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Thickness-Dependence of Block Copolymer Coarsening Kinetics

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Abstract

Despite active research, many fundamental aspects of block copolymer ordering remain unresolved. We studied the thickness-dependence of block copolymer grain coarsening kinetics, and find that thinner films order more rapidly than thicker films. Bilayer films, or monolayers with partial layers of islands, order more slowly than monolayers because of the greater amount of material that must rearrange in a coordinate fashion. Sub-monolayer films order much more rapidly than monolayers, exhibiting considerably smaller activation energies, as well as larger exponents for the time-growth power-law. Using molecular dynamics simulations, we directly study the motion of defects in these film regimes. We attribute the enhanced grain growth in sub-monolayers to the film boundaries, where defects can be spontaneously eliminated. The boundaries thus act as efficient sinks for morphological defects, pointing towards methods for engineering rapid ordering of self-assembling thin films. [In memory of Dr. Christopher Forrey (1972–2016).]

Introduction

Block copolymers (BCPs) are attractive materials for nanoscale patterning applications, owing to their spontaneous formation of well-defined nanostructures of tunable sizes (10–100 nm) over macroscopic areas.^{1, 2} The complexity of self-assembled morphologies has been increased using a variety of directing methods^{3–5} or iterative assembly.^{6–9} A host of exciting applications for these self-assembled phases have been demonstrated or proposed,^{10–12} including as patterning materials for microelectronics^{13–16} and data storage.¹⁷ In such demanding applications of self-assembly, the timescale for ordering and elimination of pattern defects is a critical factor.¹⁸ For instance, block copolymer thin films (especially large molecular weight materials) may require hours or days of thermal annealing to yield patterns with large grains and low defect densities. The slow grain coarsening kinetics in BCP thin films has inspired sustained efforts to understand and accelerate the pattern formation process. Ordering kinetics can be enhanced using solvent annealing,^{19–22}

microwave annealing,²³⁻²⁵ zone annealing,²⁶⁻²⁸ or shearing.²⁹⁻³² Yet many fundamental questions about domain ordering remain unanswered.

In this work, we measure and understand the role of block copolymer film thickness in grain coarsening kinetics, focusing on the thickness range between zero and two layers of the repeating morphology. BCP thin films exhibit commensurability effects between the film thickness and the repeat spacing of the morphology in the film normal direction.^{33, 34} For a cylindrical-phase with a parallel orientation (*i.e.* long axis lying in the film plane), the tendency to form uniform layers of hexagonally-registered cylinders will be satisfied only if the film thickness equals an integer number of cylinder row spacings.³⁵ Films cast at intermediate thicknesses will relieve frustration by partitioning the surface into regions of the two nearest integer thicknesses; so-called ‘islands’ and ‘holes’ (Figure 1). Although the effect of commensurability on BCP film structure is well-established, its influence on ordering kinetics is relatively unexplored. In BCP thin films, grain coarsening is dominated by the diffusion and annihilation of morphological defects.³⁶⁻³⁸ Naively, islands could be viewed as a form of confinement, pinning polymer material, limiting defect mobilities, and therefore inhibiting kinetics. On the contrary, we find that sub-monolayer films (*i.e.* islands forming an incomplete layer) order significantly faster than complete, uniform monolayers. Using molecular dynamics (MD) simulations, we identify island boundaries as locations where defects can be spontaneously eliminated without an annihilation partner. In this way, film boundaries act as sinks for high-energy morphological configurations. This points towards novel means of engineering self-assembly kinetics: by providing systems with intentional film discontinuities to act as outlets for disorder.

Results and Discussion

Figure 1: Schematic ordering of a cylindrical block copolymer striped pattern. A thin film of cylinder-forming BCP cast onto a flat substrate with preferential wetting leads to parallel cylinder orientations. Because of the commensurability criterion for cylinder layering, sub-monolayer thicknesses yield discrete patches of BCP material of controlled thickness. Conversely, films somewhat thicker than a monolayer will form ‘islands’ to accommodate the additional material. These different thickness regimes exhibit different ordering kinetics.

