Supporting Information for

Control of Self Assembly of Lithographically-Patternable Block Copolymer Films

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The GISAXS image shown in Figure 2b was taken slightly above the critical angle of the film at $\alpha_i = 0.125°$. The incident x-ray wavelength was set at 9.97 keV.

In other polymer systems, thin films with spherical morphology display a hexagonally close-packed (HCP) structure. An HCP sphere model is not an accurate model of this polymer thin film system. An HCP sphere system would yield a GISAXS map with a Bragg reflection at a nonzero wavevector stacked vertically above the one of the peaks on the yoneda band, not seen here.

A BCC lattice was then used to model the thin film since the (110) plane looks very similar to the HCP (001) plane. We defined the real space BCC lattice vectors as:

$$\vec{a}_1 = a\hat{x}$$
$$\vec{a}_2 = a\hat{y}$$
$$\vec{a}_3 = a\hat{z}$$

giving the following reciprocal lattice vectors:

$$\vec{b}_1 = \frac{2\pi}{a}\hat{x}$$
$$\vec{b}_2 = \frac{2\pi}{a}\hat{y} \, .$$
$$\vec{b}_3 = \frac{2\pi}{a}\hat{z}$$

We then rotated our coordinate system so that the (110) plane would be parallel to the substrate. Doing this yielded the following rotated reciprocal lattice vectors (assuming $a = 275$ Å^{-1}):

$$\vec{b}_1^{\,*} = -0.0158674\hat{y} + 0.0158674\hat{z}$$
$$\vec{b}_2^{\,*} = 0.0158674\hat{y} + 0.0158674\hat{z}$$
$$\vec{b}_3^{\,*} = -0.0224399\hat{x}$$

Using this model, we get scattering from particular planes at the following positions on the GISAXS image:

Scattering Planes	$q_{\parallel}$	q_z
(1 -1 0)	0.0323119	0.0220456502
(1 0 1)	0.0279829	0.0382015502
(1 -1 2)	0.0456959	0.0220456502

The q_z position of the scattering from the (1 0 1) planes is a bit low, after comparing with the experimental GISAXS map. This can be explained using the reasoning that in the swelled state, the polymer thin film morphology is BCC spheres. But after drying, the film shrinks in the z direction.

This changes the morphology from BCC to BCT spheres, or face centered orthorhombic. By introducing a convenient surface unit cell, we can model this shrinking in the z direction of the film while maintaining an orthogonal lattice:

$$\vec{a}_1 = \sqrt{2}a\hat{x}$$
$$\vec{a}_2 = a\hat{y}$$
$$\vec{a}_3 = 0.6a\hat{z}$$

giving the following reciprocal lattice vectors:

$$\vec{b}_1 = 0.0161559\hat{x}$$
$$\vec{b}_2 = 0.0228479\hat{y}$$
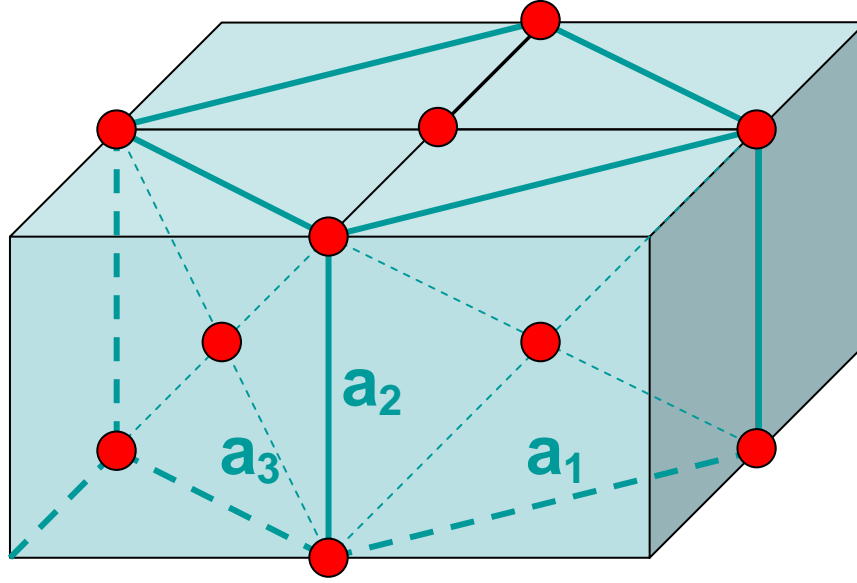$$\vec{b}_3 = 0.0326399\hat{z}$$

Figure SI-1: The FCO lattice derived from the original BCC lattice before shrinkage in the a_3 direction. Note that once the BCC lattice is rotated so the (110) plane is parallel to the surface, the (100) plane of the FCO lattice lies parallel to the surface.

Unlike before, it is not necessary that we rotate the coordinate system so that the (110) plane is parallel to the substrate surface. Using this lattice definition, the (100) plane of the FCO lattice should lie parallel to the surface as seen in Figure 2b.

Since we are using a face centered crystal structure, the allowed peaks should correspond to h,k,l being all even or all odd. With this model, we should get scattering from particular planes at the following positions on the GISAXS image:

Scattering Planes	$q_\parallel$	q_z
(2 0 0)	0.0323119	0.0220456502
(0 2 0)	0.0456959	0.0220456502
(1 1 1)	0.0279829	0.0601255502

The experimental peak positions, shown below, correspond well to the predicted values:

$q_\parallel$	q_z
0.032728	0.021705
0.045519	0.021705
0.027924	0.0594705

Thus, the theoretical model matches the observed GISAXS pattern.

References
1.   Stein, G.A.; Kramer, E. J.; Li, X.; Wang, J. Layering Transitions in Thin Films of Spherical-Domain Block Copolymers. *Macromolecules (Washington, DC, U. S.)* **2007**, *40*, 2453 -2460.