1. Bulk materials

Figure S1. SEC trace of PS-P2VP diblock copolymers.

![SEC trace of PS-P2VP diblock copolymers](image)

Figure S2. Small-angle X-ray scattering (SAXS) obtained at room temperature. The primary peak at $q^*$ suggests that the cylinder-cylinder distance is 22.0 nm.

![Small-angle X-ray scattering (SAXS)](image)
Figure S3. Inverse intensity of the scattered peak at $q^*$ (SAXS) as a function of inverse temperature (K). The abrupt change suggests that the bulk $T_{ODT} = 185 \, ^\circ C \, (\pm 5 \, ^\circ C)$.

2. Thin films:

Figure S4. Optical images of thin films corresponding to 1-, 2-, 4-, 7-, 9-layer of cylinders. The thin films are featureless with minimal island/hole formations. The scale bar corresponds to 20 µm.
Figure S5. AFM height image of 2-layer thin film prior to reactive ion etching ($O_2$). The motif without any feature suggests single-component wetting at the polymer-air interface.

Figure S6. (a) dSIMS counts corresponding to CN- and Si signals from 1-layer thin-film samples. (b) dSIMS counts corresponding to CN- and Si signals from 2-layer thin-film samples.
Figure S7. (a-d) Grazing incidence SAXS for 7-, 4-, 2-, and 1-layer samples as a function of temperature around $T_{ODT,Film}$. ($\alpha_i = 0.19$, 0.20, 0.21 °)
Figure S8. 1-dimensional density profile (across the film thickness) of the disordered (homogeneous) phase at $\zeta N=10000$, corresponding to the systems at $\zeta N=1000$ in Figure 7.

Figure S9. (a) Distribution of A segment density across the film thickness for the disordered (homogeneous) phase at commensurate thicknesses with $f_A=0.23$, $\chi N=18.6$, and $\chi_w N=-30$ from SCFT. The dotted lines denote the bulk A block fraction, $f_A=0.23$. (b) SCFT results of $(\chi N)_{ODT}$ in corresponding thin films as a function of film thickness. Dashed line indicates the ODT in bulk system.
Figure S10. Snapshots of the density profiles for commensurate monolayer and bilayer films around the order-disorder transition at $C=100$ and $C=30$ respectively.