We first present results for the self-assembly of 65 kg/mol cylinder-forming polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) block copolymer (BCP) thin films, with the PMMA cylinders oriented surface-parallel. Films were prepared via spin-coating (from 1% wt. toluene), with spin speed used to control film thickness. Nominal film thicknesses in the range of ~10 nm to 63 nm were prepared, corresponding to ~0.3 to 2.0 times the spacing between cylinder rows of

$L_0 = \sqrt{3}d / 2 = 31$ nm, where $d = 36$ nm is the inter-cylinder distance. Annealing the films (210 °C in vacuum) induced microphase-separation, appearance of parallel cylinder morphology, and (for incommensurate film thicknesses) the formation of islands and/or holes. Since the nominal/average film thickness can be misleading for BCP films with surface terracing, throughout this paper we emphasize the ‘reduced’ film thickness (h) where the average thickness is divided by the cylinder row spacing. We emphasize that for BCP cylinder phases, the row spacing (L_0) and not the cylinder-cylinder distance (d) determines the layering distance; it is for this reason that we define a reduced thickness relative to L_0 . Thus, the self-assembly process results in: a sub-monolayer covering a fraction ($h < 1$) of the surface, a uniform monolayer film ($h = 1$), a monolayer film with some bilayer islands ($1 < h < 2$), or a uniform bilayer ($h = 2$).

We measured the self-assembled stripe patterns using scanning electron microscopy (SEM), and used image analysis to compute the in-plane orientational correlation length of the striped patterns (ξ), which we use as a measure of the average grain-size.^{18, 39} For all h studied, grain sizes were observed to grow as a function of time (t) following a power-law (Figure 2a), consistent with previous studies of BCP thin films:⁴⁰⁻⁴⁴

$$\xi = kt^m \quad (1)$$

where the prefactor k contains the temperature-dependence of the coarsening, and the growth exponent m depends on grain-growth mechanism. The growth rate ($d\xi/dt$) decreases over time as defects annihilate and their density decreases. It is usually found that m is of order 0.2–0.5 in thin films,⁴⁰⁻⁴³ but may be larger for bulk materials.^{45, 46} Thermal gradients can increase this exponent, enhancing ordering kinetic by changing the ordering mechanism.^{26, 28}

We observe a systematic influence of the BCP areal coverage (h) on the coarsening rate, with films having smaller h developing larger grains for a given annealing temperature and time (Figure 2a). For example, a sub-monolayer film ($h = 0.35$) coarsens to $\xi = 661$ nm after 72 hours (at 210 °C), compared to a monolayer film ($h = 1$) which reaches only $\xi = 375$ nm (Figure 2b). Bilayer films (two layers of cylinders) appear to order even more slowly than monolayers. (These results were confirmed using a batch of similar molecular weight PS-*b*-PMMA, obtained in an independent synthesis; refer to Supplementary Figure S1.)

Figure 2: Grain coarsening for PS-*b*-PMMA (65 kg/mol) at 210 °C. (a) The orientational correlation length, ζ , was measured from SEM imagery, and is used as a measure of grain-size. Grain coarsening for a variety of film thicknesses are shown. (b) Plotting the grain-sizes as a function of film thickness highlights that the thinner films yield larger ordered domains, at a given annealing time and temperature. (c) SEM images of individual films (thicknesses noted) show how sub-monolayer films have larger grains than monolayer films. (The 500 nm scale bar applies to all images.)

