

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

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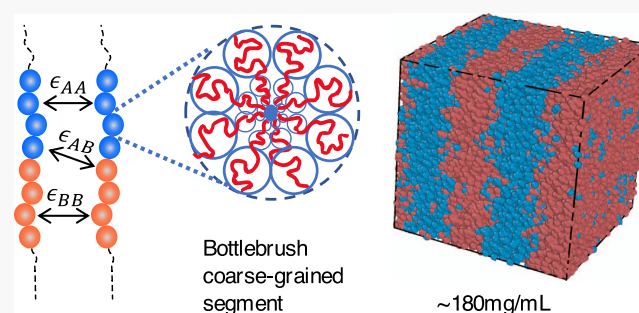
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ABSTRACT: Bottlebrush polymers are a class of macromolecules with linear backbones and densely grafted side chains, possessing unique physical properties due to strong steric interactions between the side chains. These interactions serve to both stiffen the molecular contour and impart a molecular width, leading to material properties distinct from linear counterparts. This is especially important for the case of diblock bottlebrush copolymers, where side-chain-induced stiffness leads to assembly on large length scales while simultaneously suppressing molecular entanglements that would otherwise hinder self-assembly. The resulting microphase-separated structure is thus ideal for photonic crystals, due to the formation of long-range order with features on length scales commensurate with the wavelength of visible light. Despite the usefulness of block copolymer bottlebrush materials, it remains challenging to model their self-assembly in solution due to the additional side-chain degrees of freedom, which are computationally expensive to resolve. In this paper, we develop a simulation model for bottlebrush block copolymer solution self-assembly that adapts a recently developed implicit side-chain model, accounting for the effect of side chains within a simplified, bead-rod polymer model. We further extend this model by deriving an intermolecular interaction potential from scaling arguments and show that we can predict bottlebrush self-assembly over a range of block fractions and polymer concentrations. For all architectures studied, we observe an order–disorder transition to lamellar morphologies and regions of significant compositional fluctuations in the disordered phase. We compare computational predictions of self-assembly to experiments, using diblock bottlebrush copolymers synthesized with poly(norbornene) backbones and polystyrene side chains and poly(lactic acid) side chains on each block. We show that the simulation structure factors match well with experimental scattering and indicate the emergence of self-assembly at high concentrations.



1. INTRODUCTION

Bottlebrush polymers are a class of branched macromolecules that have recently gained broad attention in the polymer community.^{1–5} These polymers are distinct from linear polymers due to the presence of side chains grafted onto a linear backbone, which introduces steric repulsion and serves to “stiffen” the molecular contour. Side-chain-induced conformational stiffening gives rise to many unique properties, such as lowered intermolecular entanglements³ and, consequently, fast self-assembly kinetics.⁶ Bottlebrush polymers with sufficiently high grafting densities, which are stiff enough to behave as rodlike molecules, have been observed to form liquid crystalline phases at high concentrations.^{7,8} In addition, the side chains impart a molecular “width” that affects the spacing between the linear backbones of two adjacent bottlebrush polymers; hence, side-chain length is a useful parameter for tuning mechanical properties.^{1,9–15} Here, the densely grafted side chains impede interpenetration, leading to a low entanglement plateau modulus in bottlebrush melts³

making them good candidates for highly deformable elastomer materials.^{15–19} The unique properties of bottlebrush polymers have also found a use for thin-film applications^{20–24} and as building blocks for self-assembled soft materials.^{25–27}

These advances in bottlebrush polymer-based materials have been driven by progress in molecular synthesis, which has led to a wide variety of ways to design architecture at the molecular level.^{26,28–36} For example, bottlebrush homopolymers have been designed over a broad parameter space and are tunable by varying backbone length, side-chain length, grafting density, and monomer chemistry.^{37–42} Bottlebrush block copolymers (BBCPs) extend this design space to include

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different branch compositions and interactions, and side chains can be arranged as block-type^{25,43,44} or mixed-type⁴⁵ sequences. In other cases, the side chains themselves can be composed of more than one component,^{46–48} leading to core–shell structures when the side chains are diblocks.

BBCPs, in particular, are attracting significant attention due to their ability to form photonic crystals, both because rapid self-assembly kinetics leads to significant long-range ordering and because the “stiff” molecules can readily reach length scales commensurate with the wavelength of light.^{6,49–51} This has led to a number of experimental protocols to form and tune self-assembled photonic crystals, using both melt- and solution-processing to engineer materials that exhibit controllable structural colors. For example, BBCPs have been used to realize a range of self-assembled structures upon micellization in poor solvents, from spherical micelles to complex hierarchical cubosomes.^{25,27,52} By optimizing polymer chemistries to exhibit refractive index differences of ~ 0.15 and domain sizes on the order of ~ 100 nm, researchers have demonstrated vibrant one-dimensional (1D) solution-cast photonic crystals with wavelength tunable by bottlebrush molecular weight^{6,53} and blend compositions.^{54,55} Recent investigations have demonstrated the use of flow-directed assembly to tune photonic properties of BBCP solutions. These include shear-induced color switching,⁵⁶ where subtle morphological rearrangements at high shear rates were implicated in significant changes in structural color. Separately, kinetic control during nonequilibrium direct-ink writing of BBCP solutions was recently demonstrated to substantially modulate domain size and photonic properties for printed thin films.⁵⁷ Taken together, these initial reports suggest that the bottlebrush architecture has significant unexplored potential for property tuning via directed self-assembly.

Concurrent with experimental efforts, theoretical and computational efforts have sought to predict the relationships between bottlebrush polymer architecture and conformation, and ultimately material properties.^{44,58–64} Early theoretical efforts used scaling arguments to predict conformations of bottlebrush polymers in dilute solutions under different solvent conditions.^{58–61} Since these initial studies, a variety of approaches have been used to understand conformational structure and dynamics of bottlebrush polymers, such as general and renormalized perturbation theories,⁶² self-consistent-field theory,^{23,24,63,65–70} density functional theory,⁴⁷ and polymer reference interaction site model (PRISM) theory.^{44,71,72} Apart from these theoretical methods, the scaling theory remains a useful tool for understanding bottlebrush structure.^{3,73–79}

Most of the efforts to computationally model bottlebrush polymers have so far been focused on determining the relationship between molecular architecture and bottlebrush conformation; in particular, Monte Carlo (MC),^{80,81} molecular dynamics (MD),^{14,44,73,76,82–89} and Brownian dynamics (BD) simulations³¹ have all been used to examine questions related to the effect of molecular parameters such as grafting density, side-chain length (N_{sc}), and backbone length (N_{bb}) on observables such as stiffness, molecular size (i.e., end-to-end distance, radius of gyration), and shape. When compared to experiments, such as via X-ray scattering or intrinsic viscosity, these simulations often perform well.^{31,90}

Despite sophistication in the modeling of individual bottlebrush polymers, it still remains a challenge to model systems composed of multiple bottlebrush polymers, either in

the melt or in a concentrated solution, since it is computationally expensive to simulate both large numbers of molecules as well as architectures with long backbone and side-chain lengths. State-of-the-art coarse-grained MD simulations, for example, are limited to a modest ($O(100)$) number of particles per chain due to the high computational cost of simulating a large number of bottlebrush chains.^{14,44,74} We recently developed a number of methods that enable coarse-grained simulations of bottlebrush polymers to address these computational limitations; we first considered an explicit side-chain (ESC) model that is analogous to the bead-rod simulation approaches and parameterized to chemistries for common bottlebrush polymers.³¹ We then demonstrated⁹¹ that these models can be systematically mapped to an implicit side-chain (ISC) representation, which uses the concept of a wormlike cylinder to simplify the molecular conformation to four quantities: a Kuhn length λ^{-1} , a contour length L , a thickness d , and an excluded volume parameter B . We can thus replace the numerous side-chain degrees of freedom with a linear bead-spring chain that has stiffness and bead size that is governed by the side-chain length. We have demonstrated that this model works well to describe both the single-chain equilibrium size,⁹¹ as well as molecular elasticity under modest stretching forces.⁹²

In this article, we develop a new method, rooted in these prior efforts, for modeling BBCP solution self-assembly that is capable of capturing both large molecular architectures (i.e., large N_{bb} and N_{sc}) and a large number of assembling molecules. This multichain simulation uses the ISC representation, and with a number of modifications is capable of matching well with experimental observations for analogous systems. We first derive a form for the pairwise potential between two bottlebrush polymers in solution from scaling arguments, and we directly include this pairwise potential into our simulations. Synthesis and characterization of BBCPs are performed, and we use phase behavior observations to parameterize the derived potential. We show that simulated self-assembly behavior for symmetric BBCPs is consistent with scattering experiments, and then map the phase behavior and lamellar spacing in these assemblies as the block fraction is changed. This method thus results in a model that can capture the microphase separation of BBCPs, even for architectures that would be otherwise intractable to model when the side chain is fully resolved (large N_{bb} , N_{sc}). This work thus sets the stage for performing simulations to understand the in- and out-of-equilibrium assembly in an increasingly broad range of bottlebrush systems, especially in solutions where the system is not well described by mean-field arguments and is known to be affected by far-from-equilibrium processing conditions.

