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Molecular Simulations of Laser Spike Annealing of Block Copolymer Lamellar Thin-Films

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ABSTRACT: We use molecular dynamics simulations to study the phase behavior of a coarse-grained lamella-forming A-*b*-B diblock copolymer under thin-film soft confinement for different heating cycle lengths, film thicknesses, and substrate– polymer affinities. This model describes the effect on thin-film morphology with a free surface (air–polymer interface) and a solid substrate. Our simulation results were first validated by showing that they capture changes for the order–disorder transition temperature with annealing conditions consistent with those found in laser spike annealing experiments, when the vertical lamella phase formed on neutral substrates. In addition, simulations with a substrate selective for a particular block revealed the formation of other phases, including a mixed vertical–horizontal lamella and a metastable island phase having horizontal but incomplete lamella layers. The nanoscale roughness features of this island phase, and hence its surface wettability, can be tuned with suitable choices of chemistry and annealing conditions.



INTRODUCTION

Block copolymers (BCPs) combine two or more chemically distinct blocks by covalently attaching them into a single polymer chain. BCPs self-assemble into ordered nanoscale morphologies through phase segregation depending on the Flory–Huggins segment–segment interaction parameter χ , the polymer chain length *N*, and the block composition. BCP ordered structures have been explored for uses involving lithographic templates,¹ bit patterned media,² filtration membranes,³ fuel cell membranes,⁴ drug delivery vectors,⁵ and adhesives.⁶

The orientation of the ordered structure of an A-*b*-B diblock copolymer (dBCP) thin film is highly sensitive to substrate wetting.^{7,8} For a symmetric dBCP and a neutral substrate that has a similar attraction to both blocks A and B, the equilibrium order phase will be a lamella phase⁹ with layers aligned vertically to the substrate. If the substrate attraction favors contacts with one particular block (A or B), the equilibrium ordered phase will be a lamella phase with layers parallel to the substrate, with the bottom layer being of the favored block type. Moreover, a peculiar island phase has been found for the horizontally aligned lamella phase, with nonperfect layers open to the air—polymer interface.^{10–15} Lastly, a hybrid lamella phase, which contains both vertically and horizontally aligned lamella, has also been found experimentally for certain film thicknesses and vapor annealing conditions.¹⁶

The structural order of dBCP films can often be improved or controlled via thermal or solvent annealing. The annealing process is often intended to provide higher mobility to individual molecules to promote faster local and cooperative rearrangements that allow the system to timely reach its most favorable (equilibrium) state. While the typical thermal annealing time scale is from minutes to hours (e.g., using vacuum-oven annealing),¹⁷ various groups have recently employed laser-spike annealing (LSA)³¹³²³³³⁴ to study the order–disorder transition of dBCPs.^{18,19} The order–disorder transition can be accelerated far in excess of what is achievable via thermal annealing by using sub-millisecond lateral gradient LSA, where the polymer experiences much higher temperatures for far shorter times. Indeed, by heating the sample up to temperature well above the order–disorder transition (ODT) temperature (T_{ODT}) for a millisecond time duration, Jacobs et al.^{18,19} explored the effect of a previously inaccessible thermal region on the kinetics of the phase segregation process. They also showed that the final structure after LSA depends on both the annealing temperature and quenching rate.

In this work, we implemented a coarse-grained model to simulate the phase behavior of a generic A-*b*-B dBCP thin film under a soft confinement. Our main goal is to understand the effect on the order–disorder transition via a fast heating– cooling protocol that mimics LSA. The ordering and disordering mechanisms of the thin film are probed by using different heating and cooling rates as well as different peak heating temperatures (below and above T_{ODT}), as was done

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with LSA. Different substrate preferences are also tested to understand the effect of substrate wetting. By controlling the cooling rate, we found that an island phase is formed by the partial "retreat" of layers from a perfect horizontal lamella phase when cooling to low temperatures. Also, we seek to understand factors that control the formation of the island phase, which can be used as a strategy to create surfaces with controlled nanoscale roughness such as in potential applications, for example, for engineering superhydrophobic surfaces.

The rest of the paper is organized as follows. First, we present the model and methods used for this study, including a description of the simulated LSA cycles and of various order parameters we adopt to track and characterize the order disorder transitions. In the subsequent section, we present the main results, describing the effect of annealing cycle conditions on thin films on either a neutral substrate or a block-selective substrate. In the last section, we summarize the main conclusions and the outlook of this study.

MODEL AND METHODS

Model Details. We adopt a simple coarse-grained model of an Ab-B dBCP thin film, following the work of Forrey et al.^{20,21} Our linear A-b-B dBCP is composed of two chemically distinct coarse-grained beads, type A and type B. We chose a polymer chain with a moderate chain length, i.e., 20 beads, having an equal number of A and B (10:10) beads to target the lamella morphology. This chain length is short enough to be computationally efficient but also long enough to allow the study of the morphological changes above the T_{ODT} with minimal evaporation. Note also that the attraction of the polymer to the substrate provides additional stability to the thin film structure even at higher temperatures.

Each dBCP coarse-grained bead represents a group of chemical units. Bonded interactions act only between bonded beads in the same chain and constrain their separation distance by a harmonic potential of the form

$$U_{\text{bond}}^{\text{harmonic}}(r) = \frac{1}{2} K_{\text{spring}} (r - r_0)^2 \tag{1}$$

where *r* is the separation distance between the bonded beads, r_0 is the equilibrium separation, and K_{spring} is the spring constant.