SEM inherently measures the structure of the film top-surface. For monolayer and sub-monolayer films ($h < 1$), this meaningfully probes the morphology and grain coarsening through the entire film thickness. However, for films with multiple cylinder layers ($h > 1$), SEM imaging alone can be ambiguous. In particular, one cannot ascertain whether the thickness-dependent ordering arises from surface behavior, or through-film behavior. Grazing-incidence small-angle x-ray scattering is able to resolve the structure through the depth of a thin film.⁴⁷ We performed both SEM and synchrotron GISAXS measurements on a series of 44 kg/mol polystyrene-*block*-poly(2-vinyl pyridine) (PS-*b*-P2VP) thin films with h varying between 1.0 and 1.5, in order to understand the ordering in this multi-layer thickness regime (Figure 3). Similar to that observed for PS-*b*-PMMA films, PS-*b*-P2VP bilayers coarsen more slowly than monolayers. The qualitatively similar ordering behavior seen in these two different BCP materials suggests that the kinetic trend is an intrinsic aspect of self-assembly, rather than a material-specific peculiarity. This coarsening trend is observed by both SEM (Figure 3a) and GISAXS (Figure 3b), and the grain-sizes measured by GISAXS are identical whether the grazing-incidence angle is above the film critical angle (*i.e.* probing all the layers in the film), or below the critical angle (*i.e.* probing only the top surface). Taken together, these results confirm the expectation that the top-layer cylinders (in the second-layer islands) are hexagonally registered with the bottom-layer cylinders; *i.e.* bilayer films order in a concerted fashion. We note that although SEM and

GISAXS results agree qualitatively, they do not yield identical measures of grain-size, because the two methods probe different aspects of long-range ordering.¹⁸ While our SEM image analysis probes the decay of orientational order, GISAXS probes the length scale over which the morphological repeat-spacing is spatially registered and coherent. For instance, a uniaxially-aligned material would have $\xi \sim \infty$ from an orientation point-of-view, but the presence of disorder, such as point defects or undulations of the morphology, would cause decorrelation and a finite ξ probed by scattering. The GISAXS provides an advantage in that it can detect extremely weak levels of order. As-cast films are highly disordered and cannot typically be measured by SEM, since the material is quenched into an incompletely phase-separated state. However, GISAXS can measure the short-range correlation even in poorly-developed morphologies.⁴⁸ Because GISAXS suggests that the as-cast ordering length scale is independent of thickness (Figure 3b), we conclude that the observed variation in grain-sizes during annealing is due to a modification in the coarsening process, and not due to an intrinsically different starting configuration for films of differing thickness.

Figure 3: Ordering for PS-*b*-P2VP (44 kg/mol) at 170 °C. (a) Grain-size estimated from SEM demonstrates that thinner films order more rapidly for this BCP material. (b) Corresponding grain-size estimates from GISAXS confirm the trend. (c) Individual GISAXS images for two representative films (after 24 hr annealing) show a narrowing of the peak arising from the BCP morphology, indicating a larger correlation length in thinner films.

To probe the mechanism of ordering, we measured grain-sizes in PS-*b*-PMMA (67 kg/mol) thin films as a function of film coverage, annealing time and temperature (Supplementary Figures S1–S3). Fitting the grain growth as a function of time allows extraction of the mechanistic exponent m (c.f. Eq. 1); Figure 4a shows the scaling of m for grain coarsening at 232 °C in oven annealing. There is evidence for an increase in m for sub-monolayer films, suggesting that a new ordering mechanism is available in this regime. The influence of temperature (T) is embedded in the prefactor k . It is often assumed that BCP grain coarsening is Arrhenius:^{27, 37, 44, 49-51}

$$k = Ae^{-E_a/k_B T} \quad (2)$$

where k_B is the Boltzmann constant, E_a is the activation energy for defect annihilation, and A is a prefactor that accounts for other aspects of ordering, such as defect mobility. By measuring the temperature-dependence of k , we extract estimates for E_a (Figure 4b), while noting that the grain

coarsening is likely not strictly Arrhenius, as it involves multiple energy barriers^{52, 53} and temperature-dependent material properties.^{49, 54, 55} The activation energy decreases markedly in sub-monolayer films, dropping to zero (within the experimental uncertainty) for $h < 0.6$. This implies that sub-monolayer films have access to a defect-removal mechanism with a very small activation energy; this mechanism would naturally dominate the coarsening, compared to the conventional grain-annihilation mechanism, which involves a substantial energy barrier.^{52, 53} In sub-monolayer films, grain coarsening would thus be relatively insensitive to temperature, which is indeed what we observe experimentally.

