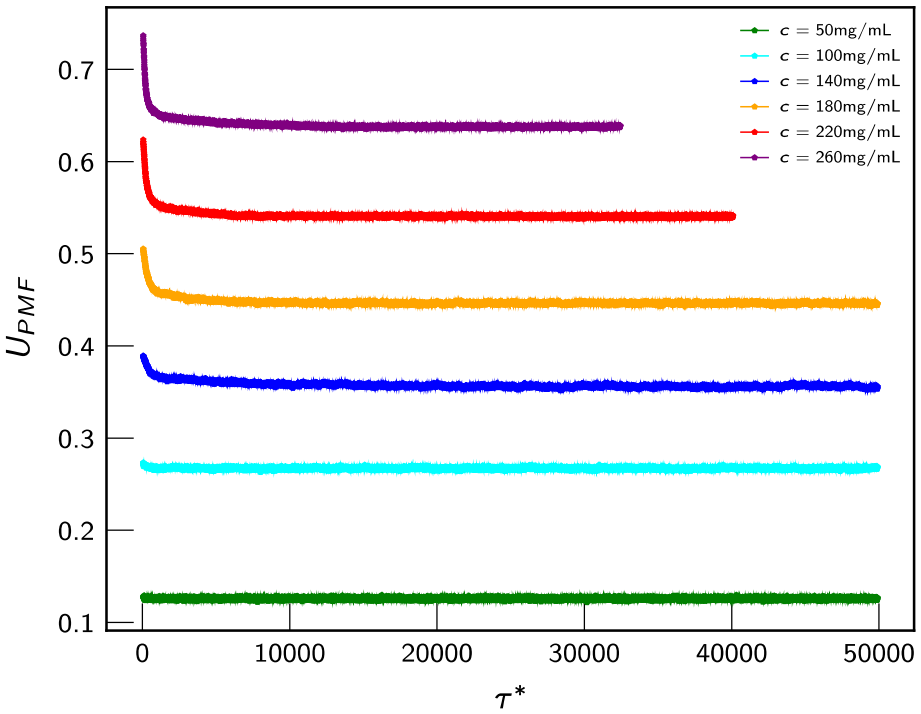


Figure S3: Total energy from pair-wise interactions as a function of simulation time. Here we fix the interaction parameters and run simulations under different concentrations from 50-260 mg/mL. The total energy from pair-wise interactions reaches a stable state after sufficiently long time in all cases, suggesting that these simulations are at equilibrium.

References

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