2. MODEL AND METHODS

2.1. Experimental Materials and Methods. 2.1.1. Material Synthesis. Well-defined polystyrene-*b*-poly(lactic acid) (PS-*b*-PLA) diblock bottlebrush polymers with poly(norbornene) backbones were produced via a previously developed route.^{34,56,57} In brief, the methodology involves the synthesis of PS macromonomers via an anionic polymerization of styrene initiated by *sec*-BuLi (M_n : 4500 g mol⁻¹, $\bar{D}$: 1.03) and PLA macromonomers via an organocatalyzed 1,8-diazabicycloundec-7-ene (DBU) ring-opening polymerization of lactide (M_n : 4100 g mol⁻¹, $\bar{D}$: 1.05).^{32,33,56,93–96} Sequential addition ring-opening metathesis polymerization (ROMP) was then used to synthesize the targeted symmetric diblock bottlebrush polymers with a targeted total backbone length of 400 repeat units. Size-exclusion chromatography (SEC) analysis of the synthesized diblock revealed a

bimodal peak and residual macromonomer (unfunctionalized PS arms, 1 wt %). The major peak was determined to be the targeted diblock polymer (95 wt % of the sample). It presented a narrow molecular weight distribution of M_w/M_n : 1.05 and light scattering SEC gave an absolute molecular weight of 1700 kg mol^{-1} . The smaller peak was determined to be a PS bottlebrush. This polymer sample (12 g batch) was used for all of the following material studies. Details of general methods and material, synthesis procedure, and additional polymer characterization can be found in the [Supporting Information](#).

2.1.2. Small-Angle X-ray Scattering (SAXS). SAXS experiments were conducted in two sets of overlapping concentration ranges at beamline 12-ID-B of the Advanced Photon Source (Lemont, IL), with a beam energy of 13.3 keV and the distance between the sample and the Pilatus 2M two-dimensional (2D) detector set to 3.6 m. Q-calibration was performed using a silver behenate standard. Solutions of PS-*b*-PLA diblock bottlebrush polymers were prepared by direct dissolution in toluene (a good solvent) at room temperature. After at least 2 h of stirring, solutions were sequentially scanned in transmission mode (from lowest to highest concentration) using a single quartz capillary flow cell, beginning with pure toluene for a background scan. Reduction of 2D scattering data and background subtraction were performed using the Nika and Irena packages^{97,98} developed by J. Ilavsky for Igor Pro (WaveMetrics, Lake Oswego, OR). Correction to the nominal concentration was made by enforcing overlap of the concentration-normalized curves at $q = 0.07 \text{ \AA}^{-1}$.

2.2. Molecular Model of Bottlebrush Assembly. We use an ISC model based on a discrete wormlike cylinder model to represent diblock bottlebrush polymers. This model was originally developed for homopolymer bottlebrush polymers in our earlier work,⁹¹ which we adapt here for the case of diblocks. This model represents a bottlebrush as a series of connected beads, only implicitly including the effect of the side chains by imposing a strong bending potential on the chain. The diameter of the beads d reflects the length of the side chain, and the backbone contour L is represented with $N = L/d$ beads. [Figure 1](#) illustrates the correspondence between the ISC model and

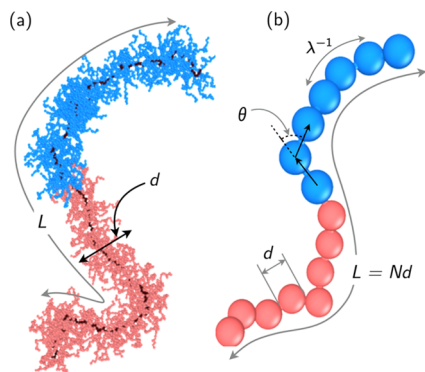


Figure 1. (a) Simulation snapshot of a diblock bottlebrush based on the ESC model, showing the length of the contour L and width d . (b) Simulation snapshot of a diblock bottlebrush based on the ISC model, showing the L , d , and λ^{-1} equivalent to the ESC model. The angle θ controls the bending penalty, which appears as a result of coarse-graining out the side chains.

an ESC model, the latter including the side-chain degrees of freedom. The latter model is significantly more computationally expensive but was used earlier⁹¹ to parameterize the more coarse-grained ISC model by determining three key descriptors of the bottlebrush structure that all depend on side-chain interactions: the width d , the length L , and the Kuhn length λ^{-1} . This mapping allows us to perform large-scale simulations of bottlebrush self-assembly. In our previous work,⁹¹ we showed that the ISC model is capable of capturing single-molecule properties of bottlebrush polymers in solution, and here we address the remaining challenge of modeling bottlebrush–bottlebrush interactions that were only included as an additional excluded volume parameter B in the single-chain case.

2.2.1. Bottlebrush–Bottlebrush Interactions. Bottlebrush self-assembly is driven by the interactions between nearby bottlebrush polymers, in particular the repulsion between side chains that are coarse grained out of the ISC model. This side-chain-induced repulsion is analogous to the interactions between micelles or polymer-grafted nanoparticles,^{99,100} in that overlapping chains significantly restrict their conformational degrees of freedom. The subsequent entropic repulsion can be captured with a soft, pairwise potential of mean force that has been derived using scaling arguments and demonstrated to be an effective descriptor of spherical brushlike particles.¹⁰¹ We seek a similar expression for the potential of mean force between nearby bottlebrush particles. While in principle it is possible to perform an explicit side-chain simulation to determine this potential of mean force, we instead choose to derive a potential that builds on scaling arguments established by Witten and Pincus⁹⁹ and Wang and Safran.⁶¹ The schematic of the scaling arguments along with several key scaling relations are shown in [Figure 2a](#).

We first recapitulate a scaling argument for cylindrical brushes made by Wang and Safran,⁶¹ based on the classical Daoud–Cotton model,¹⁰² that relates grafting density and side-chain length to brush dimensions. An average distance l_G is first defined between the number p of grafted side chains per length of backbone h , $l_G = h/p$. Each side chain extends radially from the backbone, forming thermal blobs that are space-filling and thus have a radially dependent size $\xi(r)$. This means that, at any radial position r , the cylindrical surface area around a length of backbone h ($A \sim \pi hr$) should be equivalent to the area of all thermal blobs by all side chains ($A \sim \pi p \xi^2(r)$). Equating these two areas $p \xi^2 \sim hr$ provides an expression for the radial dependence of the thermal blob size, $\xi(r) \sim l_G^{1/2} r^{1/2}$.

This length scale $\xi(r)$ designates the extent to which a flexible side chain can exhibit self-avoiding or random walk statistics before it is confined by neighboring side chains. The relationship between this length scale and the number of monomers in a thermal blob g is thus $\xi(r) \sim g^\nu b$, where b is the monomer size and ν is the Flory exponent, which is related to solvent quality. Since the chemistry of both blocks used in our experiments are in a good solvent, we use $\nu = 3/5$, also in line with the original derivation from Wang and Safran.⁶¹ We can thus write a radially dependent number of monomers per blob $g \sim \xi^{5/3} b^{-5/3}$ and the corresponding number density of monomers $\rho(r) \sim g(r)/\xi^3(r) \sim \xi(r)^{-4/3} b^{-5/3} \sim l_G^{-2/3} b^{-5/3} r^{-2/3}$.