Figure 4: Mechanism of BCP thin film ordering. (a) The exponent of grain coarsening ($\zeta = kt^m$) is larger in sub-monolayer films, implying a different grain annihilation mechanism is available in this regime (data for cylinder-forming PS-*b*-PMMA, 67 kg/mol, at 232 °C). (b) The Arrhenius-like activation energy (E_a) was computed from the temperature-dependence of the coarsening kinetic prefactor (k). This analysis suggests that the barrier for defect annihilation drops substantially for sub-monolayer films.

Molecular dynamics (MD) simulations provide significant insight into the mechanism underlying the observed coarsening behavior. In the simulations, block copolymer chains are simulated as freely-jointed linear chains of beads, with chemical incompatibility between blocks enforced by adjusting the relative interaction potentials between beads.^{56, 57} The number ratio between the distinct bead types is selected so that the system spontaneously forms a cylinder phase. An in-plane BCP orientation is similarly enforced using the substrate-interaction parameters, reproducing the experimentally-observed substrate wetting behavior. We simulate and compare

the time evolution of striped patterns formed by a monolayer film ($h = 1$), as well as a film slightly thinner ($h < 1$), and slightly thicker than this ($h > 1$). The thicker film spontaneously generates islands on the film as the MD simulation proceeds, while the sub-monolayer simulation has, by construction, a distinct in-plane boundary, leaving regions where the substrate is exposed. Snapshots as a function of simulation time (Figure 5a) show robust coarsening of the stripe pattern grains in all cases. We visualize only the minority component (in black), making the morphology clearly evident. We analyze the images using the exact same orientational analysis to determine the correlation length (ξ), as done previously for the SEM data. Simulations of thicker films (more material than required to form a monolayer) show an initial single-layer morphology, with the eventual formation of islands (after an incubation time^{58, 59}), which coalesce and grow as observed experimentally.^{60, 61} For these bilayer films, the offset between the first and second layer of cylinders makes these regions look black in the visualization. Consistent with our experiments, the quantitative grain-size depends on film coverage (Figure 5b). Sub-monolayer films exhibits remarkably faster grain-growth compared to monolayers. Films with surface islands are somewhat slower in ordering than monolayers.

Figure 5: Molecular dynamics study of cylinder-forming BCP thin films. (a) Snapshots of the MD simulation for three different film thicknesses (time runs along horizontal). (b) The grain-size measured from the simulated morphologies (each curve is the average of 4 independent MD runs). Consistent with experiment, the sub-monolayer films coarsen more rapidly. (c) Snapshots of ordering for a sub-monolayer film (time runs along horizontal). A defect near the film boundary is highlighted (orange). Over time, this defect can diffuse into the boundary, and vanish. By comparison, a defect deep within the film interior (purple) does not disappear over the same simulation timescale. (d) Snapshots of ordering for a monolayer film. Two nearby defects are highlighted (purple circles). In bulk films, defects can only disappear by finding a partner and annihilating. This process involves a considerable energy-barrier to the distorted intermediate states, and is thus quite slow.

The MD simulations allow us to directly investigate the origin of the enhanced kinetics in sub-monolayer films. The ordering in monolayer stripe patterns is limited by topological defects, which are quasi-particles that can diffuse through the film through collective rearrangements of polymer chains. Eliminating defects in these films is only possible through pair-wise defect annihilation (Figure 5d), a process involved several high-energy intermediate states. Fredrickson *et al.* quantified the thermodynamic and kinetic aspects of defects using simulation methods,^{52, 53}

