Supporting Information for the Effect of Film Thickness and Domain Spacing on Defect Densities in Directed Self-Assembly of Cylindrical Morphology Block Copolymers

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Effect of fluctuations

The absence of long range translational order in smectics arises from fluctuations in layer displacements which are logarithmically divergent in 3D.¹ If $u(\mathbf{r})$ is the layer displacement field at a position $\mathbf{r}$, then in the harmonic approximation, the mean-square value of fluctuations of wave vector $\mathbf{q}$ has been shown to be^{2,3}

$$\langle u^2(q) \rangle = \frac{k_B T}{Bq_z^2 + Kq_x^4} \quad (\text{S1})$$

where $u(\mathbf{q})$ is the Fourier transform of the layer displacement field $u(\mathbf{r})$, q_z and q_x are the wave vector components along and perpendicular to the layer normal, respectively. The sample size

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limits the wave displacement vectors to $2\pi/L < q_z < 2\pi/a$ and $2\pi/W < q_x < 2\pi/d$, where L and W are the sample size normal to the layers and in-plane, respectively, d is the lateral molecular spacing and a is the layer spacing. In the limit that $W \gg L$ and $a > d$ (which is realized in most experimental situations) the mean-squared layer displacement $\langle u^2(r) \rangle$ approximates to

$$\langle u^2(r) \rangle = \frac{k_B T}{8\pi\sqrt{KB}} \ln\left(\frac{L}{a}\right) \quad (\text{S2})$$

where K is the splay elastic constant and B is the compressional modulus normal to the layers. For infinitely large smectic systems, $\langle u^2(r) \rangle$ diverges implying that there is no long range translational order. This is known as the Landau-Peierls instability. If monolayers of cylindrical morphology block copolymers follow the same physics as liquid crystals, it will be impossible to achieve long range order over infinitely large scales through block copolymer assisted patterning. However grapho-epitaxy which involves physical confinement of the block copolymer within topographic patterns can potentially cut off long wavelength phonon modes responsible for the destruction of order. Bilayers in contrast are similar to columnar phases where the mean square fluctuation in layer displacement for columnar liquid crystals is

$$\langle u^2(r) \rangle = \frac{k_B T}{4\pi B \sqrt{\lambda a}} \left(1 - \left(\frac{a}{L}\right)^5\right) \quad (\text{S3})$$

where the columns are oriented along the z axis and L is the linear dimension of the lattice in the x - y plane.⁴ Since the fluctuations do not diverge as $L \rightarrow \infty$, columnar liquid crystals have better order than smectics. Hence the behavior of cylindrical morphology block copolymer thin films under confinement cannot be easily predicted and there is a need to study the nature of ordering in these systems to identify fundamental features of their assembly.

Size characterization

The size and composition of the block copolymers used in this study were obtained using ^1H -nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC), the data for which is shown in Figure S1, Figure S2 and Figure S3. Both the composition and the overall molecular weight quoted in this paper was obtained from NMR analysis, however the gel permeation chromatography data is also shown in Figure S4 for completeness.

Figure S1: ^1H -NMR for PS-PVP_{0.22} block copolymer

Figure S2: ^1H -NMR for PS-PVP_{0.23} block copolymer

Figure S3: ¹H-NMR for PS-PVP_{0.26} block copolymer Figure S4: Gel permeation chromatographs for PS-PVP_{0.22}, PS-PVP_{0.23} and PS-PVP_{0.26} block copolymers

Determination of the bulk order-disorder transition temperature

Temperature varying SAXS data to determine the ODT for the PS-PVP_{0.26} block copolymer is shown in Figure S5. The ODT is estimated to be approximately $260 \pm 10^\circ\text{C}$. Higher temperatures could not be employed as the sample underwent a color change upon heating further, possibly due to degradation of the block copolymer. The bulk ODT determination for PS-PVP_{0.23} was done by Hammond *et al.* and is reproduced in Figure S6.

Figure S5: Temperature variable SAXS for PS-PVP_{0.26} block copolymer in bulk to determine the bulk ODT

Bilayer order-disorder transition

AFM micrographs for bilayer thick films of PS-PVP_{0.22} films are shown in Figure S7. The atomic force micrographs clearly show the gradual destruction of translational and orientational order by growth of density of thermally generated defects, similar to the monolayer order-disorder transition shown in the manuscript.

Figure S6: Temperature variable SAXS for PS-PVP_{0.23} block copolymer in bulk. Reproduced with permission from Macromolecules, 2005, 38 (15), pp 6575–6585, Copyright © American Chemical Society 2005.

Figure S7: Atomic force micrographs of the structure in a bilayer of PS-PVP_{0.22} cylindrical morphology block copolymer as a function of temperature (in °C). Scale bar = 200 nm

Determination of a_0

Our experiments showed that a well ordered arrangement of cylinders with domain spacing approaching 20 nm was not accessible using PS-PVP block copolymer monolayers. Combining our SCFT calculations with this experimental result, we can obtain an approximate dependence of the smallest attainable cylinder spacing in a monolayer as a function of χN and ϕ .

$$\text{Since } n_d \sim \frac{1}{a_c^2} \exp^{-E_d/k_B T}$$

For an ordered structure

$$\begin{aligned} \frac{E_d}{k_B T} &> \left[\frac{E_d}{k_B T} \right]_o \\ &\equiv C \\ \Rightarrow \frac{0.03 B a^3}{T} &> k_B C \\ \Rightarrow 0.03 \frac{B \bar{V}}{RT} a^3 &> k_B C \frac{\bar{V}}{R} \end{aligned}$$

We then express the compression modulus B in terms of χN and volume fraction ϕ , to allow us to define a limit on ‘ a ’ for monolayer films in terms of χN and ϕ . By fitting values obtained from the SCFT simulations, we can extract the dependence of B on ϕ at constant χN (from Figure 12) and B on χN at constant ϕ (from Figure 13)

$$\begin{aligned} \frac{B \bar{V}}{2RT} &\propto (\chi N - 18)^{0.5} \text{ for } \phi = 0.22 \\ \frac{B \bar{V}}{2RT} &\propto (\phi - 0.197)^{0.08} \text{ for } \chi N = 30 \\ \text{Assuming } \frac{B \bar{V}}{RT} &\propto (\chi N - 18)^{0.5} (\phi - 0.197)^{0.08} \text{ for } \chi N > 18, \phi > 0.197 \end{aligned}$$

$\therefore$ condition for a_0 is

$$a_0 = \frac{c \bar{V}^{1/3}}{(\chi N - 18)^{0.167} (\phi - 0.197)^{0.026}}$$

From our experimental results we can infer that a_0 for PS-PVP block copolymers would correspond to the PS-PVP_{0.22} block copolymer. At $T = 150^\circ\text{C}$, χN for this block copolymer is ~ 25 , $\bar{V} \sim 0.027 \text{ m}^3/\text{mol}$ and a_0 is approximately 20 nm. Thus we can evaluate the proportionality constant 'c' in the above relation to be approximately 3.6×10^{-9} . Note that a_0 scales with molar volume $\bar{V}$, which is proportional to N and depends on the specific polymer, but as an approximation we treat it as a constant $\bar{V} \sim 0.027 \text{ m}^3/\text{mol}$ to obtain a general form for a_0 (Eqn 4) in terms of χN and ϕ alone.

$$a_0(\text{nm}) = \left(\frac{25}{(\chi N - 18)^{0.167} (\phi - 0.197)^{0.027}} \right) \quad (\text{S4})$$

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