The radial extent (i.e., thickness, d) of the brush is determined by integrating over this density, to obtain the overall number of monomers for a given side-chain length N_{sc}

$$N_{sc} \sim 2\pi l_G \int_b^d r \rho(r) dr \sim l_G^{1/3} b^{-5/3} d^{4/3} \quad (1)$$

Here, the last relationship assumes that $b \ll d$. We can thus write the scaling relationship $d \sim N_{sc}^{3/4} l_G^{1/4} b^{5/4}$, as well as a free energy per unit length of chain

$$\frac{f}{k_B T h} \sim 2\pi \int_b^d r \xi^{-3}(r) dr \sim l_G^{-3/2} d^{1/2} \sim l_G^{-13/8} b^{5/8} N_{sc}^{3/8} \quad (2)$$

These results stem from the premise that the free energy per blob is $k_B T$ and is the same as what was derived by Wang and Safran.⁶¹

To convert this result to a potential of mean force $W(r)$, we interpolate between the free energy of two nonoverlapping chains and the free energy of two chains where the backbones are immediately adjacent; the key idea of this latter case is that they effectively form a single bottlebrush with twice the grafting density. Here, we adapt an argument made by Witten and Pincus,⁹⁹ which carries out the same procedure for two grafted colloids, in the limit that the grafted chains are long.⁹⁹ We first note that we are interested in the change in free energy as related to the potential of mean force, such that $W(r > d) = 0$; so, we consider a change in free energy of bottlebrush polymers as $\Delta f(r) = f(r) - f_0$, where $f_0/(k_B T h) \sim l_G^{-13/8} b^{5/8} N_{sc}^{3/8}$ is the scaling relationship given above. For the special case of $r = b$, which is where two bottlebrush polymers are right next to each other, we use the same relationship but make the replacement $l_G \rightarrow l_{G/2}$ such that the

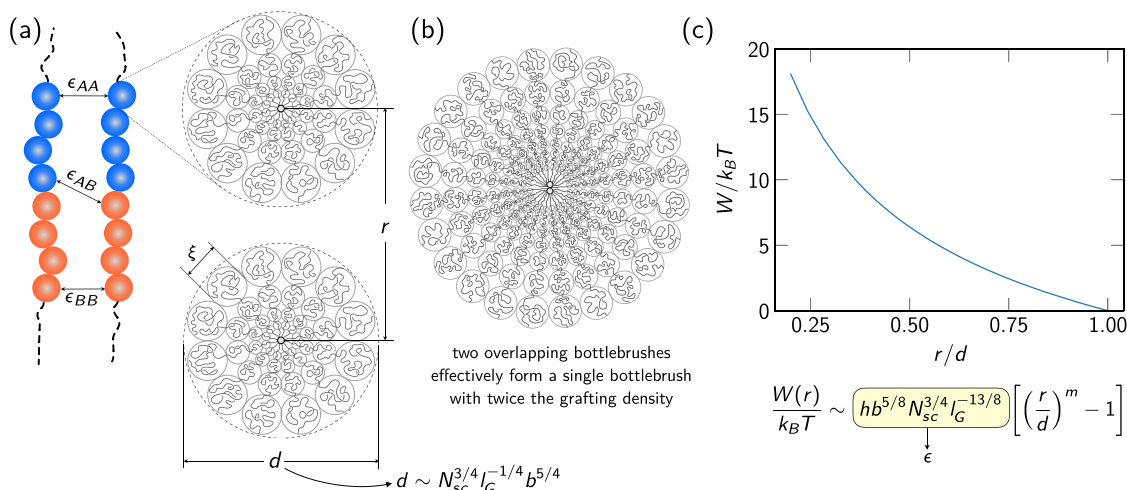


Figure 2. Schematic showing several key aspects of bottlebrush–bottlebrush interactions. (a) (Left) Schematic of interactions among diblock bottlebrush segments. The blue and red spheres stand for segments of diblock bottlebrush polymers. The ϵ 's correspond to the prefactors in the potential formula in (c). (Right) Cross-sectional view of two interacting bottlebrush coarse-grained units. Each of the units contains side chains that extend radially from the backbone, forming thermal blobs that are space-filling with a radially dependent size ξ . The dashed circles bounding those blobs indicate the range of interaction between the coarse-grained units. The diameter d is a function of grafting density l_G^{-1} , monomer size b , and side-chain length N_{sc} . (b) Schematic of two overlapping bottlebrush polymers when the two backbones are adjacent to each other. They effectively form a single bottlebrush with twice the grafting density. (c) Profile of bottlebrush–bottlebrush interactions with arbitrary parameters. The formula below the graph is the analytical expression of the potential. The boxed portion is the prefactor, which contains information such as grafting density, monomer size, and side-chain length.

“effective” grafting density is twice as large. This leads to the result for the adjacent bottlebrush polymers

$$\frac{\Delta f}{k_B T h}(r=b) \sim b^{5/8} N_{sc}^{3/8} [(l_G/2)^{-13/8} - l_G^{-13/8}] \quad (3)$$

At $r=d$, the value of $\Delta f/(k_B T h)$ should be zero, so to interpolate between these results we suggest the following form as an ansatz

$$\frac{\Delta f}{k_B T h}(r=b) \sim b^{5/8} N_{sc}^{3/8} [(\phi(r/d) l_G)^{-13/8} - l_G^{-13/8}] \quad (4)$$

Here, we assume a function $\phi(x) = x^n$ is a power law of the dimensionless bottlebrush separation r/d , which interpolates between $\phi(1) = 1$ and $\phi(b/d) = 1/2$. This relationship can be written out ($b/d = 1/2$ and solved for $n = -\ln 2 / \ln(b/d)$ to obtain the exponent n . When placed into eq 4, we finally obtain the potential of mean force between two segments of length h

$$\frac{W(r)}{k_B T} = \frac{\Delta f(r)}{k_B T} \sim h b^{5/8} N_{sc}^{3/4} l_G^{-13/8} \left[\left(\frac{r}{d} \right)^m - 1 \right] \quad (5)$$

where the exponent $m = \frac{13 \ln 2}{8 \ln(b/d)}$. This key result is also plotted in Figure 2c using arbitrary parameters. For the purposes of this paper, we will consider the prefactor to be a fixed constant (for a given grafting density l_G^{-1} , unit of bottlebrush length h , and side-chain length N_{sc}) that is open to parameterization while keeping the form of the potential as dependent only on the known value of d for which r is rendered dimensionless and is included in m . We will test this form of potential in future works, but here we show that it allows us to reproduce the self-assembly characteristics seen in the experiment.

We note that this scaling analysis assumes an architectural symmetry between the interacting bottlebrushes, such that both coarse-grained beads contain side chains with the same length N_{sc} and grafting density l_G . This will be sufficient for this paper, where we are comparing experimental data from BCCPs with blocks of comparable N_{sc} and l_G ; however, it is in principle possible to generalize the analysis to consider asymmetric architectures. For example, length disparities would be accounted for by considering a more complicated adjacent-backbone geometry, with two distinct regions of blobs. The region around the backbone would consist of blobs of both long and

short side chains, while the region far from the backbone (i.e., beyond the reach of the short side chains) would only consist of long side-chain blobs.

2.2.2. Simulation Model. Our simulation model of bottlebrush polymers has been established in our prior work,⁹¹ with only minor modifications. Each bottlebrush consists of a sequence of touched beads, which in our case is a linear chain of N_A A-beads (the PS block) followed by N_B B-beads (the PLA block). We perform MD simulations in the canonical (NVT) ensemble using the Langevin thermostat in the LAMMPS package,¹⁰³ where the solvent is treated implicitly. The damping parameter is chosen to be 100 time units since the simulations are under equilibrium condition and no temporal information is acquired. The motion of each bead i on polymer j with position $\mathbf{r}_{ij}$ is governed by a potential U for the system, which is given by

$$U = U_b + U_\theta + U_{PMF} \quad (6)$$

Here, the potential consists of three contributions: the bonding potential U_b between beads in the same chain, a bending potential U_θ that reflects the side-chain-induced stiffness of the bottlebrush, and a pairwise potential of mean force U_{PMF} between bottlebrush polymers that is informed by the derivation in the previous subsection. The bonding potential is simply a Hookean spring between the $N = N_A + N_B$ connected beads on n chains

$$\tilde{U}_b = \frac{\tilde{\kappa}_b}{2} \sum_j^n \sum_i^{N-1} \left(\frac{2|\mathbf{r}_{i+1,j} - \mathbf{r}_{i,j}|}{(d_{i,j} + d_{i+1,j})} - 1 \right)^2 \quad (7)$$

We introduce a Hookean spring constant $\tilde{\kappa}_b = 200$ that only needs to be sufficiently large to act as a constraint that keeps beads at a distance $(d_{i,j} + d_{i+1,j})/2$, where $d_{i,j}/2$ is the radius of bead i of polymer j . In the writing of this and subsequent potentials, we use tildes to denote the use of simulation quantities that have been rendered dimensionless by an energy scale $k_B T$. We write the bending potential in a similar fashion

$$\tilde{U}_\theta = \frac{\tilde{\kappa}_\theta}{2} \sum_j^n \sum_i^{N-2} \theta^2(\mathbf{r}_{i,j}, \mathbf{r}_{i+1,j}, \mathbf{r}_{i+2,j}) \quad (8)$$

Table 1. Simulation Model Parameters for Diblock Bottlebrush Polymers

	α	DP _{bb}	N _{bb}	DP _{sc}	N _{sc}	d_a/b	L/b	N _a	d_a/σ	m	$\tilde{\kappa}_\theta$
PS	A	200	182.82	45	22	24.06	206.59	8	2.0	−0.36	3.84
PLA	B	200	182.82	60	29	28.63	206.59	7	2.38	−0.34	4.27

In this potential, the bending constant $\kappa_\theta = (2\lambda d)^{-1}$ is chosen to reflect the Kuhn length λ^{-1} of the bottlebrush induced by the implicit side chains. The angle θ is between two subsequent bonds in the chain and is given by

$$\theta = \arccos \left[\frac{4(\mathbf{r}_{i+2,j} - \mathbf{r}_{i+1,j}) \cdot (\mathbf{r}_{i+1,j} - \mathbf{r}_{i,j})}{(d_{i,j} + d_{i+1,j})(d_{i+1,j} + d_{i+2,j})} \right] \quad (9)$$