finding that each defect incurs an energy penalty of order $10\text{--}150\ k_B T$, and elimination of a single defect pair involves a pathway with 1–4 energy barriers, of height $\sim 1\text{--}20\ k_B T$, giving rise to the observed activation energy (E_a). Increasing temperature increases the diffusion velocity of defects, and also provides the necessary energy to overcome the barrier to annihilation. Our MD simulations demonstrate an additional pathway for healing defects in sub-monolayer films. In addition to pair-wise defect annihilation within the film interior, it is also possible for defects to migrate to the film boundary and essentially vanish without finding a topological partner (Figure 5c, orange highlight). Thus, the perimeters of islands act as sinks for defects, where the morphology can rearrange into a defect-free configuration without any energy barrier ($E_a \sim 0$), consistent with the experimental behavior of sub-monolayer films (Figure 4b). Coarsening in sub-monolayer films is evidently dominated by the migration of defects to the island boundaries. This accelerates the grain coarsening, while making the process less temperature-sensitive. Overall, this represents a different coarsening mechanism, consistent with the change in m in thinner films (Figure 4a).

Combined, our experimental and simulation results suggest that the thickness-dependence of striped pattern coarsening kinetics arises from different regimes with correspondingly different mechanisms. Monolayer films coarsen through random diffusion of topological defects, which can annihilate with one another to improve overall order. Thicker films inherently order more slowly, because the morphology in surface islands is registered with the underlying monolayer. The two must order in concert, which introduces a larger energy-barrier for the requisite rearrangements to annihilate defects. Thus, we would expect thicker films to order progressively more slowly. At a sufficient thickness, interface-induced preferential orientation no longer dominates, and the material becomes a three-dimensional isotropic powder, instead of a constrained two-dimensional system. At this point, different ordering kinetics would dominate.

Sub-monolayer films exhibit enhanced ordering, relative to monolayers, because they have access to an extremely efficient defect-removal pathway. At the boundary of the film, the morphology is unconstrained, with an associated freedom to rearrange. In particular, topological defects can spontaneously vanish at this interface, even without finding a partner for annihilation. One can also imagine the symmetry-breaking interfaces as ‘infinitely defective’ boundaries, which can thus easily annihilate any incident defects. Importantly, defect-removal at boundaries apparently involves no energy barrier, making this a highly favorable pathway. Overall, films with discontinuities thus order more rapidly, because the boundary is an efficient sink for defects. This mechanistic understanding explains the experimentally-observed trends in m and E_a , and moreover suggests that these trends should be universal across different BCP materials. That is, while different systems will exhibit different quantitative values of E_a , we predict that the decrease of E_a towards zero for sub-monolayer films should be a universal property of BCP grain coarsening.

We note that during grain coarsening, there is likely to be a simultaneous growth of the average island size, as islands merge to minimize their perimeters.⁶² This decrease in perimeter-to-area ratio will correspondingly decrease the enhancement afforded by the film boundary. Thus, we expect the enhanced grain coarsening to exhibit progressive depression as ordering proceeds.

The long-time kinetic behavior of films should converge for all film thicknesses, though the quantitative grain sizes will differ substantially owing to differences in early-stage kinetics. The influence of surface restructuring implies that the grain kinetics reported herein—and reported more generally in the literature—are in fact a convolution of the intrinsic grain coarsening, and the kinetics of island/hole coalescence. In our molecular dynamics simulation of the sub-monolayer regime, we were careful to construct a system with an initial film edge; this edge was then conserved over the course of the experiment. By maintaining the perimeter-to-area ratio in this simulation, we confirm that the enhanced kinetics arise specifically from this film edge, and not from the confounding influence of island/hole growth kinetics. Experimentally, measured coarsening kinetics could be separated into the convolved contributions from intrinsic coarsening and island/hole growth, since the kinetics of the latter have been studied in detail. The formation of islands/holes is preceded by a short incubation phase where the film is nominally flat.^{58, 59} Once these surface features form, they grow through coalescence following a power-law,⁶¹ with growth occurring on a timescale of hours.^{63, 64} Interestingly, these kinetics are also dependent on film thickness, though in this case this is directly related to BCP commensurability. Near-commensurate film thicknesses exhibit long (>10 h) incubation times, while highly incommensurate thicknesses (midway between two commensurate conditions) rapidly nucleate surface features (tens of minutes). An avenue for future investigation is to quantitatively separate the kinetic contributions from these two sources.

