Controlled spacing between nano-patterned regions in block copolymer films obtained by utilizing substrate topography for local film thickness differentiation

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Figure S1. SEM images of PS-*b*-PMMA films assembled on topographically modified substrates showing dot-patterned regions separated arbitrarily by patternless domains of arbitrary width (a-c) and over large areas (d). (a,b) 23 nm-thick film assembled on substrates featuring 20 nm-deep trenches, (c) 23 nm-thick film with 13 nm-deep trenches, and (d) 25 nm-thick film with 38 nm-deep trenches. Trench/plateau lateral widths: (a) 2,000/160 nm; (b) 2,000/640 nm; (c) 640/320 nm; (d) 1,500/160 nm.



Figure S2. SFM images of thin PS-*b*-PMMA films cast at different thicknesses (top right corner) on flat SiOx substrates.



Figure S3. Illustration of the simulation cell: (a) The volume filled by the copolymer film; (b) location where the surface field acts (blue and white grid points denote $\Lambda N=11$ and $\Lambda N=20$ for the bottom and sidewalls of the trench, respectively). Lengths are measured in units of R_e . The grid, shown in this figure, is coarser than the grid used to evaluate the non-bonded interactions by a factor of 2.



Figure S4. Simulation results showing the dual morphology on substrates that consist of adjacent plateau and trench with the same parameters used in Figure 4a,b after extended run ($T=3.1\times10^7$ Monte-Carlo steps).

The disjoining pressure and the shape of the free surface

The simulation model cannot describe the free surface in contact with the vapor phase; therefore, we extracted the geometry from the experimental measurements. In the experiment the free surface of the film is not flat but the shape is dictated by a balance of capillary forces: the Laplace pressure tends to even out the curvature of the film surface, whereas the disjoining pressure, $\Pi(h)$, which quantifies the forces of interaction between the free polymer-vapor surface and the substrate, tends to maintain preferred film thicknesses over different parts of the substrate (i.e., plateaus and trenches). The disjoining pressure is comprised of a negligible, short-range contribution that decays exponentially with the film thickness *h*, and two long-range contributions, $\Pi_{it}(h)$:

$$\Pi_{\rm lr}(h) = \frac{\sqrt{N}k_B T}{R_{\rm e}^3} \widetilde{\Pi}\left(\frac{h}{R_{\rm e}}\right) - \frac{A_{\rm H}}{6\pi h^3} \tag{S1}$$

where $\tilde{\Pi}(h/R_e)$ is a scaling function and $A_{\rm H}$ is the Hamaker constant. The first term – the morphological contribution – stems from the preference of the copolymer morphology for a particular film thickness if it exhibits a nontrivial structure perpendicular to the substrate (such as the neck-like shapes of the PMMA domains found in our study). For example, this morphological contribution gives rise to the formation of island-and-hole structures in thick lamellar films (as illustrated below). Its strength is set by the free-energy density of the film, and its spatial variation only depends on the dimensionless film height h/R_e . The second, long-range contribution – Hamaker contribution – arises from van-der-Waals interactions. The specific form of the equation above refers to a simple planar substrate. Generalizations to layered substrates¹⁻² or corners are available.³

To illustrate the morphological contribution, we consider the known behavior of block copolymer film coarsening that leads to island-and-hole structures. For a lying lamellar structure with p internal AB interfaces parallel to the substrate, the scaling function takes the form:⁴

$$\widetilde{\Pi}(x) = \frac{3\pi^2}{8p^2} x^2 - \frac{3}{4} \left(\frac{\pi^2}{3} \chi N\right)^{1/3}$$
(S2)

in the strong segregation limit. The first term arises from the thickness-dependent stretching of the chain conformations, whereas the second term arises from the chemical potential. There is no explicit contribution from the interfaces because the interface free energy is independent of the film thickness h at fixed p. This provides a simple analytic description of the morphology inside the trenches. Unfortunately, no such explicit form is available for the complex neck-like hexagonal morphology on the plateaus, but we expect that its magnitude is similar.

In the case of an island-hole morphology the film surface is locally planar. Thus the Laplace pressure vanishes and the force balance requires $\Pi(h)=0$. The relative strength of the morphological and Hamaker contributions to the long-range part of the disjoining pressure is dictated by the dimensionless quantity, $\sqrt{N}k_BT/A_H$. Neglecting the Hamaker contribution, the condition $\Pi(h^*/R_e) = 0$ identifies the well-known preferred film thickness, h^* , of the island-hole structures (with a non-preferential free film surface).

An order-of-magnitude estimate of the relative strength of the morphological and Hamaker contributions to the disjoining pressure can be obtained from the following consideration. Using $\sqrt{\overline{N}} = 128$ and $R_e \approx L_0/1.83 \approx 46$ nm, we obtain for the order of magnitude of the morphological contribution $\Pi_{\text{morph}} \approx 5 \times 10^3$ J/m. The Hamaker constant between an organic polymer and silicon oxide¹⁻² is on the order of $A_{\text{H}} \approx 2 \times 10^{-20}$ J and thus we obtain $\Pi_{\text{VdW}} \approx 10^2$ J/m³ for a film of h = 20nm. Thus, even for these ultrathin films, the morphological contribution dominates over the Hamaker contribution. Additionally, we note that the Laplace pressure is on the order $\Pi \approx 2.4 \times 10^3$ J/m³ (using $\gamma = 40$ mN/m as the surface tension of the polymer and 6×10^{-5} nm⁻¹ as the curvature of the films on top of the plateaus, which was estimated using SFM profiles). Hence, the Laplace pressure is chiefly compensated by the morphological contribution to the disjoining pressure.

In case of the plateau-trench structure the experiments demonstrate: (i) that the polymer film is continuous and (ii) that the free film surface is slightly corrugated. The first observation indicates that no pinned, three-phase contact line exists between the polymer, substrate and vapor at the borders of the plateaus. The latter observation suggests that there is a non-vanishing Laplace pressure that is balanced by disjoining pressure (cf. Equation (1) in the main text). Our rationale thus points towards a strategy for obtaining flat-top films by using a top-coat that does not dewet and has a higher interfacial tension with the polymer film than the surface tension of the polymer (i.e., $\gamma_{topcoat/BCP} > \gamma_{BCP/air}$).

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