Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

1. Bulk materials

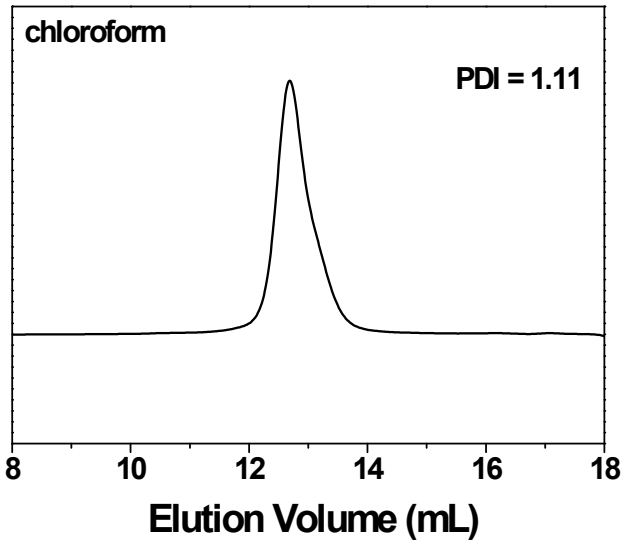

Figure S1. SEC trace of PS-P2VP diblock copolymers.

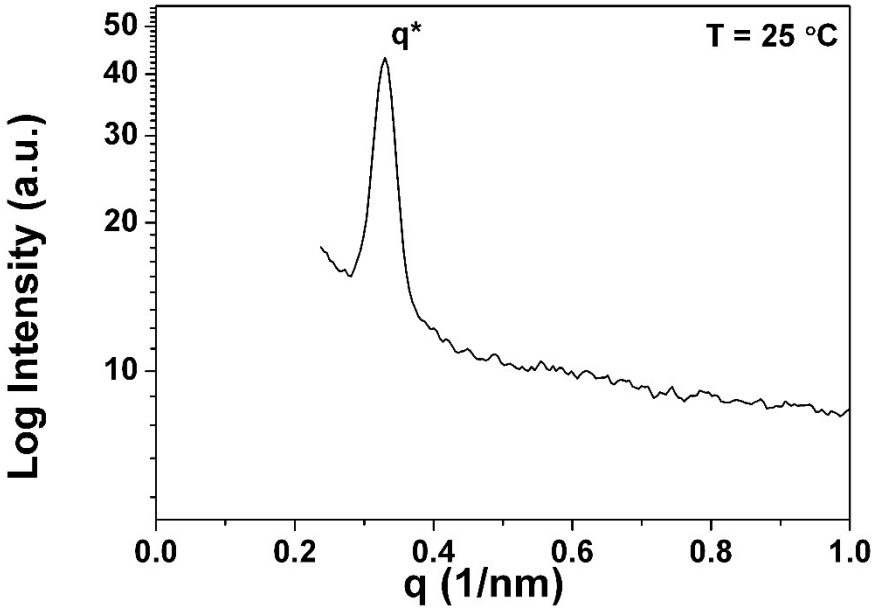

Figure S2. Small-angle X-ray scattering (SAXS) obtained at room temperature. The primary peak at q* suggests that the cylinder-cylinder distance is 22.0 nm.

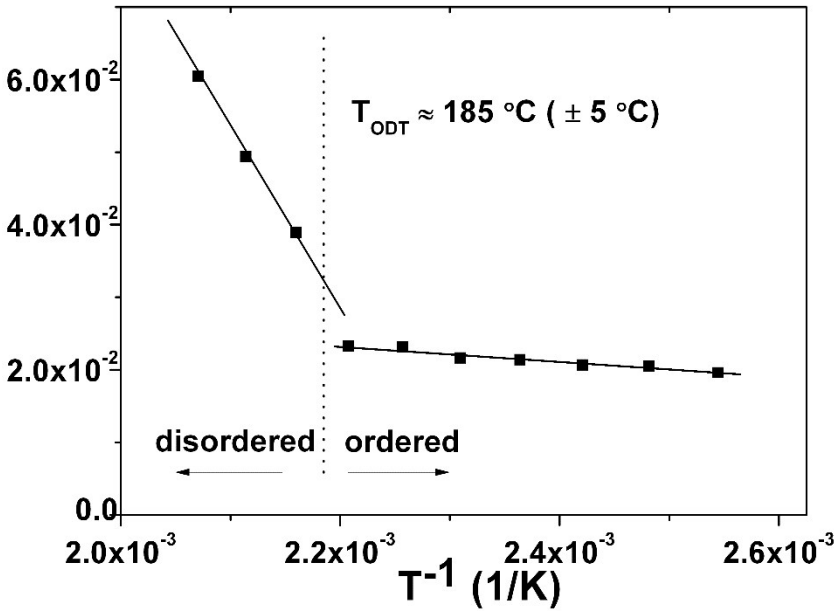

Figure S3. Inverse intensity of the scattered peak at q* (SAXS) as a function of inverse temperature (K). The abrupt change suggests that the bulk T_{ODT} = 185 °C (±5 °C).