Finally, the potential of mean force takes the form of eq 5, derived in the previous subsection

$$\tilde{U}_{\text{PMF}} = \sum_{i,j} \sum_{k \neq l} \tilde{u}_{\text{PMF}}(\mathbf{r}_{i,k}, \mathbf{r}_{j,l}) \quad (10)$$

This is a sum over all pairwise interactions u_{PMF} between beads i and j on different chains k and l . The pairwise potential has a form related to the distance between those beads $r_{ij,kl} = |\mathbf{r}_{i,k} - \mathbf{r}_{j,l}|$, the sum of radii of the beads $d_{ij,kl} = (d_{i,k} + d_{j,l})/2$, and the bead “types” (i.e., A versus B), α and β

$$\tilde{u}_{\text{PMF}}(r_{ij,kl}) = \begin{cases} \tilde{\epsilon}_{\alpha,\beta} \left[\left(\frac{r_{ij,kl}}{d_{ij,kl}} \right)^m - 1 \right], & \text{if } r_{ij,kl} < d_{ij,kl} \\ 0, & \text{if } r_{ij,kl} \geq d_{ij,kl} \end{cases} \quad (11)$$

The exponent m was defined in the previous subsection, and the quantity $\tilde{\epsilon}_{\alpha,\beta}$ reflects the prefactor $h b^{5/8} N_{\text{sc}}^{3/4} l_G^{-13/8}$ that includes information related to the side-chain degrees of freedom and grafting density. We will discuss the parameterization of $\tilde{\epsilon}_{\alpha,\beta}$ later; we do note here that, because the solvent is “good” for both PS and PLA blocks, we will make a simplifying assumption that $\tilde{\epsilon}_{A,A} = \tilde{\epsilon}_{B,B} = \tilde{\epsilon}_0$. We then define a parameter $\gamma = \epsilon_0/\epsilon_{A,B}$, where $\gamma < 1$ denotes a stronger repulsion between dissimilar blocks that can serve as a driving force for phase separation.

This model can be parameterized from values determined in our prior efforts;⁹¹ specifically, we use the bottlebrush thickness d , length L , and Kuhn length λ^{-1} . We invoke the important assumption that both blocks in the diblock are well described by parameterizations on the same explicit side-chain model used in Dutta et al.³¹ This assumption is justified in part by noting that the original development of the coarse-grained, explicit side-chain model in Dutta et al.³¹ was possible upon consideration only of the C_∞ for the chemistry. We pursue the same strategy here, to determine the equivalent mapping for PS ($C_\infty = 9.5$)¹⁰⁴ to the same simplified coarse-grained model used for PLA.³¹ There may be additional nuanced differences that will affect this parameterization, in particular the key role that excluded volume differences may play in affecting bottlebrush stiffness; we will also provide an a posteriori argument, based on comparison with scattering data, that this assumption is reasonable within the scope of molecular assembly. The key results in Dutta et al.⁹¹ that are relevant to this work are the parameters of the ISC model with grafting density of $l_G^{-1} = 1$, from which we use linear interpolation to determine parameters describing our experiments. For example, if the fine-grained number of side-chain repeat units, N_{sc} , is between 20 and 32, then the Kuhn length will be linearly interpolated between 182.4 and 351.84, and the diameter will be linearly interpolated between 22.755 and 30.59.⁹¹ By applying those rules, the parameters listed in Table 1 have been obtained.

Here, DP_{bb} and DP_{sc} correspond to the degrees of polymerization in the experimental system, while N_{bb} and N_{sc} are the corresponding coarse-grained model parameters for the explicit side-chain model considered in previous efforts by Dutta et al.^{31,91} that are not performed in this paper. Distances d and L are also provided in units of b as a reflection of these explicit side-chain models, which is needed

for the quantity d/b that is required for the calculation of the exponent m . Note that we assign $d_A/2 = \sigma$ as the basic simulation length unit. Key parameters for the ISC model include the number of coarse-grained beads N_a for each block type. In this case, we note that $N_A \neq N_B$ due to the slight differences in the coarse-grained unit size d_A versus d_B . The quantities d_a , m , and $\tilde{\kappa}_\theta$ are all also important for defining the total potential U in eq 6. This parameterization is used throughout most of this paper due to its connection with the experimental system, but we will also consider different block fractions by changing N_A and N_B while keeping $N_A + N_B = 15$, defining a block fraction $x_A = N_A/(N_A + N_B)$.

It is possible to match the solution concentration in the simulation model with experiments. The mass of an individual chain is the same as the molecular weight of a single bottlebrush molecule. The diameter of coarse-grained beads of the PS block is set to $d_a = 2\sigma = 24.06b$. From our previous work,³¹ we know the monomer size of the explicit side-chain model is $b = 0.67$ nm. Thus, we have $\sigma = 8.08$ nm, relating the simulation length units with real units.

Simulations are run starting from an initial configuration at concentration $c = n/V$, produced by placing n coarse-grained bottlebrush chains randomly in a simulation box of volume V . We use two different box sizes—(i) $50\sigma \times 50\sigma \times 50\sigma$ and (ii) $20\sigma \times 100\sigma \times 100\sigma$. The choice of simulation box size will be discussed in the context of the results. The number of chains is chosen so that an experimentally relevant range of solution concentrations can be obtained. The pair potential $\tilde{u}_{\text{PMF}}$ in eq 11 was provided to LAMMPS as a tabulated potential with a spatial discretization of $10^{-4}\sigma$. All simulations were performed at the reduced temperature $T^* = k_B T/\epsilon = 1.0$ for least 2×10^6 time steps, each time step corresponding to $\Delta t = 0.005\tau^*$, where $\tau^* = (\epsilon/m\sigma^2)^{1/2}t$ is the reduced time unit for Lennard-Jones type of particles. The smallest interaction distance was tested against this time step for all concentrations to ensure that the distance between any two particles was not less than $10^{-4}\sigma$ as the simulation progresses.

The total simulation duration was $2\text{--}5 \times 10^6$ time steps for equilibrium, with data collected over at least a further 1×10^6 time steps. The equilibrium standard is based on the degree of mixing reaching stability, which will be introduced and discussed in detail in the next subsection. We provide the time evolution of the degree of mixing as well as total energy from pairwise interactions in the Supporting Information, which both suggest that these simulation times are sufficiently long to observe equilibrium structure. A minimum of 20 independent configurations were collected for further analysis, the configurations being sampled every 5×10^4 time steps.

2.3. Simulation Analysis. To characterize the morphological features of bottlebrush assembly, and compare with the experiment, we directly calculate the static structure factor $S(\mathbf{q})$ from MD simulations using the following formula

$$\begin{aligned} S(\mathbf{q}) &= \frac{1}{N} \left\langle \sum_{j=1}^n \sum_{i=1}^{N_A} \exp(-i\mathbf{q} \cdot \mathbf{r}_{i,j}) \sum_{j=1}^n \sum_{i=1}^{N_A} \exp(i\mathbf{q} \cdot \mathbf{r}_{i,j}) \right\rangle \\ &= \frac{1}{N} \left\langle \left| \sum_{j=1}^n \sum_{i=1}^{N_A} \cos(\mathbf{q} \cdot \mathbf{r}_{i,j}) \right|^2 \right. \\ &\quad \left. + \left| \sum_{j=1}^n \sum_{i=1}^{N_A} \sin(\mathbf{q} \cdot \mathbf{r}_{i,j}) \right|^2 \right\rangle \end{aligned} \quad (12)$$

Here, $\mathbf{r}_{i,j}$ denotes the coordinates of monomer i on chain j . For the purposes of this paper, we plot the structure factor versus only the