Nonbonded interactions are determined by pairwise Lennard-Jones potentials that include an attractive tail between all bead types

$$U_{ij}^{\rm LJ}(r) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right], \ r < 3\sigma_{ij}$$
(2)

where *i* and *j* represent the bead type, *r* is the bead separation, ε_{ij} is the depth of the potential well, and σ_{ij} is the distance where the interparticle potential is zero. A-type beads are tuned to have a higher self-attraction than B-type beads, while the attraction between A and B beads is even weaker to drive phase segregation. Unlike the commonly used Kremer–Grest bead spring model,²² in which the potential between dissimilar beads is purely repulsive (known as the Weeks–Chandler–Andersen potential²³), here, we use an attractive well between all bead types to ensure film cohesion in the presence of a free surface. The parameters used in this model are presented in Table 1. All units are in LJ units: temperature, $T^* = Tk_{\rm B}/\varepsilon$, where $k_{\rm B}$ is the Boltzmann's constant; pressure, $P^* = P\sigma^3/\varepsilon$; length, $L^* = L/\sigma$; and time, $t^* = t(\varepsilon/m\sigma^2)^{0.5}$.

Note also that the Lennard-Jones self-interaction parameter ε_{AA} (=1.9) is set to be higher than ε_{BB} (=1.6) to provide a driving force for wetting the free surface by the lower-surface energy bead B. Our choice of ε_{AB} ensures a tendency for microphase separation via a positive interaction mismatch parameter χ , which relates to ε as

$$\chi \approx \frac{-(\varepsilon_{\rm AB} - 0.5(\varepsilon_{\rm AA} + \varepsilon_{\rm BB}))}{k_{\rm B}T} \tag{3}$$

Table 1. Simulation Parameters

type	parameter	value
bond stretching	<i>r</i> ₀	1
	K _{spring}	500
Lennard-Jones interaction	\mathcal{E}_{AA}	1.9
	$\varepsilon_{ m BB}$	1.6
	\mathcal{E}_{AB}	0.8
	$\mathcal{E}_{substrate(neutral)}$	3.5
	$\mathcal{E}_{\text{substrate to favored bead}}$	4.5
	$\mathcal{E}_{\text{substrate to unfavored bead}}$	0.75
	$\mathcal{E}_{\text{substrate to substrate}}$	0
	σ_{ij}	0.84

Simulations were performed via the LAMMPS molecular dynamics (MD) simulation package²⁴ using a canonical (NVT) ensemble with a reduced time step of $0.005t^*$. VMD was used for visualization.²⁵ The simulation box was $55 \times 55 \times 70.5$ (L* units) in the x, y, and z directions. Different system sizes were studied by using 3000, 4000, or 6000 chains to probe the effect of film thickness. Also, 8868 substrate beads were placed below the thin film with a hexagonal close-packed arrangement to form two layers of the solid substrate. All substrate beads were immobilized by a harmonic potential (with the same $K_{\rm spring}$ value given in Table 1) to only allow small fluctuations around their lattice positions; these substrate beads only interact with the polymer beads and not among themselves. Different values of $\varepsilon_{substrate}$ were tested to study the effect of substrate preference. Since our model targets the lamella phase, its orientation depends on the substrate selectivity. Periodic boundary conditions were applied in the xy plane, while the z direction was made to be nonperiodic. Reflective walls were applied at both the lower and upper bounds of the zdimension of the box.

We will report reduced temperatures defined as $T_r = T^*/T_{ODT}^{bulk}$ where T_{ODT}^{bulk} is the order-disorder temperature (T_{ODT}) for the bulk system in LJ units, which is taken to be $T_{ODT}^{bulk} = 2.8$, based on our bulk-phase simulation results presented in Supporting Information (SI), section S1. Configurations with locally segregated blocks were obtained following the spin-cast procedure described by Forrey et al.²⁰ and were used as initial configurations for disordered thin films. Simulation runs at $T_r = 0.54$ were performed with different substrates until the lamella phase was formed, and then, the system was cooled to $T_r = 0.36$ (or $T^* = 1$) and annealed for 10^6 steps for later use as the initial ordered configurations, as illustrated in Figure 1. We note that for our ensuing discussion the value of $T_r = 0.36$ will just be referred to as T_0 and is a value representing a very "cold" system, below room temperature but above its glass transition temperature, where any microsegregated structure can be considered "arrested" or "locked" so that no further significant morphological rearrangements take place.

We use $T_{\text{ODT}}^{\text{bulk}}$ to calibrate the T_{r} temperature scale for convenience since the actual T_{ODT}^{film} value for a polymer film with soft confinement will depend on the film thickness and substrate interactions. In section S2 in the SI, we show some sample calculations to estimate $T_{\rm ODT}^{\rm film}$ for a 3000-chain system on either a neutral substrate (forming a vertical lamella like in Figure 1b) or a selective substrate (forming a horizontal lamella like in Figure 1c). Expectedly, $T_{ODT}^{film} < T_{ODT}^{bulk}$, with disorder nucleating from the free-surface layer down (see section S2). For the neutral surface case, we find an approximate 2% decrease in the ODT, which is rather minor for the film thickness involved; this is likely due to the absence of lateral expansion in our film (set by the presence of the rigid substrate) and the stabilizing effect of the substrate attraction, which hinders lateral distortions of the vertical lamella layers with increasing temperature. For the horizontal lamella case, we find that while the bottom layer remains pinned to the selective substrate, the top layer breaks up into partial layers for temperatures $>0.8T_{ODT}^{bulk}$

Annealing Cycle Details. The simulation procedure is illustrated in Figure 2. The simulation system can be considered as a small area of the experimental thin film scanned by the laser. Thus, to simulate the laser annealing experiment, we tested the ordered phase with



Figure 1. Snapshots of the (a) disordered phase, (b) vertical lamella phase formed on a neutral substrate, and (c) horizontal lamella phase formed on a B-bead selective substrate.