2. Thin films:

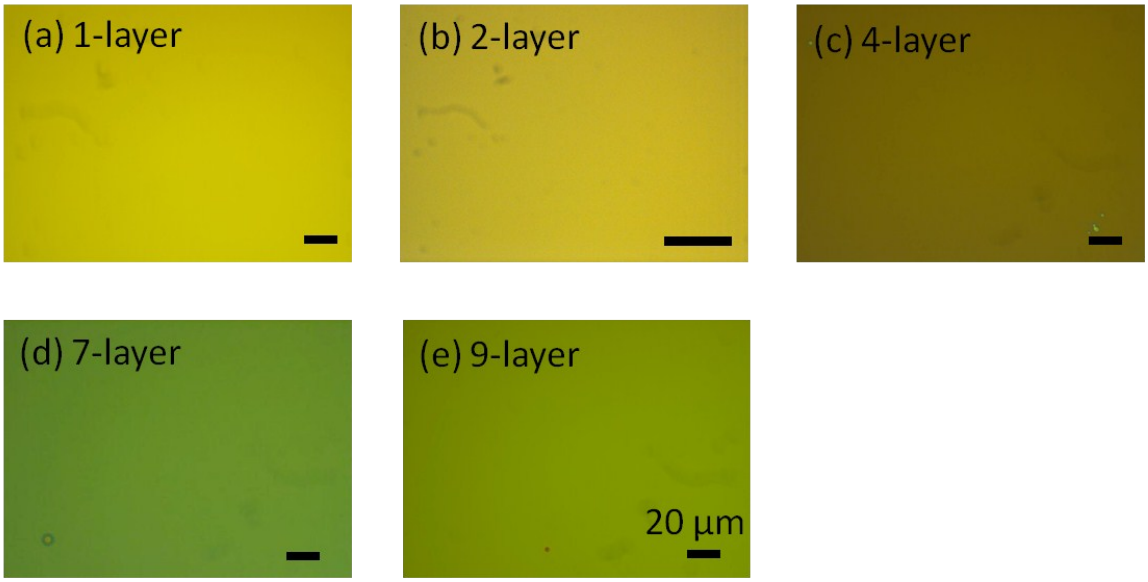

Figure S4. Optical images of thin films corresponding to 1-, 2-, 4-, 7-, 9-layer of cylinders. The thin films are featureless with minimal island/hole formations. The scale bar corresponds to 20 µm.

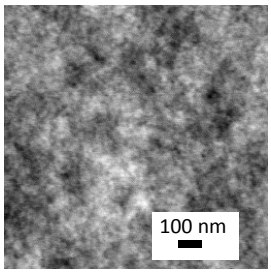

Figure S5. AFM height image of 2-layer thin film prior to reactive ion etching (O_2). The motif without any feature suggests single-component wetting at the polymer-air interface.