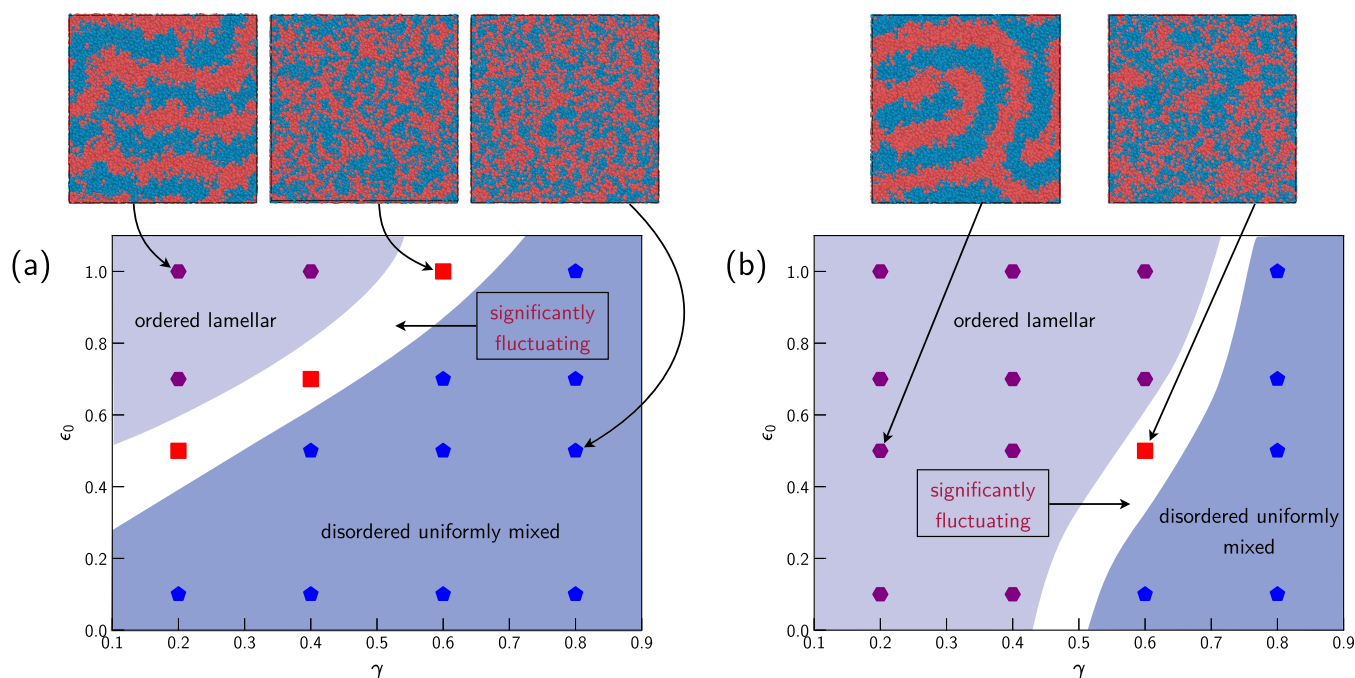


Figure 3. Phase maps as a function of interaction parameters γ and ϵ_0 at two different concentrations: (a) 50 and (b) 100 mg mL⁻¹. Purple symbols indicate ordered, lamellar phase; red symbols indicate significantly fluctuating regime; and blue symbols indicate disordered, uniformly mixed phase. The color-coded regions denote the approximate extent of each phase. On increasing ϵ_0 at fixed γ or decreasing γ at ϵ_0 , the system gradually transitions from a disordered, uniformly mixed phase to a significantly fluctuating regime, followed by another transition to an ordered, lamellar phase. For all subsequent simulations, we fix $(\gamma, \epsilon_0) = (0.6, 0.5)$. Representative simulation snapshots of the structures are also shown, which we observe at the points indicated by arrows, providing visual evidence of the existence of the three phases. For all snapshots, the experimental concentration of ~ 80.0 mg mL⁻¹ corresponds to a simulation number density of $1.0\sigma^{-3}$.

magnitude of $|\mathbf{q}| = q$ and average over similar $\mathbf{q}$ -vectors to produce a smoothed structure factor $S(q)$ analogous to what is seen from scattering experiments. Here, we assume complete contrast between the two blocks (calculating the scattering function only from the A-blocks). We restrict the chosen q -vectors to integer multiples of $2\pi/L_{\text{box}}$ on all three dimensions (L_{box} is the length of box), accounting for periodicity in these systems.

We quantify the extent of phase separation in the simulations via the magnitude of compositional fluctuations in a manner analogous to other simulation models of polymer phase separation.¹⁰⁵ We first define a global number density of the $i = \text{A}$ and B components, $\bar{\rho}_i = N_i(V)/V$, where the quantity $N_i(V)$ is the overall number of particles in the box volume V . We then divide the system into cubic subcells j of volume $\Delta V = (5\sigma)^3$, define a local density $\rho_{i,j} = N_i(\Delta V)/\Delta V$, and define a normalized particle fraction $f_{i,j} = \rho_{i,j}/\bar{\rho}_i$. This quantity is chosen so as to ensure that all systems comparably have $\langle f_i \rangle = 1$ for both components, where the angle brackets denote averaging over all subcells and at multiple snapshots at the same conditions (i.e., concentration and block fraction). This allows us to define a degree of mixing, $\langle f_A f_B \rangle$, that ranges from 1 for homogeneously mixed systems to 0 for completely demixed systems.

3. RESULTS AND DISCUSSION

The molecular model developed in this paper combines the ISC representation of bottlebrush polymers, featuring implicit side chains and bending potentials to minimally represent the wormlike structure of BBCPs, and also a scaling argument for the pairwise interaction between nearby bottlebrush polymers in solution. The former aspect of this model is informed by the ESC models of individual bottlebrush polymers and has been shown to be in agreement with the dilute solution properties of bottlebrush polymers.³¹ We can demonstrate that, with appropriate parameterization of the latter aspect of the

model, i.e., the pairwise bottlebrush–bottlebrush interaction, we can qualitatively reproduce key experimental observables. Our results can then be used to map out and characterize BBCP phase behavior as a function of block fraction and solution concentration, thus providing simulation predictions over an array of molecular parameters beyond those involved in the initial parameterization.

3.1. Interaction Parameters in Bottlebrush Solution Assembly. In our description of the model in Section 2.2.2, we introduced the parameters ϵ_0 and γ that govern bottlebrush–bottlebrush repulsion. The magnitude of the repulsion between chemically identical (i.e., A–A or B–B) brushes is determined by ϵ_0 , and then the chemically different repulsion is determined by γ (a value of $\gamma < 1$ corresponds to an increased repulsion between dissimilar blocks), and thus drives microphase separation. We note that this choice of parameters is informed by the chemistry of the experimental system; toluene is a good solvent for both the PS and PLA blocks,^{106,107} so we do not consider the alternative that self-assembly is driven by one of the blocks being solvophobic. With this in mind, we will consider ϵ_0 and γ as analogous to χ in traditional self-assembly, in that they are phenomenological parameters that can be determined by fitting experiments to a model. In this case, we will use SAXS data to inform our choice of ϵ_0 and γ .

We map the microstructure of BBCP solutions as a function of ϵ_0 and γ , for a number of concentrations, in Figure 3. Using noncubic simulation boxes ($20\sigma \times 100\sigma \times 100\sigma$), we distinguish between three different types of observed morphologies—(i) ordered, lamellar phase (given as purple symbols), (ii) disordered, uniformly mixed phase (blue symbols), and (iii) an intermediate significantly fluctuating

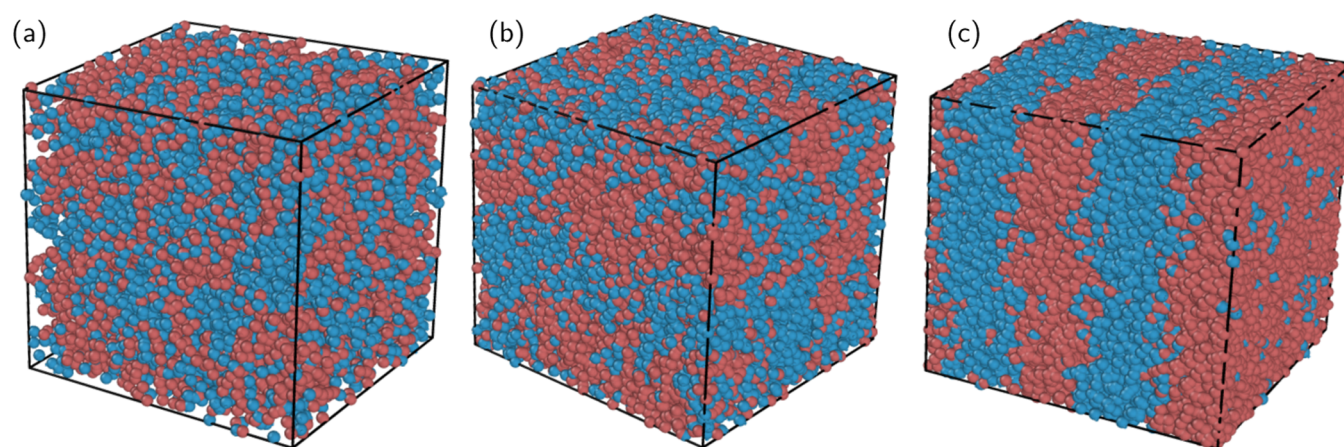


Figure 4. Simulation snapshots showing phases observed in self-assembled diblock bottlebrush solutions at different concentrations: (a) disordered, uniformly mixed phase, 50 mg mL⁻¹; (b) significantly, fluctuating regime, 100 mg mL⁻¹; and (c) ordered, lamellar phase, 180 mg mL⁻¹. While the disordered, uniformly mixed phase (a) and the significantly fluctuating regime (b) are visually similar, there exist nontrivial differences in compositional fluctuations between these two regimes. For all snapshots, the experimental concentration of ~ 80.0 mg mL⁻¹ corresponds to a simulation number density of $1.0\sigma^{-3}$.

regime (red symbols) that is still disordered but exhibits significant compositional fluctuations. Representative simulation snapshots are shown in Figure 4 for cubic boxes ($50\sigma \times 50\sigma \times 50\sigma$), demonstrating these three regimes. We note that it is more efficient to use noncubic simulation boxes to distinguish between the three regimes, motivating their use, as the equilibration time for these simulations is generally shorter than simulations with cubic boxes. For both the box sizes, we do not see any qualitative difference in the observed microstructure when other aspects of the simulations are the same.