Figure 2. Schematics of the simulated thermal cycle. System was heated up to peak temperature, T_{peak} , with different ramp periods for heating, τ_{h} , and cooling, τ_c , with $\tau_{\text{h}} = \tau_c \equiv \tau$. A 10⁵ step run was performed before τ_{h} and after τ_c at T_0 . After-cycle outcomes will often be reported for the "final structure" collected at the point indicated in the plot.

different ramp periods, τ , namely 10⁵, 10⁶, 2×10^6 , and 4×10^6 time steps, and with different peak temperatures T_{peak} below and above the bulk T_{ODT} , namely from $T_r = 0.82$ to $T_r = 1.18$. Each simulation cycle consisted of an initial 10⁵ step period at $T_0 = 0.36$ followed by a heating period τ_h up to T_{peak} , a cooling period τ_c back to $T_0 = 0.36$, and a final 10⁵ step period at $T_0 = 0.36$ to produce the final structures. Cooling and heating rates were identical in magnitude (albeit opposite in sign) as we set $\tau = \tau_h = \tau_c$.

Our preliminary runs showed that $T_{\text{peak}} < 0.82$ was too low for our annealing cycle to cause any appreciable effect, and the system remained essentially unchanged from the initial morphology. On the other hand, $T_{\text{peak}} > 1.18$ was too close to the boiling temperature, and the thin film became unstable, resulting in most of the chains evaporating to fill the entire simulation box.

To quantitatively compare the simulation heating/cooling ramp periods to the experimental laser annealing cycle time scale, we calculated the relaxation time of our dBCP model from the response of a bulk system to shear deformation. This relaxation time captures the linear viscoelastic behavior of the dBCP as the time required to respond to the applied stress to reach the steady state. Details of this calculation are given in the section S3, and the results listed in Table S1 in the SI. These show that our simulated heating/cooling ramp period is of the same order of magnitude as the experimental laser annealing time scale. Such a consistency is important because this allows us to employ an approximate model that forsakes the need to explicitly model specific heat transfer processes, whose physical mechanisms and rates are embodied in the experimentally accessible LSA time scales. The results in Table S1 also help illustrate the idea that laser annealing times are long enough to allow chains to locally relax and to control heat transfer but not too long to dwarf the (temperature-dependent) time scale of the order—disorder transition; otherwise, any heating cycle with $T_{\rm peak} > 1$ would likely result in complete disordering of the lamellar phase.

Order Parameters. P_2 *Order Parameter.* To characterize the global order of the thin film, we adopted the algorithm described by John et al.²⁶ for the global order parameter to measure the order of the system, \overline{P}_2 , which is defined as

$$\overline{P_2} = \frac{\max}{n} \frac{1}{N_a} \sum_i \frac{1}{2} (3\langle |\mathbf{u}_i \cdot \mathbf{n}|^2 \rangle - 1) = \frac{\max}{n} \frac{1}{N_a} \sum_i \frac{1}{2} (3\langle \cos^2 \theta_i \rangle - 1)$$
(4)

where N_a is the number of chains, $\mathbf{u}_i = \begin{bmatrix} u_{i,xy} & u_{i,yy} & u_{i,zz} \end{bmatrix}$ is the unit vector along the end-to-end vector of chain i, $\mathbf{n} = \begin{bmatrix} n_{xy} & n_{yy} & n_z \end{bmatrix}$ is the director unit vector for which \overline{P}_2 is maximized, θ_i is the angle between vectors \mathbf{n} and \mathbf{u}_i , and $\langle \rangle$ represents the ensemble average. For a disordered system, the chains have no preferred alignment direction, and P_2 approaches 0. For an ordered system where all the chains lie parallel (perpendicular) to a reference direction, P_2 approaches 1 (-0.5).²⁷ On the basis of our bulk-system simulations, the end-to-end vectors tend to align normal to the lamella plane, and the histogram showed a large P_2 value for both end-to-end vectors and centroid of blocks vectors, as illustrated in Figure S3 in the SI.

Average Alignment of End-to-End Vectors. While P_2 can quantify the global extent of order in a system, it cannot discriminate between two systems with similar ordered structure but with chains oriented in different direction with respect to the substrate. Capturing such difference is crucial for systems undergoing a thermally induced order \rightarrow disorder \rightarrow order transformation since the ordered states may have

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Figure 3. Schematics of surface area calculations. The surface area is computed as the sum of the area of the triangles formed by triangulating over the preset pixels.



Figure 4. Snapshots, 2D structure factor of the final structure at T_0 , and Φ history for a $\tau = 10^5$ step period of heating/cooling for $T_{\text{peak}} = 0.82$ (a), 1.0 (b), and 1.18 (c). Φ exhibits the largest drop near $\tau + 10^5 = 2 \times 10^5$ steps when the thermal cycle reached T_{peak} (see Figure 2).

different features. To quantify the orientation of the system, we adopted an order parameter Φ defined as

$$\Phi = \frac{1}{N} \sum_{i}^{N} |\mathbf{u}_{i} \cdot \mathbf{n}_{r}|$$
(5)

where N is the number of chains, \mathbf{u}_i is the unit end-to-end vector, and \mathbf{n}_r is the reference unit vector. Φ measures how well the molecules align along \mathbf{n}_r . For systems with vertical lamella, \mathbf{n}_r was chosen to be the maximum lamella alignment direction calculated from the recipe described by John et al.,²⁶ while for systems with horizontal lamella \mathbf{n}_r was the z-direction (normal to the substrate).

If the ordered direction is aligned parallel (perpendicular) to \mathbf{n}_r , $\Phi \rightarrow 1$ (0). As a result, for both Φ close to 1 or 0, the system is ordered. For Φ close to 0.5, the system is typically disordered since it would indicate no preferential alignment. We can track the evolution of Φ to see whether the system becomes fully disordered during heating. If the system maintains the initial order, then $\Phi \rightarrow 1$. If the system becomes fully disordered, the final structure will be independent of the initial configuration, and Φ will show a distinctive drop to values close to 0.5.