Finally, we note that the reported kinetic trends are no doubt convolved with other aspects of BCP ordering that influence kinetics. Block copolymer ordering is known to depend strongly on interfacial interactions, both with respect to the substrate and the free surface. Interfacial interactions can give rise to altered morphology⁶⁵ or morphological alignment.^{56, 66} The strength of interfacial interactions can also influence ordering kinetics. Strong substrate interactions will pin material at interfaces and slow kinetics,⁶⁷ while neutralized⁶⁸ or even antagonistic⁶⁹ interactions will ‘lubricate’ the BCP-substrate interface, and increase ordering rates. Undoubtedly, substrate interactions are playing a role in setting the overall scale of kinetics measured in our experiments. Moreover, the measured kinetics must be a convolution of the kinetics arising from multiple sources, including interfacial interactions, island/hole growth, and the ‘film edge’ effects we identify here. An interesting possibility for future studies is to exploit these phenomena to engineer ordering. For instance, one can purposefully pattern films to exhibit numerous discontinuities—enforced using preferential substrate interactions—and thereby engineer fast assembly kinetics.

Conclusions

We experimentally probed the thickness-dependence of grain-size growth rates in block copolymer thin films. We find that bilayer films order more slowly than monolayers, due to the greater amount of material which must rearrange in a coordinated manner. Conversely, sub-monolayer films order at greatly enhanced rates, because the film edge acts as an efficient sink for topological defects, which can migrate to these boundaries and be spontaneously eliminated with a small energy barrier. We confirmed this mechanistic explanation using molecular

dynamics simulations, which show that defects can disappear at interfaces, and do so far faster than the annihilation of defect-pairs in the bulk of a film. We confirmed these results in independent material batches, and observe qualitatively similar behavior for different BCP materials, which—combined with the molecular dynamics results—confirms that the kinetic enhancement is generic to block copolymer self-assembly and not material-specific. Overall, these results point towards new methods for engineering rapid assembly of polymer morphologies: purposefully inserting film discontinuities should maximize coarsening rates.

Methods

Polymer films. Substrates were 500 μm thick, boron-doped $\langle 100 \rangle$ oriented silicon wafers. Substrates were plasma-cleaned for 5 minutes (March CS-1701, 100 mT of oxygen, 20 W RF power). In order to confirm that the observed behaviors were not generic and not system-specific, we studied a variety of cylinder-forming (composition majority:minority $\approx 7:3$) block copolymer materials (with polystyrene as majority component). The inter-cylinder spacing (d) was measured using a Fourier transform of SEM imagery (and checked for consistency with GISAXS peak position), from which we compute the layering distance between cylinder rows using $L_0 = \sqrt{3}d/2$. We present results for PS-*b*-PMMA (provided by C. Hawker), of molecular weight $M_w = 65$ kg/mol (44 kg/mol PS, 21 kg/mol PMMA), polydispersity PDI = 1.15, inter-cylinder spacing of $d = 36$ nm ($L_0 = 31$ nm); these were confirmed using an independent batch of similar PS-*b*-PMMA (obtained from Polymer Source, Inc.), $M_w = 67.1$ kg/mol (46.1 kg/mol PS, 21.0 kg/mol PMMA), PDI = 1.09, $d = 37$ nm ($L_0 = 32$ nm); we also show results for PS-*b*-P2VP $M_w = 44.0$ kg/mol (23.6 kg/mol PS, 10.4 kg/mol PMMA), PDFI = 1.04, $d = 29$ nm ($L_0 = 22$ nm). Films were spin-cast from toluene solutions ($\sim 1\%$ by weight), at speeds ranging from 2000–6000 RPM, to achieve different film thicknesses. Samples were annealed in a vacuum oven (<1 Torr) at temperatures ranging from 180°C to 230 °C, and times ranging from 2 h to 72 h.

SEM. Scanning Electron Microscopy images were acquired on a Hitachi S-4800. To improve SEM imaging, the PS phase was crosslinked by UV irradiation, and the PMMA block partially etched by exposure to acetic acid, followed by rinsing with deionized water.