The difference between the disordered uniformly mixed phase and significantly fluctuating regime is not indicative of a true phase boundary and is merely empirical; however, we find it a useful distinction that is clear both visually and in our characterization of this system. To quantitatively distinguish between these two regimes, we consider the compositional fluctuations as quantified by the degree of mixing $\langle f_A f_B \rangle$. We plot the degree of mixing as a function of simulation time in the Supporting Information, showing that this quantity can be used to check that we have reached an equilibrium state. We illustrate how this parameter is used to determine the existence of significant compositional fluctuations in Figure 5, plotting $\langle f_A f_B \rangle$ as a function of c for $\epsilon_0 = 0.5$ and $\gamma = 0.6$. The degree of mixing parameter monotonically decreases from a well-mixed ($\langle f_A f_B \rangle \approx 1$) to demixed ($\langle f_A f_B \rangle \approx 0$) as concentration c increases, with a broad transition between the two limits. Here, we choose two values to be the boundaries for distinguishing the three regimes. The first is $\langle f_A f_B \rangle = 0.85$, above which we identify the system as disordered uniformly mixed phase; the second is $\langle f_A f_B \rangle = 0.65$, below which we identify the system as ordered, lamellar phase. This choice is informed by the work of Mao et al.,¹⁰⁵ who related an analogous mixing parameter to both the breakdown of mean-field theory of semiflexible polymers prior to microphase separation, and the order–disorder transition. Their choice of mixing parameter is scaled differently (varying instead between 0 and 0.25) but exhibits near-identical trends.¹⁰⁵ We thus extract and rescale the values that they identify,^{105,108} leading to the aforementioned boundaries of $\langle f_A f_B \rangle = 0.85$ and 0.65 , as indicated in Figure 5. Although the definition of degree of mixing in this paper is

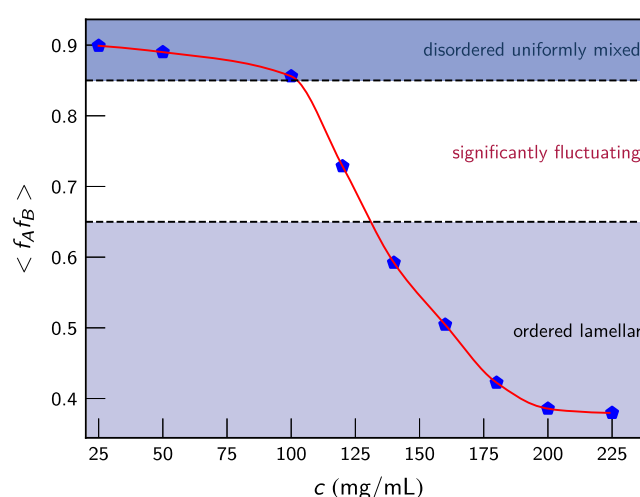


Figure 5. Degree of mixing $\langle f_A f_B \rangle$ as a function of concentration c . The red line serves to guide the eye. By definition, $\langle f_A f_B \rangle = 1$ is the well-mixed limit. The degree of mixing monotonically decreases with concentration c , with clearly visible plateau values at the low and high c limits. The black dashed lines mark the phase boundaries, at $\langle f_A f_B \rangle = 0.85$ and 0.65 , respectively. The colored regions denote the approximate extent of each phase.

slightly different from that prior work,¹⁰⁵ it is reasonable to use those two values since they are similar in their physical meanings. We will show later that these criteria are consistent with features in the structure factor, determined both in simulation and the experiment.

Figure 3a,b shows two different concentrations, $c = 50$ and 100 g mL⁻¹, respectively. Noticeably, the region of microphase separation increases to a larger set of molecular parameters at higher concentrations. This trend is consistent with the solution assembly of standard block copolymers¹⁰⁹ and arises due to the increased number of less favorable interactions between the chemically dissimilar blocks at higher concentrations. For both cases, microphase separation occurs at large values of ϵ_0 and small values of α . This is unsurprising, as this combination of parameters increases the strength of the pairwise interactions while simultaneously maximizing the repulsion between dissimilar blocks.

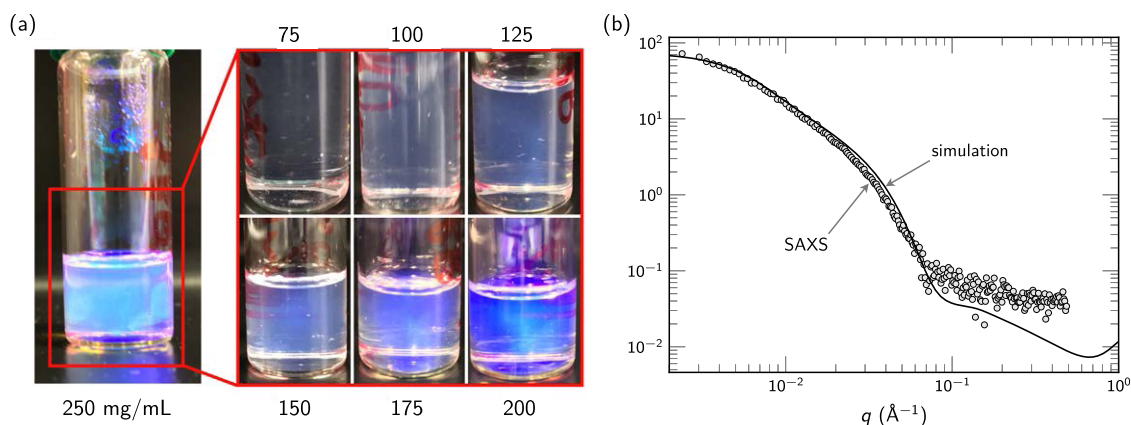


Figure 6. (a) Photographs of BBBCP solutions prepared at various concentrations. The emergence of strong blue/turquoise reflection at concentrations exceeding $\sim 125 \text{ mg mL}^{-1}$ coincides with the formation of long-range order notes by SAXS and simulation (Figure 7). (b) Structure factor for homopolymer bottlebrush molecules ($N_{bb} = 320$, $N_{sc} = 20$) at the dilute limit (isolated molecule) computed from simulations using explicit side chains from ref 91 (solid line) compared to SAXS data for diblock bottlebrush polymers at 1 mg mL^{-1} (markers).