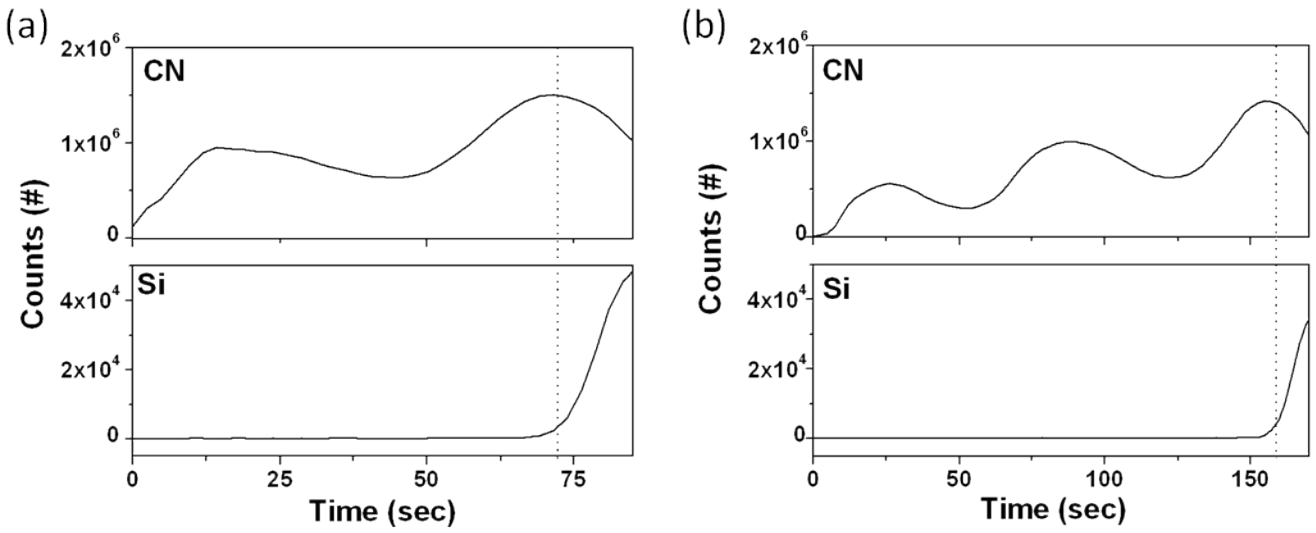

Figure S6. (a) dSIMS counts corresponding to CN- and Si signals from 1-layer thin-film samples. (b) dSIMS counts corresponding to CN- and Si signals from 2-layer thin-film samples.