A local Φ can also be used to quantify the ordering mechanism of the thin film at varying distance from the substrate. For this, we divided the thin film into four equal thickness layers in the *z* direction, bottom (layer 1), intermediate (layers 2 and 3), and surface (layer 4), and calculated Φ versus time to examine changes in the ordering profile during the annealing cycle.

2D Structure Factor. To detect translational order in the system, we calculate the structure factor based on eq $6:^{28}$

$$S(\vec{q}) = \frac{\left(\sum_{j} \cos(\vec{q} \cdot \vec{r_{j}})\right)^{2} + \left(\sum_{j} \sin(\vec{q} \cdot \vec{r_{j}})\right)^{2}}{N}$$
(6)

where \vec{q} is the wave vector, $\vec{r_j}$ is the position vector of each bead, and N is the number of beads. \vec{q} is restricted to integer numbers of wavelengths within the simulation box, namely $\vec{q} = 2\pi \left(\frac{n_x}{L_x}, \frac{n_y}{L_y}\right)$, and

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Figure 5. Snapshots, 2D structure factor of the final structure at T_0 , and Φ history for a $\tau = 10^6$ step period of heating/cooling for $T_{\text{peak}} = 0.82$ (a), 1.0 (b), and 1.14 (c). Φ exhibits the largest drop near $\tau + 10^5 = 1.1 \times 10^6$ steps when the thermal cycle reached T_{peak} (see Figure 2).

the peak locations are given by $m = \sqrt{n_x^2 + n_y^2}$, which, for lamella phase, follow the ratios (1:2:3:4:5...). To better visualize S(q) and allow comparison to experimental GISAXS results,²⁹ we average over the film thickness to plot S(q) as a function of q_x and q_y .

Roughness Parameter. To quantitatively capture the extent of surface roughness, we defined an order parameter "RP". For this, we divided the *xy* plane into 2500 pixels (50×50) and calculated the maximum height of each pixel. The order parameter RP is defined as the ratio of the standard deviation of the grid heights (*H*) and the thickness of the initial flat lamella phase:

$$RP = \frac{\sqrt{\langle H^2 \rangle - \langle H \rangle^2}}{H_{\text{Initial Horizontal Lamella}}}$$
(7)

If the phase is close to having fully horizontal lamella layers, the surface will be nearly flat and smooth, and $RP \rightarrow 0$.

Surface Area Parameter. The coordinates of the xy plane pixels used for RP are further used to estimate the surface area by a triangulation that uses the pixel centers as triangle vertices (i.e., two triangular areas are defined by four neighbor pixels, as illustrated in Figure 3). The area of each triangle was found from the cross product of the vectors forming two edges of a triangle. While the results depend on the chosen grid size, for a fixed grid size, the relative trends for changes in the surface area with annealing conditions will be similar. The relative surface area parameter "SP" is defined as the ratio of the surface area of the system to that of the initial horizontal lamella phase:

$$SP = \frac{Surface area of island phase}{Surface area of initial horizontal lamella phase}$$
(8)

RESULTS AND DISCUSSION

Heating/Cooling for Different Ramp Periods on a Neutral Substrate. 3000-Chain System with $\tau = 10^5$ Steps (Fast Heating and Cooling). We tracked the effect of temperature on the structure of each layer (bottom \rightarrow surface) by computing Φ . Figure 4 shows these results for different T_{peak} values (from 0.82 to 1.18).

At low T_{peak} (=0.82), only the surface layer was affected upon heating, as indicated by a small drop in the Φ value (0.85 \rightarrow 0.75) during heating while the remaining layers (bottom, layer 2, and layer 3) stayed ordered with an average of $\Phi >$ 0.85 over the entire heating and cooling periods. The system was able to go back to the initial ordered state after cooling. Figure 4 (a) shows, from top to bottom, a snapshot, a 2D structure factor color map (both for the final ordered phase after the cycle), and the variation of Φ for each layer during the heating and cooling process for T_{peak} = 0.82. As T_{peak} increased $(1 \le T_{\text{peak}} \le 1.14)$, a large drop in Φ was observed due to the disordering of all upper layers during heating, with only the bottom layer being able to largely retain the initial order, as Figure 4 (b) illustrates. The final structure obtained in this $T_{\rm peak}$ range was similar to the initial lamella phase with some defects in the layer spacing, as detected in the 2D structure factor color map by the diffuse parallel peaks. If T_{peak} is even higher (=1.18), the system fully disorders, and the final structure stays disordered due to the short cooling period, as shown in the snapshot and the ring-shaped 2D structure factor in Figure 4 (c).

3000-Chain System with $\tau = 10^6$ Steps (Slow Heating and Cooling). We found that not only the structure of the surface layer was affected but also the structures of layers 2 and 3 because of the larger amount of energy dumped into the system during the longer heating period. This effect was apparent even for the low $T_{\text{peak}} = 0.82$ but was more marked for $T_{\text{peak}} = 1.0$, where all the layers showed a larger decrease in the Φ values while heating, indicative of higher and widespread disorder (see Figure 5). While the system ordered back to the initial lamella phase after cooling for $T_{\text{peak}} = 1.0$, it stayed

disordered for $T_{\text{peak}} = 1.14$. Note that the T_{peak} value for which lasting disorder ensued is now lower (1.14) than with fast heating (1.18 for $\tau = 10^5$) because a comparable amount of thermal energy can be absorbed by the system at lower temperatures if the cycle is longer.

Relationship Between Peak Heating Temperature and Heating/Cooling Period. We now evaluate the apparent T'_{ODT} at different heating and cooling ramp periods using P_2 and Φ order parameters to compare with the experimental trends reported by Jacobs et al.¹⁹

To quantitatively examine the effect of T_{peak} and τ on structure disordering, P_2 values were calculated for the final structure after the heating/cooling cycle, as shown in Figure 6.