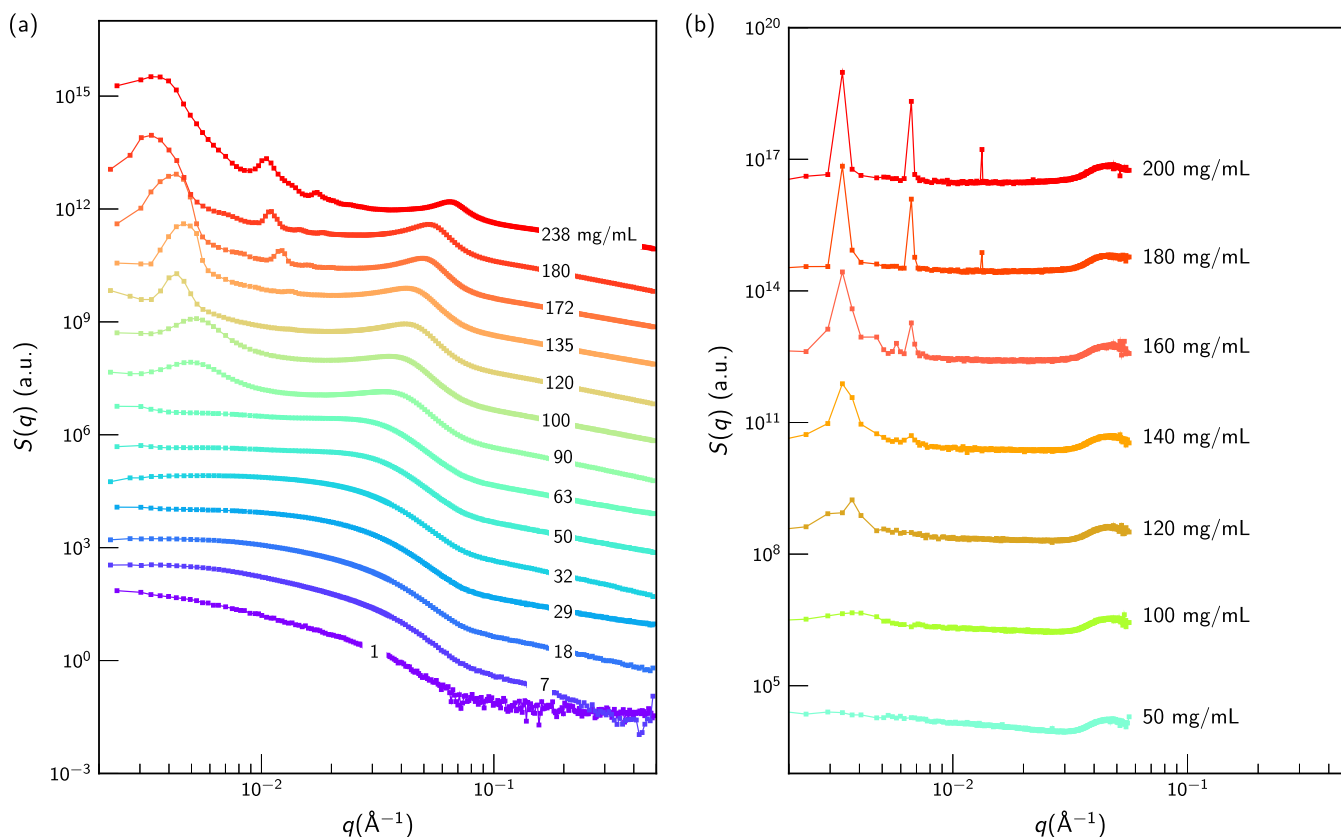


Figure 7. Structure factor curves for symmetric bottlebrush polymers (block fraction $x_A = 0.53$). The graphs for different concentrations have been vertically shifted for visual clarity. (a) SAXS data: Below 50 mg mL^{-1} , form factor of the dilute bottlebrush solution is observed. As the concentration increases beyond 90 mg mL^{-1} , a structure factor peak first emerges at high- q regime, indicating the length scale related to the interaction between adjacent bottlebrush polymers. This peak shifts to higher q as the concentration increases due to the crowding of bottlebrush polymers. At 90 mg mL^{-1} , a diffuse peak at low q emerges, which indicates compositional fluctuations. Beyond 135 mg mL^{-1} , multiple diffraction peaks emerge at integer multiples of the fundamental peak position, indicating a lamellar phase. (b) Simulation data: the trends qualitatively agree with the experimental data, except that simulations cannot resolve q higher than 0.06 Å^{-1} , as the coarse-grained model no longer contain the information below the length scale of bottlebrush width.

We show a number of characteristic simulation snapshots in Figure 3 as well, corresponding to several selected points in the plot. We first note that, in both cases and for all combinations of ϵ_0 and γ , the ISC model is essentially space-filling and thus assembly occurs when there is significant overlap of the bottlebrush arms. This justifies our use of the soft potential

that we derived rather than assume an “effective” hard-core potential of size d , which would be unable to reach these experimentally realized concentrations. Indeed, despite the apparent high concentration of these bottlebrush solutions, each coarse-grained bead represents a branched structure that contains a significant amount of solvent within its span, so

these are at rather low-volume fractions. In fact, if we use the PS coarse-grained beads as an example, the weight fraction of polymers within these beads is only $\sim 80.0 \text{ mg mL}^{-1}$, which we take to be equivalent to the simulation units of $1.0\sigma^{-3}$. We can also see that simulation snapshots align excellently with the categorized phases, which again strengthens our choice of boundary values of $\langle f_A f_B \rangle$. As a final note, we observe that lamellar structures readily form defect states, as can be seen for $(\gamma, \epsilon_0) = (0.2, 1.0)$ in Figure 3a and $(\gamma, \epsilon_0) = (0.2, 0.5)$ in Figure 3b. We attribute this both to the long relaxation times of the morphology, as well as the imposed boundary conditions; we do not expect these features to affect our results in the remainder of the manuscript.

3.2. Scattering from Block Bottlebrush Solutions.

Small-angle X-ray scattering was performed on solutions of well-defined PS-*b*-PLA diblock bottlebrush polymers, consisting of 400 repeat units along the backbone with a block fraction of $x_A = 0.5$. Scattering data was obtained for a series of solution concentrations, shown in Figure 7a spanning a large range of concentrations from 1 to 238 mg mL^{-1} . Systematic increase in concentration reveals a succession of scattering features corresponding to the emergence of higher-level ordering. At concentrations below $\sim 20 \text{ mg mL}^{-1}$, scattering yields the form factor of a dilute bottlebrush solution, consistent with form factors determined in the literature from the experiment and simulation.^{90,110} The comparison between experimental structure factor and that determined based on explicit side-chain simulation (from ref 91) in the dilute limit is shown in Figure 6. While the simulation data is for a slightly smaller backbone length, qualitative agreement between the simulation and experiments is excellent.

As concentration increases beyond 90 mg mL^{-1} , a structure factor peak appears in the high- q region, which we attribute to the interaction between adjacent bottlebrush backbones (across the radial direction). This peak monotonically sharpens and shifts to higher q (i.e., smaller correlation length) as concentration increases further, reflecting the increased crowding of adjacent bottlebrush polymers. At 90 mg mL^{-1} , a diffuse peak at low q emerges which is attributed to compositional fluctuations typically observed in the disordered block copolymer phase near the order–disorder transition (see ref 111 and the references therein). Finally, for concentrations greater than 135 mg mL^{-1} , multiple diffraction peaks are visible at integer multiples of the fundamental peak position (in q), indicating the presence of a long-range-ordered lamellar phase.

We use these SAXS structure factors to delineate different regimes in bottlebrush assembly. There is initially a uniformly mixed state at low concentrations, characterized by the lack of any discernible low- q peaks that exist in this case for $c < 90 \text{ mg mL}^{-1}$. This eventually transitions to a regime of lamellar-ordered structures, characterized by multiple diffraction peaks above the order–disorder transition at $c > 135 \text{ mg mL}^{-1}$. Intermediate concentrations $90 \leq c \leq 135 \text{ mg mL}^{-1}$ are characterized by a broad peak, and we call this a significantly fluctuating regime. These are the designations used earlier in mapping phase behavior in Figure 3.

It is possible to compare these experimental observations with results from simulation. We first choose values of $\epsilon_0 = 0.5$ and $\gamma = 0.6$ for all subsequent simulations, as this choice of parameters corresponds well with the sequence of morphologies—and concentration transitions—seen in experimental SAXS measurements. These points are directly observed in the

phase maps in Figure 3a,b as disordered, uniformly mixed phase and significantly fluctuating regime, for example. We run simulations at the block composition described in Table 1 ($x_A = 0.53$) in a cubic box ($50\sigma \times 50\sigma \times 50\sigma$). The cubic box is chosen to prevent the box geometry from playing a role in determining the eventual morphology, though we nevertheless observe lamellar morphologies for all ordered structures at this block composition. We perform these calculations at a number of concentrations ranging from 50 to 200 mg mL^{-1} .

The resulting structure factors are plotted in Figure 7b and correspond well to the experimental data. First, we can match the locations of the transitions between disordered, uniformly mixed phase to significantly fluctuating regime, which for our case occurs between 50 and 100 mg mL^{-1} , as evidenced by the emergence of a broad peak at $c = 100 \text{ mg mL}^{-1}$. This is consistent with the experiment, which puts this transition at $c = 90 \text{ mg mL}^{-1}$. The multiple diffraction order peaks begin to appear at $c = 140 \text{ mg mL}^{-1}$, a characteristic of the order–disorder transition. This is again consistent with the transition in the experiment, which is seen to occur at roughly $c = 135 \text{ mg mL}^{-1}$. While this agreement is in part due to the deliberate choice of parameters, we note that it was not apparent that these transitions would be so well aligned by just tuning these two parameters.

More strikingly, we see agreement between many of the key features of the structure factors. In addition to the emergence of a broad low- q peak that sharpens and gives rise to diffraction-ordered peaks, which are seen in both sets of data, the positions of these peaks are in general agreement. Both the broad fluctuation peak and the lowest- q ordered peaks occur between 0.003 and $0.005 \text{ \AA}^{-1}$. For the ordered lamellar phase, the subsequent peaks are positioned at integer factors of the lowest- q peak, consistent with lamellar ordering; this is true for both the simulation and experimental data. These results are also in agreement with our characterization of the significantly fluctuating and disordered, uniformly mixed regimes by the parameter $\langle f_A f_B \rangle$, and we indicate approximate locations of these boundaries, determined from the structure factors, in Figure 5.