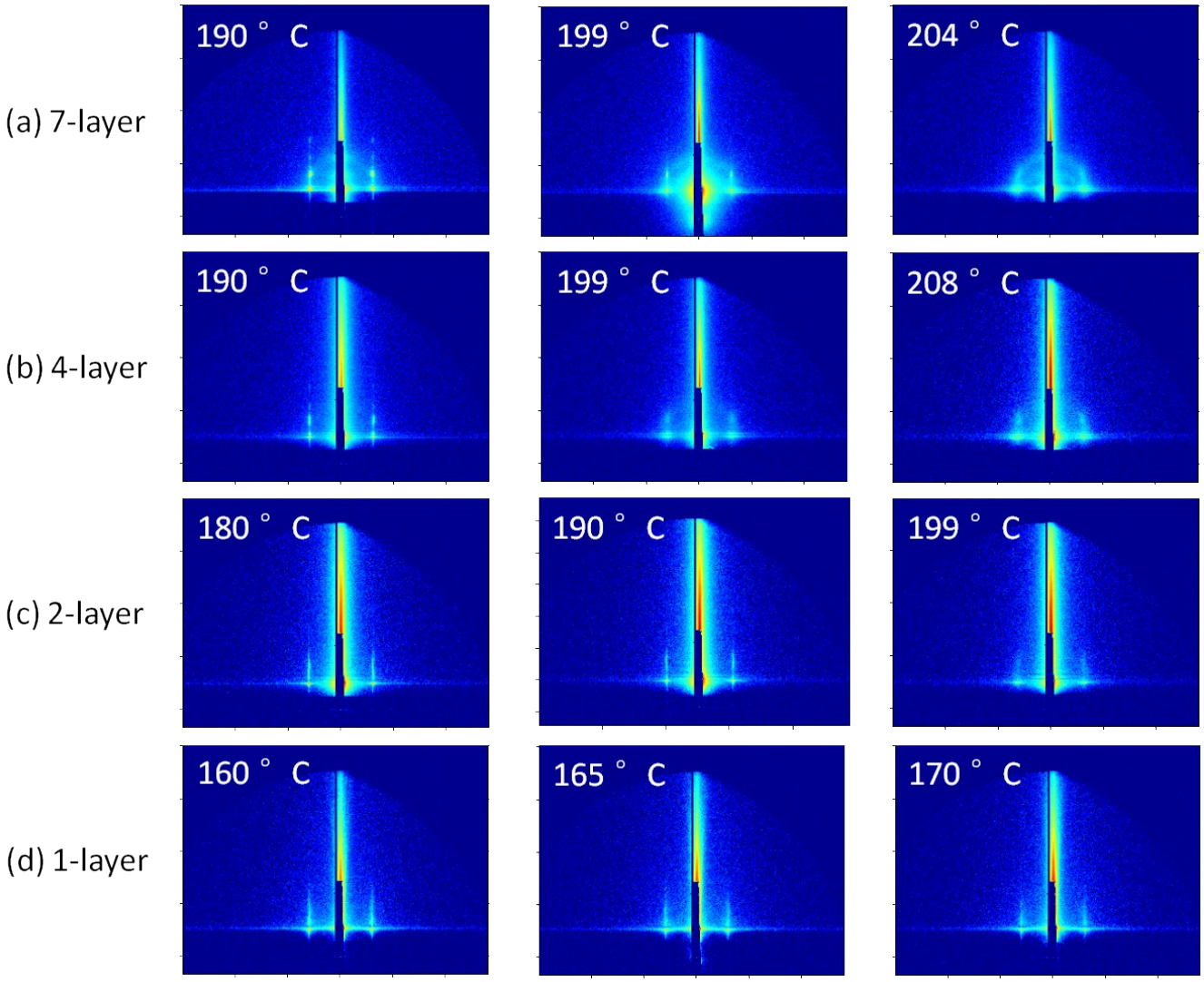

Figure S7. (a-d) Grazing incidence SAXS for 7-, 4-, 2-, and 1-layer samples as a function of temperature around T_{ODT_Film}. (α_i = 0.19, 0.20, 0.21 °)

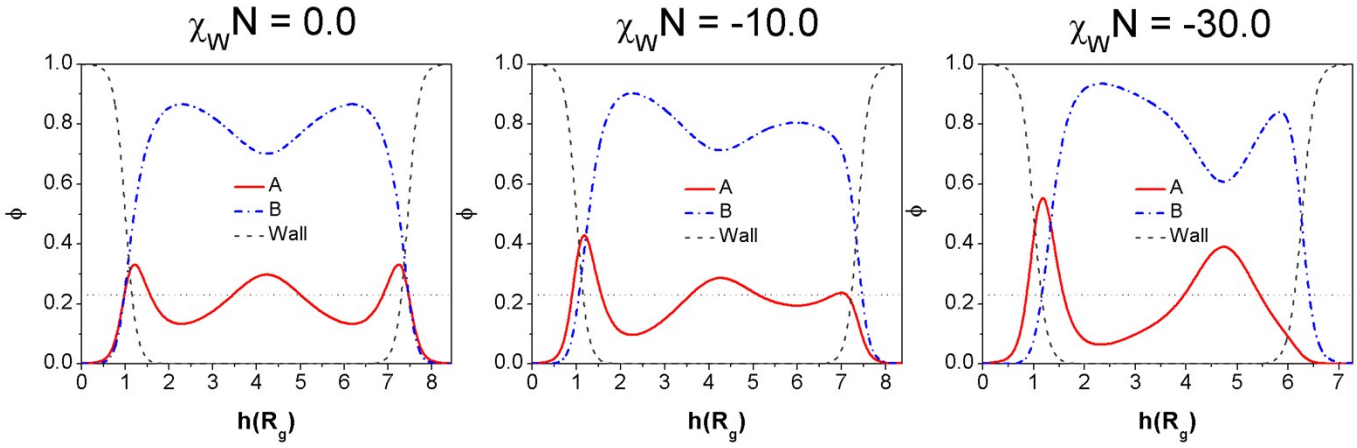

Figure S8. 1-dimensional density profile (across the film thickness) of the disordered (homogeneous) phase at ζN=10000, corresponding to the systems at ζN=1000 in Figure 7.

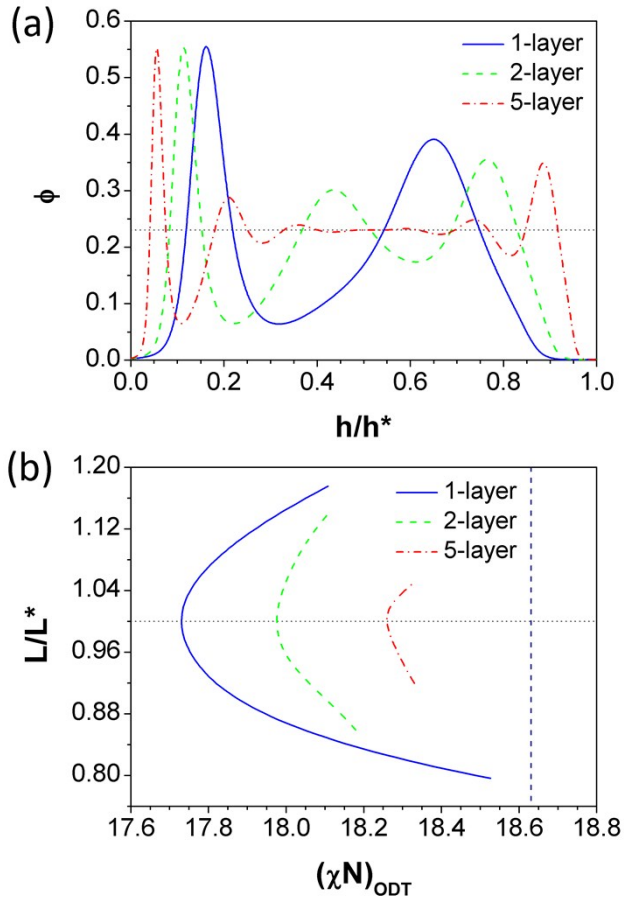

Figure S9. (a) Distribution of A segment density across the film thickness for the disordered (homogeneous) phase at commensurate thicknesses with f_A=0.23, χN=18.6, and χ_wN=-30 from SCFT. The dotted lines denote the bulk A block fraction, f_A=0.23. (b) SCFT results of $(\chi N)_{ODT}$ in corresponding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