Figure 6. P_2 of the final structure at T_0 after different heating/cooling ramp periods as a function of the imposed peak heating temperature in the thermal cycle (see Figure 2) for the 3000-chain system.

Note that for T_{peak} = 1.15, for example, there is a clear reversal in the trend of P_2 with increasing τ , wherein P_2 initially decreases and then increases. This reflects a competition of kinetic effects, where a longer heating period favors disordering while a longer cooling period favors reordering; for $\tau > 10^6$, it is the latter effect that would start prevailing (even if the reordering is incomplete). If we assign, for convenience, the temperature at which the onset of disorder occurs, or of "partial disorder", i.e., the point where P_2 first decreases below ~0.55 (or Φ < 0.8), as the apparent T'_{ODT} then it is clear that as τ increases, T'_{ODT} decreases and approaches the equilibrium T_{ODT}^{film} value (~0.96 T_{ODT}^{bulk} , see section S2 in the SI). For the longest heating and cooling ramp period ($\tau = 4 \times 10^6$ steps), the T'_{ODT} occurs between $T_r = 0.94$ and 0.96, with P_2 dropping from 0.6 to 0.53 while forming a final partially ordered structure

By combining our criterion above for detecting "partial disorder" with another criterion for "complete" disorder, e.g., the point where P_2 or Φ dropped significantly ($P_2 < 0.35$ or Φ < 0.65), we can combine in Figure 7 the results from Figure 6 for P_2 and Φ for the long ramp period of 4×10^6 steps (see Figures S6 and S7, considering that the system was able to reorder into a different lamella orientation after having been fully disordered). In this manner, Figure 7 maps the approximate relationship between the different cycle conditions $(T_{\text{peak}} \text{ and } \tau)$ where incipient and extensive disordering occurs; the general decaying trends are qualitatively consistent with those of experimental results for LSA on an initially ordered vertical lamella (Figure 6a in ref 19). For conditions below the partial-disorder line, the system tends to retain its original ordered structure (with $T_{peak} \rightarrow T_{ODT}^{film}$ for long τ). For conditions above the full-disorder line, any reordering results



Figure 7. Correlation between the imposed peak temperature (see Figure 2) and the heating period τ (*x* axis) at which the system started to become disordered and became fully disordered (T'_{ODT}). A shorter heating/cooling ramp period corresponds to a higher T'_{ODT}.

from the quench period. For conditions between these two lines, the system exhibits various degrees of transitional order.

The effect of film thickness was probed by using systems with 4000 and 6000 chains while keeping the substrate area constant (Figures S8, S9, and S10). The 4000-chain system exhibited a similar order–disorder transition trend as that with the 3000-chain system, while the ordered structure of the 6000-chain system showed more stability during the heating cycle, leading to a higher T'_{ODT} even for a longer heating/ cooling ramp period. These results clearly illustrate the expected relationship between the film thickness and T'_{ODT} .

Heating/Cooling under Different Ramp Periods on Selective Substrates. 3000-Chain System with $\tau = 10^5$ (Fast Heating/Cooling). We found that the bottom layers of the horizontal lamella phase remained largely unperturbed, indicating that the substrate attraction was strong enough to effectively anchor the selective domain segments. The chains in the top layers were much more mobile and tended to expand to the free surface at high temperatures. The disordered surface structure created during heating did not recover a state of order after the rapid cooling period (see Figure S11).

Slower Heating/Cooling: Formation of an Island Phase. We found that the system formed a peculiar "island" phase upon cooling for $\tau = 10^6$ and 2×10^6 steps. In this phase, imperfect horizontal lamella layers were obtained whether we started from an initially ordered or disorder system and whether A or B favored the substrate. Forrey et al.²⁰ has provided an explanation for the island phase formation while heating a dBCP film from an initially disordered phase. The energetic (substrate) interactions that favor the fully horizontal lamella phase compete with the entropic effects that favor chain stretching and disorder; the islands formed when chain stretching are more dominant. However, here we find that the islands could also form even if the system did assemble a fully horizontal lamella phase when reaching the $T_{\rm peak}$ point in the cycle. As shown in Figure 8, the lamella layers retreated to leave lamella "islands" during cooling.

To understand the mechanism of island formation, we first studied the bulk phase behavior reported in section S1 in the SI. In the bulk phase, there is a clear tendency of lamella thinning and a reduction of chain area density with temperature, as shown in Figure S2. Such tendencies must also be at play even in the system under soft confinement. Indeed, as the initial disordered phase is heated to a high temperature, the system will tend to form a fully horizontal

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Figure 8. Illustration of an island phase formed after cooling from a fully horizontal lamella phase with a $\tau = 10^6$ step cycle.



Figure 9. Illustration of island phase formed from an initial horizontal lamella phase.

lamella phase with "thin" layers. As the temperature is decreased during cooling, χN and the attraction between like blocks increases, and the system begins to favor thicker lamella (containing more chains in each layer). At some point, the system would reach a structural instability that tends to rearrange the formerly formed horizontal lamella, causing some layers to retreat or partially disappear. The surface islands can then be seen as resulting from the freer surface layer being only partially incorporated into a deeper layer.

The island phase may also form from an initially ordered phase, as shown in Figure 9. As temperature increased, the chain density per layer per unit area decreased. The initial lamella phase (and layer spacing) destabilized as the block segregation strength became milder; hence, some chains were "squeezed out" to form a new layer on top. During cooling, these expelled chains were not able to penetrate back into the original layers due to a large free energy barrier associated with chains crossing unfavorable block domains. Thus, these chains remained kinetically trapped on the top and became part of the islands; indeed, clear evidence of the metastability of the island phase is the fact that they have a larger potential energy than the equilibrium horizontal lamella phase at same temperature condition ($T_0 = 0.36$), as illustrated in Figure 10 (see also Figure S12 for a reheating test showing that the islands are difficult to anneal away). Note also that the area of these islands shrunk after cooling, an observation consistent with the experimental results of Croll et al.³⁰

Quantifying the Roughness of the Island Phase. The rough topography of the island phase and the concomitant increase of the surface area could be exploited for applications where nanoscale features are desirable, as in creating superhydrophobic surfaces (via a mechanism akin to the lotus leaf effect) or enhancing another type of surface activity.



