Supporting Information


Rectangular Symmetry Morphologies in a Topographically Templated Block Copolymer

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Trends of changing morphology

Figure S1. SEMs that show how the spherical morphology appears from cylinders by increasing the post period from the left to right. White and light grey colors represent HSQ and ox-PDMS, respectively.

Figure S2. SEMs showing how the perforated lamellae appear from the superstructure morphology by increasing the period of the posts from left to right. White and light grey colors represent HSQ and ox-PDMS, respectively.

Analytical calculation of PDMS microdomain size

In this section, we show how the size of the PDMS microdomains in the templated BCP relates to that in the untemplated film. For the case of a film consisting of a single layer
of PDMS cylinders, the volume fraction (ratio of the volume of PDMS to the volume of the unit cell) is:

\[ V_{PDMS} = \frac{\pi R_0^2 L_0}{t} \]  

where \( R_0, L_0 \) and \( t \) represent the radius of the ox-PDMS cylinders, the cylinder period, and the thickness of the BCP film, respectively.

In a film templated by a rectangular array of posts to form spheres of PDMS, Figure S3 shows a schematic of a unit cell of the template. The volume of the unit cell occupied by the BCP (\( V_u \)) is:

\[ V_u = [P_x P_y - \pi (r + T)^2]t. \]

where \( r, T, P_x \) and \( P_y \) are the radius of the posts, the thickness of the PS brush, and dimensions of the unit cell in the \( x \) and \( y \) directions, respectively, assuming the posts are at least as tall as the film thickness. The volume of PDMS per unit cell is given by:

\[ V_{PDMS} = \frac{\pi R_0^2 [P_x P_y - \pi (r + T)^2]}{L_0}. \]

When \( P_x \) and \( P_y \) are equal the PDMS can form spheres which have radius \( R_s \):

\[ V_{PDMS} = \frac{4}{3} \pi R_s^3. \]

Eq. (3) and (4) give

\[ R_s = \left( \frac{3 R_0^2 [P_x P_y - \pi (r + T)^2]}{4 L_0} \right)^{\frac{1}{3}}. \]

For the case of a thicker BCP film that forms two layers of cylinders, the volume of PDMS is:

\[ V_{PDMS} = \frac{\pi (R_{01}^2 + R_{02}^2)}{L_0 t} \]

where \( R_{01} \) and \( R_{02} \) are the radii of the ox-PDMS cylinders in the two layers. The radius of the templated PDMS sphere (\( R_s \)) can be calculated as follows:
\[
R_s = \left(\frac{3(R_1^2 + R_2^2)}{4L_0} [P_x P_y - \pi (r + T)^2]\right)^{\frac{1}{3}}. \quad (7)
\]

In Fig. 5a,b,c, the measured periods are 38 nm, 17 nm, and 35 nm, respectively; the cylinder radii are 9 nm for Fig. 5a; 1.5 nm and 2.5 nm for the two layers of Fig. 5b; and 7.5 and 9 nm for Fig. 5c; the periods of the posts are 40 nm, 25 nm, and 40 nm and their radii are 10.5 nm, 6.5 nm, and 6.5 nm. The thickness of the PS brush was 3 nm for Fig. 5a,c and 1 nm for Fig. 5b. Eq. 5 and 7 give \( R_s = 24 \) nm, 11 nm and 31.5 nm for Figure 5a-c, similar to the experimental results (24 nm, 11 nm, and 32 nm).

**Figure S3.** A plan view schematic of a template unit cell.

**Figure S4.** Schematic of the field boundary conditions of a unit cell used in 3D SCFT simulations. The purple area is where the fields are constrained to prohibit the polymers from evolving in the simulation to model the posts and bottom substrate. The orange area is where the fields are constrained to be attractive to the majority block (PS) and repulsive to the minority block (PDMS) to model the PS brush layer used in the experiment. The light blue area is where the fields are constrained to be attractive to the minority block to model the air interface wetting behavior of the PDMS observed in the experiment. Boundary conditions are periodic in the \( x \)- and \( y \)-directions. \( P_x \) and \( P_y \) were varied from \( 0.7L_0 \) up to \( 2.0L_0 \) in the simulations and \( t \) was kept constant at a film thickness of \( 1.5L_0 \). The post diameter and height were set to \( 0.7L_0 \) and \( 1.0L_0 \) respectively to best model the physical posts.