We do see some important differences, however, that we attribute to limitations in both simulation and the experiment. First, we note that our molecular model coarse-grains the bottlebrush side chains and is not reliable in the high- q limit. This prevents reproducing the trend toward higher q for the peak associated with the bottlebrush width, as the spacing between adjacent chains decreases. This trend has been well characterized in both the bottlebrush and analogously in the polyelectrolyte literature,^{112,113} but we do not resolve it here. We speculate that the origin of this disparity is that we expect the Kuhn length λ^{-1} to vary as a function of the local polymer concentration, with a shorter persistence length occurring at higher concentrations due to screening of excluded volume.¹¹² These differences would be most apparent at intermediate concentrations, where screening is significant and chain–chain segregation is relatively weak and thus most sensitive to changes in the persistence length. We also note that the peaks in the experimental SAXS data are broader, likely due to the significantly larger system size and molecular weight distribution in the synthesized molecules. Simulation data comes from relatively small, periodic boxes but with monodisperse chains, leading to much sharper peaks. Finally, simulation data assumes complete contrast between the two

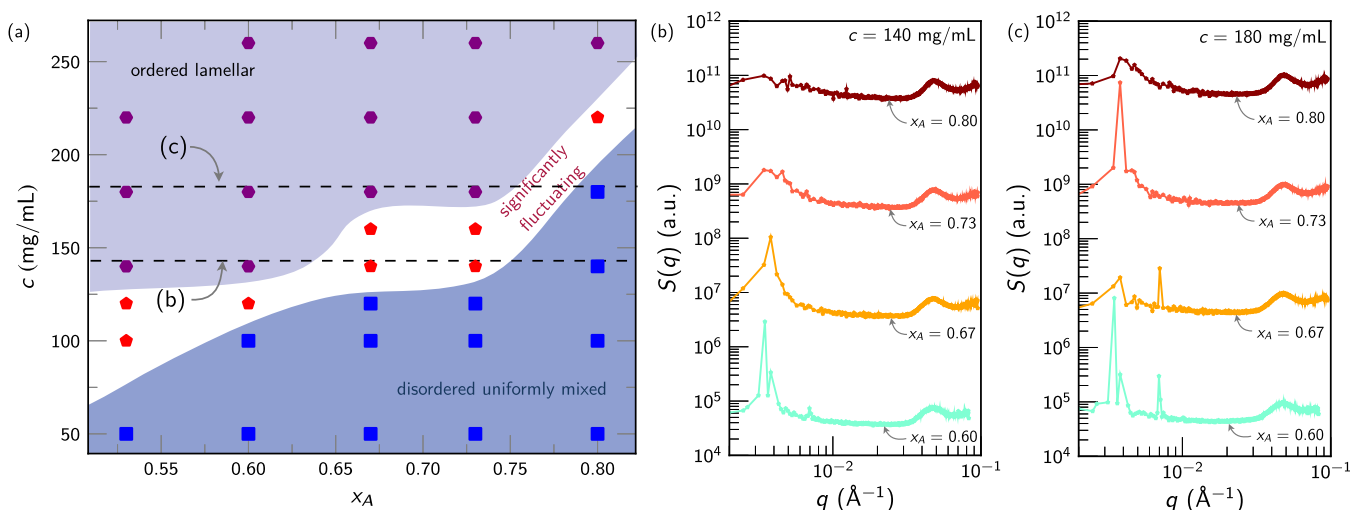


Figure 8. (a) Phase diagram for different bottlebrush architectures showing a disordered, uniformly mixed phase (blue symbols), a significantly fluctuating regime (red symbols), and an ordered, lamellar phase (purple symbols). The colored regions denote the approximate extent of each phase. As the block fraction moves away from $x_A = 0.53$, a higher concentration is needed to observe microphase separation. (b) Structure factor curves for different block fractions at a fixed concentration $c = 140$ mg mL⁻¹. Lamellar morphology is observed at $x_A = 0.6$, and significantly fluctuating morphology is observed at $x_A = 0.67$ and 0.73 . (c) Structure factor of various block fractions with fixed concentration $c = 180$ mg mL⁻¹. Disordered morphology is seen at $x_A = 0.8$ and lamellar morphology prevails at $x_A = 0.73$, 0.67 , and 0.6 .

blocks, contributing to the quantitative differences between the experiment and simulation.

These agreements between simulations and experiments show the strength of this ISC model; there are some limitations to be addressed by further refinement of the model and comparison with a wider range of architectures, but we nevertheless show that we can capture many key features despite such a high level of coarse-graining. Removing a large number of degrees of freedom in the system provides benefits of reducing computational cost, and the simulations conducted in this section generally take under 7 days to complete on a single-core central processing unit (CPU). An analogous ESC calculation would be much more computationally expensive for bottlebrush polymers of this size.

3.3. Phase Diagrams in Bottlebrush Block Copolymer Solution Assembly. Given the qualitative agreement between molecular simulation and experimental SAXS data, we use our model to predict a phase diagram for BBCP solutions. We use the same procedures used for the $x_A = 0.53$ case, using the same molecular interaction parameters $\epsilon_0 = 0.5$ and $\gamma = 0.6$, but for a variety of different block fractions x_A and concentrations c ; these include simulating in narrow ($20\sigma \times 100\sigma \times 100\sigma$) boxes, to ensure that we have sufficient numbers of lamellae to obtain an accurate structure factor. Structure factor data is used to categorize the morphologies, using the features highlighted in the previous subsection. We map in Figure 8a the observed morphology from simulation, as a function of concentration c versus block fraction x_A , with approximate phase boundaries determined by visual inspection. We show structure factor data at fixed concentrations $c = 140$ and 180 mg mL⁻¹ in Figure 8b,c, respectively. We observe that at $c = 140$ mg mL⁻¹, only the system with the lowest block fraction (closest to the symmetry) forms a lamellar phase; when the concentration increases to $c = 180$ mg mL⁻¹, the system with the most asymmetry still does not form any ordered morphology.

We show that, as the block fraction moves away from $x_A = 0.53$, a higher concentration is needed to observe microphase

separation. This is analogous to the expectation for solution self-assembly of linear block copolymers, in that as one of the blocks becomes smaller, there are less unfavorable interactions between dissimilar blocks that drive assembly. The primary difference here is twofold: (i) the interactions between blocks are more complicated than simple block–block contact and arise due to the multiple simultaneous interactions between side-chains. This coarse-grained model does not resolve these interactions explicitly but instead uses the soft potentials derived earlier in this manuscript. (ii) The side-chain-induced stiffness of the bottlebrush structure decreases the ability of the blocks to deform and adapt to nonlamellar morphologies, and we thus do not see any evidence of nonlamellar morphologies even at large block fraction disparities. We acknowledge that it is not possible, however, to rule out all possibilities as we are not able to compare, for example, the free energies between competing morphologies with particle-based calculations in a manner that is common in field-theoretic approaches.¹¹⁴

4. CONCLUSIONS

In this paper, we studied the self-assembly behavior of bottlebrush block copolymer solutions using experiments and simulations. First, we prepared symmetric bottlebrush polymers with poly(norbornene) backbones with polystyrene side chains and polylactide side chains on each block. We used the scaling theory to derive an analytical expression of bottlebrush–bottlebrush interactions in good solvent conditions. By systematically varying the potential parameters in MD simulations with Langevin thermostat, we were able to obtain a phase diagram with respect to ϵ_0 and γ . We used the degree of mixing to characterize the degree of microphase separation and established quantitative criteria for distinguishing different morphologies. We then calculated the structure factor from simulations and found a good agreement with scattering results in the low wave vector regime. Despite that the simulations are not able to capture high wave vector behavior due to the nature of the coarse-grained model, we still

showed that the structure factor enabled us to capture many structural features in our system, such as lamellar spacing.

Finally, we extended our simulation model to asymmetric architectures, where the block with polystyrene side chains (A block) is longer in backbone contour length than the block with polylactide side chains (B block). We found that the block fraction has an effect on the concentration dependence of phase behavior. Specifically, we showed that the more asymmetric the architecture is, the higher concentration it takes for an order–disorder transition to happen. Also, we found no evidence of morphologies other than lamellar structures in a high concentration regime, which we attribute to the side-chain-induced stiffness of the bottlebrush structure decreasing the ability of the blocks to deform and adapt to nonlamellar morphologies.

Overall, we developed a coarse-grained implicit side-chain model for bottlebrush block copolymers in solution and showed its ability to match to experiments with specific chemistry. This model is able to predict the phase behaviors of such a system correctly, with the advantage of relatively low computational cost. The model is versatile and can be adapted to different architectures such as asymmetric architectures. This is potentially useful as the chemistry and architecture of bottlebrushes become increasingly complex, and this type of coarse-grained model can provide valuable predictions to guide materials design.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.1c00336>.

Materials and characterization methods, synthesis procedures, characterization data, and equilibrium validation in molecular simulations (PDF)

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Notes

The authors declare no competing financial interest.

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