Figure 10. System potential energy (U_{total}) of the final structure at T_0 after different heating/cooling ramp periods as a function of T_{peak} . The U_{total} of the horizontal lamella phase at $T_0 = 0.36$ is shown for comparison. The system has 3000 chains.

Our calculations of RP for the island phase showed that the roughness depends on both T_{peak} and τ . Likewise, our results for the surface metric SP show that the surface area increases with the heating temperature, as shown in Figure 11. Expectedly, the trends of RP are similar to those of SP, as both metrics are correlated.

A higher T_{peak} leads to the formation of more horizontal lamella layers, as the layers get thinner (see also Figure S13). These extra layers will partially remain as islands after cooling and cause the roughness to increase but only up to a point (i.e., increases taper to a plateau value, see Figure 11.) A longer cooling period provides more time for the chains to rearrange in an attempt to locally reach the optimal lamella spacing, which resulted in the formation of islands at a lower temperature (i.e., for the initial disordered system at $T_{\text{peak}} = 0.86-0.96$, see Figure 11 (a)) and more variation in the height



Figure 11. Roughness parameter (filled symbols) and surface area parameter (open symbols) of the island phase at T_0 for a system initially (a) disordered and (b) ordered as a function of T_{peak} for 3 heating/cooling ramp periods.



Figure 12. Snapshots and Φ as a function of time step for (a) the perfect horizontal lamella phase formed at $T_r = 0.54$ and (b) the hybrid phase formed after heating/cooling at $T_{\text{peak}} = 0.93$ for $\tau = 10^6$ steps. Note that the thermal cycle reaches T_{peak} at $\tau + 10^5 = 1.1 \times 10^6$ steps (see Figure 2).

(i.e., RP ≈ 60 for $\tau = 2 \times 10^6$ compared to RP ≈ 50 for $\tau = 10^6$, as shown in Figures 11 and S14).

Finite Size Effects. We note that the topographical lengthscale of the islands and their shapes is constrained by the finite lateral size of our systems (and the periodic boundary conditions used). Our results for a 4-times larger system (with double side length) exhibited more complex and broader island contours (see section S9 and Figure S15 in the SI) than in the smaller system described above; however, similar general trends were observed of the roughness increasing with T_{peak} and with a longer ramp period as well as the surface area increasing with T_{peak} (see Figures S16 and S17). Formation of Hybrid Phase for Thicker Films. To explore the effect of film thickness, we increased the film thickness by using a larger system size while keeping the substrate area fixed. For an initially disordered 6000-chain system, we found that a hybrid structure formed having both horizontal and vertical lamella layers after the heating/cooling cycle. Note, however, that this system forms a fully horizontal lamella phase after annealing at $T^* = 1.5$ for $\tau = 5 \times 10^6$ steps. A comparison of the hybrid phase and horizontal lamella phase is shown in Figure 12. The hybrid phase shows the effect of local arrangements favored by both the substrate and free surface simultaneously. As before, the strong attraction to the substrate induces the formation of a horizontal lamella by the bottom

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layers. As the temperature increased during heating, the upper layers tended to expand to the free volume above, and being far from the substrate, they tended to decouple from the bottom layers and the associated tendency for horizontal alignment. As a result, the upper layers arranged vertically next to the free surface in a similar way as they would next to a neutral substrate.

The orientation of the lamella phase can also be changed for thicker films with different heating/cooling cycles ,as illustrated for the 6000-chain system in Figure 13. With a higher T_{peak} , the



Figure 13. (a) Morphology of the 6000-chain system and (b) system potential energy at T_0 after the heating/cooling cycle, showing the effect of T_{peak} and heating/cooling ramp period on the lamella orientation of the final structure.

surface layer will gain sufficient freedom to arrange in a way that favors the lower surface-tension beads to come on top, forming an extra horizontal layer. With a longer τ , the system has more time to rearrange and form the island phase, absorbing the large energy dumped into the system during the heating cycle. Thus, the horizontal lamella alignment could be formed (albeit giving rise to the island phase) with a higher T_{peak} and a slower heating and cooling rate, as illustrated with the result for $\tau = 2 \times 10^6$ steps and $T_{\text{peak}} = 1.18$. Note, however, that the mixed horizontal/vertical lamella morphology like the one shown in Figure 13a would likely be the most thermodynamically stable phase at T_0 given that it has the lowest potential energy (as shown in Figure 13b) compared to the other morphologies.

CONCLUSIONS AND OUTLOOK

Motivated by recent findings from an experimental laser annealing study,¹⁹ our simulation work investigated the dBCP thin film morphology under different heating cycles and substrate conditions using a simple coarse-grained model.²⁰ In particular, we explored the lamellar phase behavior with respect to changes in the peak temperature and heating/ cooling ramp period. Our simulation results capture a similar trend for the order—disorder transition as in experiments, where faster heating/cooling rates are associated with higher disordering temperatures for the vertical lamella phase formed on neutral substrates.

Simulations with a selective substrate revealed the formation of a long-lived metastable phase having horizontal but incomplete layers that give rise to a rough surface topography. This island phase forms after relatively long heating/cooling ramp cycles (independent of the initial structural order and block-substrate selectivity) and is hard to eliminate by reheating once formed, but its degree of roughness is tunable by the features of the annealing cycle.