Image analysis. We compute the in-plane orientational correlation length (ξ), and use this as an estimate of the grain-size, by analyzing the SEM images.^{18, 39} This was performed using custom-written Python code, which exploits libraries for image manipulation (Python Image Library), numerical computations (numpy⁷⁰), and plotting (matplotlib⁷¹). The procedure has been described previously in the literature;^{26-28, 42, 72} briefly, image gradients are used to determine the local orientation vector of the morphology. The correlation length is computed by fitting the decay of the orientational correlation function to an exponential. For images with incomplete coverage of the BCP morphology, the image was first segmented into regions with morphology and without (by using the local mean absolute image gradient to differentiate regions). The

correlation length was computed only using pixels within the morphology regions (high local gradient).

Mechanistic analysis. The grain coarsening exponent was obtained by fitting $\log(\zeta)$ vs. $\log(t)$ to a linear function, and equating the slope to m and the exponential of the intercept to the kinetic prefactor (k). The Arrhenius-like activation energy (E_a) was estimated by measuring k for a variety of films at different thicknesses and different temperatures (182 °C, 205 °C, 232 °C). A plot of $\log(k)$ vs. $1/T$ was used to extract E_a from the slope.

GISAXS. Synchrotron Grazing-Incidence Small-Angle X-ray Scattering (GISAXS) experiments were performed at the X9 undulator beamline of the National Synchrotron Light Source at Brookhaven National Laboratory. Two-dimensional scattering images were collected using a fiber-taper charge-coupled device (MarCCD). Samples were measured under vacuum using an x-ray beam of 13.5 keV ($\lambda = 0.0918$ nm). GISAXS data were collected across a range of incidence angles (0.07° to 0.20°). The data presented in the manuscript are for 0.20°. The scattering patterns had the same features above and below the critical angle, implying that order at the surface and below the surface (*e.g.* for bilayer films) were similar. Silver behenate powder was used as a standard for data conversion to q -space. In-plane correlation length was computed using the peak width, after accounting for grazing-incidence geometry and instrumental resolution.⁷³

Molecular Dynamics. We simulated the behavior of block copolymer thin films using our previously-described molecular dynamics (MD) methods and parameters.^{56, 57} Briefly, polymers chains are coarse-grained as linear chains of beads of two distinct types, segregated lengthwise along the chain into two blocks (using a 3:7 ratio to give rise to a cylinder morphology). The two bead types have distinct self-cohesive interaction strengths, such as the two phases spontaneously phase-separate as the molecular dynamics simulation proceeds. The majority bead type exhibits preferential substrate-interactions, leading to an overall parallel orientation for the cylinder domains. Due to overall cohesive interactions between all beads, and the underfilling of the simulation box, the chains spontaneously organize into a thin film wetting the substrate interface, with a free film-vacuum interface. Simulations were performed using the LAMMPS package⁷⁴ made available by Sandia National Laboratories using the canonical (NVT) ensemble, and periodic boundary conditions in both in-plane directions. Care was taken to ensure that the inplane box dimensions were sufficiently large to avoid any commensurability effects. Molecular dynamics simulations were run for at least 300 000 000 MD steps. System configuration was saved every 500 000 MD steps; each snapshot was evaluated by outputting a projection of the simulation volume (viewed along the film normal direction), where the minority beads are black and the majority beads are invisible. This has the result of generating visible stripe patterns of the morphology. These images were subjected to image analysis in a fashion identical to the experimental SEM data. Three different film thickness regimes were simulated. Each regime was replicated four times (with different random seeds for the chain starting configurations); the presented kinetic results are the average of the independent simulation runs. In the case a sub-monolayer film, the simulated chains forms an ‘island’ connected across one of the in-plane periodic dimensions, but exposing two film boundaries in the orthogonal in-plane direction. Owing to the periodic boundary conditions of the simulation box in this direction also, the box

size and chain filling was regulated so that these two boundaries were far apart (and thus non-interacting).

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