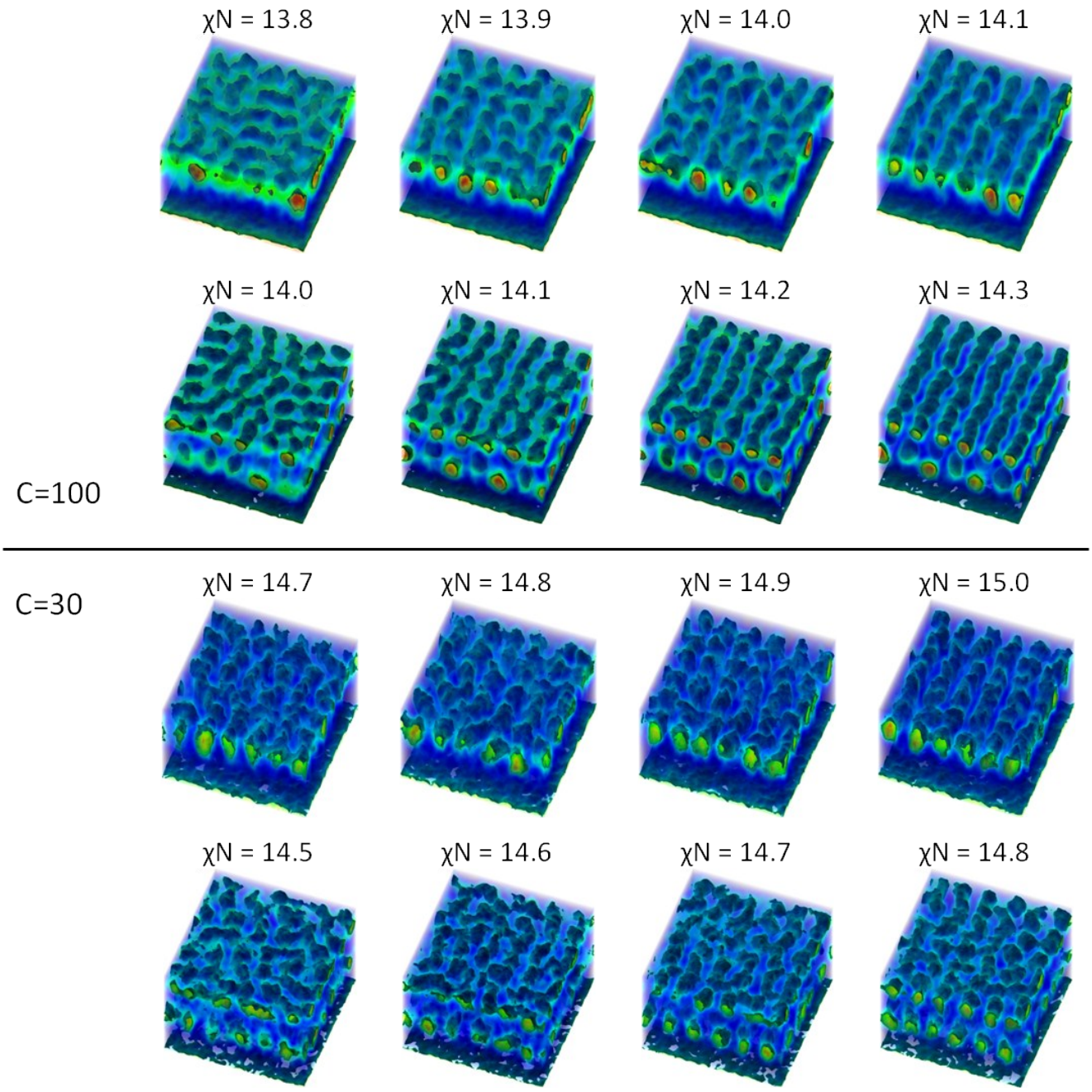

Figure S10. Snapshots of the density profiles for commensurate monolayer and bilayer films around the order-disorder transition at C=100 and C=30 respectively.