For bulk and thin-layer lamellar systems, a general trend observed is that the lamella thickness decreases (and the chain surface density hence decreases) with temperature, which can result in the formation of new (potentially incomplete) lamella layers. This domain-thinning phenomenon can be seen as a stage preceding the domain disintegration and mixing that occurs above the order—disorder temperature for all systems. In a thin-film favoring horizontal lamella where additional surface layers formed during heating, the subsequent cooling increases the block segregation strength, which thermodynamically promotes the consolidation of layers but kinetically favors the trapping of some of the outer layers in partially filled states.

A hybrid phase having both vertical and horizontal lamellar layers formed for thicker systems containing 6000 chains on a selective substrate, upon a heating/cooling cycle. This phase manifested the different structural motifs favored by both the substrate and free surface simultaneously: the selective substrate induces a horizontal lamella for the bottom layers, while the neutral free surface favored a vertical lamella for the top layers. The system can also form a horizontal lamella phase or an island phase, the latter being favored by increasing the heating temperature and the heating/cooling ramp period. Overall, these results illustrate the tenet that the thin-film morphology can be controlled by both polymer-interface interactions and processing variables (film thickness and annealing cycle).

The simple coarse-grained model used in this work captures the generic behavior of lamella thin film under idealized laser annealing conditions. It would also be of interest to explore simulation models that would allow studying other thin film morphologies by employing asymmetric dBCP chains or triblock terpolymers. Also, a longer chain length model could be employed to study the effect of entanglements on the time scale of phase rearrangements, while polymer models with blocks having disparate glass transition temperatures would allow targeting thermal deformations to specific blocks only. The nanoscale roughness features of the island phase could be used to modulate the wettability of surfaces. More generally, it would be of interest to explore whether the ability to "write" with a laser "pen" nanoscale featured with different superficial shapes, depths, interfacial chemistries, and roughness on a dBCP film could be exploited to create surfaces with improved antifouling properties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.0c00423..

Results for bulk phase system, calibration of annealing cycle time scale, and additional results for thin layers with different conditions, given by Table S1 and Figures S1-S17 (PDF)

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Notes

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REFERENCES

(1) Bates, C. M.; Maher, M. J.; Janes, D. W.; Ellison, C. J.; Willson, C. G. Block copolymer lithography. *Macromolecules* **2014**, 47, 2–12.

(2) Hellwig, O.; Bosworth, J. K.; Dobisz, E.; Kercher, D.; Hauet, T.; Zeltzer, G.; Risner-Jamtgaard, J. D.; Yaney, D.; Ruiz, R. Bit patterned media based on block copolymer directed assembly with narrow magnetic switching field distribution. *Appl. Phys. Lett.* **2010**, *96*, 052511.

(3) Dorin, R. M.; Phillip, W. A.; Sai, H.; Werner, J.; Elimelech, M.; Wiesner, U. Designing block copolymer architectures for targeted membrane performance. *Polymer* **2014**, *55*, 347–353.

(4) Meier-Haack, J.; Taeger, A.; Vogel, C.; Schlenstedt, K.; Lenk, W.; Lehmann, D. Membranes from sulfonated block copolymers for use in fuel cells. *Sep. Purif. Technol.* **2005**, *41*, 207–220.

(5) Guo, X. D.; Tan, J. P.K.; Kim, S. H.; Zhang, L. J.; Zhang, Y.; Hedrick, J. L.; Yang, Y. Y.; Qian, Y. Computational studies on selfassembled paclitaxel structures: Templates for hierarchical block copolymer assemblies and sustained drug release. *Biomaterials* **2009**, 30, 6556–6563.

(6) Rastogi, A. K.; St. Pierre, L. E. Interfacial phenomena in macromolecular systems. *J. Colloid Interface Sci.* **1969**, *31*, 168–175. (7) Suh, H. S.; Kang, H.; Nealey, P. F.; Char, K. Thickness dependence of neutral parameter windows for perpendicularly oriented block copolymer thin films. *Macromolecules* **2010**, *43*, 4744–4751.

(8) Peters, R. D.; Yang, X. M.; Kim, T. K.; Nealey, P. F. Wetting behavior of block copolymers on self-assembled films of alkylchlorosiloxanes: Effect of grafting density. *Langmuir* **2000**, *16*, 9620–9626.

(9) Hu, H.; Gopinadhan, M.; Osuji, C. O. Directed self-assembly of block copolymers: a tutorial review of strategies for enabling nanotechnology with soft matter. *Soft Matter* **2014**, *10*, 3867.

(10) Maher, M. J.; Self, J. L.; Stasiak, P.; Blachut, G.; Ellison, C. J.; Matsen, M. W.; Bates, C. M.; Willson, C. G. Structure, Stability, and Reorganization of 0.5 L0Topography in Block Copolymer Thin Films. *ACS Nano* **2016**, *10*, 10152–10160.

(11) Fasolka, M. J.; Mayes, A. M. Block Copolymer Thin Films: Physics and Applications. *Annu. Rev. Mater. Res.* 2001, 31, 323-355.

(12) Smith, A. P.; Douglas, J. F.; Meredith, J. C.; Amis, E. J.; Karim, A. Combinatorial study of surface pattern formation in thin block copolymer films. *Phys. Rev. Lett.* **2001**, *87*, 4–7.

(13) Pickett, G. T.; Balazs, A. C. Equilibrium Orientation of Confined Diblock Copolymer Films. *Macromolecules* **1997**, *30*, 3097–3103.

(14) Heier, J.; Kramer, E. J.; Groenewold, J.; Fredrickson, G. H. Kinetics of individual block copolymer island formation and disappearance near an absorbing boundary. *Macromolecules* **2000**, 33, 6060–6067.

(15) Green, P. F.; Limary, R. Block copolymer thin films: pattern formation and phase behavior. *Adv. Colloid Interface Sci.* 2001, 94, 53–81.

(16) Zhang, X.; Berry, B. C.; Yager, K. G.; Kim, S.; Jones, R. L.; Satija, S.; Pickel, D. L.; Douglas, J. F.; Karim, A. Surface Morphology Diagram for Cylinder-Forming Block Copolymer Thin Films. *ACS Nano* **2008**, *2*, 2331–2341.

(17) Li, Y.; Kaito, A. Highly oriented structure formed in a lamellaforming diblock copolymer with high molar mass. *Eur. Polym. J.* **2006**, *42*, 1986–1993.

(18) Jacobs, A. G.; Jung, B.; Ober, C. K.; Thompson, M. O. Control of PS-b-PMMA directed self-assembly registration by laser induced millisecond thermal annealing. *Proc. SPIE* **2014**, *9049*, 90492B–90492B-7.

(19) Jacobs, A. G.; Liedel, C.; Peng, H.; Wang, L.; Smilgies, D.-M.; Ober, C. K.; Thompson, M. O. Kinetics of Block Copolymer Phase Segregation during Sub-millisecond Transient Thermal Annealing. *Macromolecules* **2016**, *49*, 6462–6470.

(20) Forrey, C.; Yager, K. G.; Broadaway, S. P. Molecular Dynamics Study of the Role of the Free Surface on Block Copolymer Thin Film Morphology and Alignment. *ACS Nano* **2011**, *5*, 2895–2907.

(21) Yager, K. G.; Forrey, C.; Singh, G.; Satija, S. K.; Page, K. A.; Patton, D. L.; Douglas, J. F.; Jones, R. L.; Karim, A. Thermally-induced transition of lamellae orientation in block-copolymer films on "neutral" nanoparticle-coated substrates. *Soft Matter* **2015**, *11*, 5154–5167.

(22) Grest, G. S.; Lacasse, M.; Kremer, K.; Gupta, A. M. Efficient continuum model for simulating polymer blends and copolymers. *J. Chem. Phys.* **1996**, *105*, 10583–10594.

(23) Weeks, J. D.; Chandler, D.; Andersen, H. C. Role of repulsive forces in determining the equilibrium structure of simple liquids. *J. Chem. Phys.* **1971**, *54*, 5237–5247.

(24) Plimpton, S.; Pollock, R.; Stevens, M. J. Particle Mesh Ewald and rRESPA for Parallel Molecular Dynamics Simulations. In Proceedings of the Eighth Siam Conference on Parallel Processing for Scientific Computing, Minneapolis, Minnesota, March 12–14, 1997; SIAM, 1997; pp 1–13.

(25) Humphrey, W.; Dalke, A.; Schulten, K. Visual molecular dynamics. J. Mol. Graphics 1996, 14, 33–38.

(26) John, B. S.; Juhlin, C.; Escobedo, F. A. Phase behavior of colloidal hard perfect tetragonal parallelepipeds. *J. Chem. Phys.* 2008, 128, 044909.

(27) Zheng, Z.; Liu, H.; Shen, J.; Liu, J.; Wu, Y.; Zhang, L. Tailoring the Static and Dynamic Mechanical Properties of Tri-Block Copolymers through Molecular Dynamics Simulation. *Polymers* **2016**, *8*, 335.

(28) Zhang, K. On the Concept of Static Structure Factor. *arXiv* preprint **2016**, arXiv:1606.03610.

(29) Zhang, J.; Posselt, D.; Smilgies, D. M.; Perlich, J.; Kyriakos, K.; Jaksch, S.; Papadakis, C. M. Lamellar diblock copolymer thin films during solvent vapor annealing studied by gisaxs: Different behavior of parallel and perpendicular lamellae. *Macromolecules* **2014**, *47*, 5711–5718.

(30) Croll, A. B.; Matsen, M. W.; Shi, A. C.; Dalnoki-Veress, K. Kinetics of layer hopping in a diblock copolymer lamellar phase. *Eur. Phys. J. E: Soft Matter Biol. Phys.* **2008**, *27*, 407–411.

(31) Majewski, P. W.; Yager, K. G. Millisecond Ordering of Block Copolymer Films via Photothermal Gradients. *ACS Nano* **2015**, *9*, 3896–3906.

(32) Yamamoto, T.; Kubo, T.; Sukegawa, T.; Takii, E.; Shimamune, Y.; Tamura, N.; Sakoda, T.; Nakamura, M.; Ohta, H.; Miyashita, T.; Kurata, H.; Satoh, S.; Kase, M.; Sugii, T. Junction Profile Engineering with a Novel Multiple Laser Spike Annealing Scheme for 45-nm Node High Performance and Low Leakage CMOS Technology. *IEEE International Electron Devices Meeting* **2007**, 143–146.

(33) Singer, J. P.; Lin, P.-T.; Kooi, S. E.; Kimerling, L. C.; Michel, J.; Thomas, E. L. Direct-Write Thermocapillary Dewetting of Polymer Thin Films by a Laser-Induced Thermal Gradient. *Adv. Mater.* **2013**, *25*, 6100–6105.

(34) Fung, S.; Huang, H.; Cheng, S.; Cheng, K.; Wang, S.; Wang, Y.; Yao, Y. Y.; Chu, C.-M.; Yang, S. J.; Liang, W. J.; Leung, Y. K.; Wu, C. C.; Lin, C. Y.; Chang, S. J.; Wu, S.-Y.; Nieh, C. F.; Chen, C. C.; Lee, T. L.; Jin, Y.; Sun, Y. C.; 65nm CMOS high speed, general purpose and low power transistor technology for high volume foundry application. In *Digest of Technical Papers. 2004 Symposium on VLSI Technology*, Honolulu, Hawaii, June 15–17, 2004; IEEE, 2004; pp 92–93.

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