## Supplementary Information

The Perpendicular Cylinder Orientation of Block Copolymer Mixtures throughout the Whole Sample Thickness

The perpendicular cylinder orientation throughout the whole sample thickness can be more clearly confirmed by etching experiments using an excimer laser.[S1] Note that such etching experiments identically correspond to the cross-sectional TEM experiments because both the PS and PI block components are simultaneously ablated during the KrF excimer laser irradiation. As an example, the perpendicular cylinder orientation observed on the surface of untreated 10 μm-thick SIS+PS12k was also identically obtained after the 100 pulses of KrF excimer laser irradiation with 130 mJ/cm^2 of fluence even though the sample thickness was reduced to ~7 μm after the excimer laser ablation. As shown in Figure S1 (a) and (b), the surface orientation of SIS+PS12k was not notably different from its ~3 μm-depth orientation, suggesting that the cylinder orientation perpendicular to the surface is not a local orientation confined only at the sample-superstrate or sample-substrate interfaces, but overall orientation dominant on the whole sample thickness.
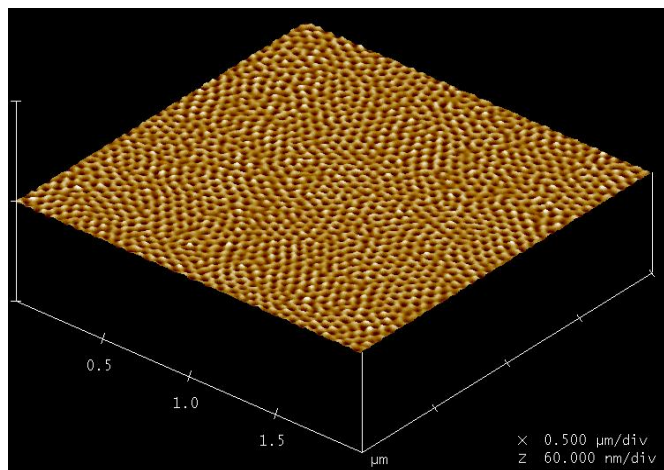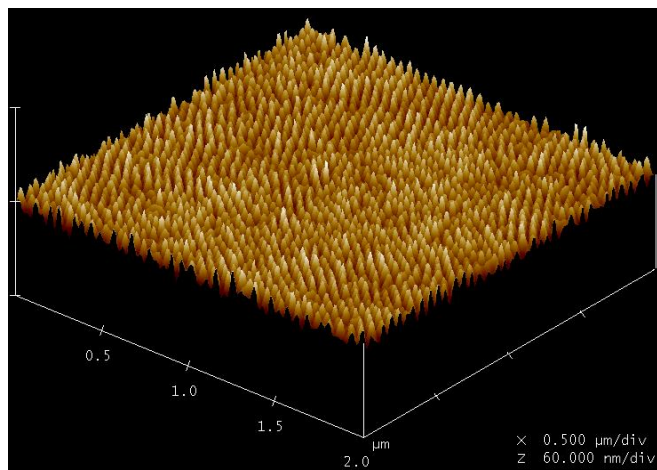
(a)   (b)

Figure S1.   AFM images of SIS+PS12k annealed on the Teflon substrate at 130°C for 50 h:

(a) Untreated SIS+PS12k and (b) After 100 pulses of KrF excimer laser irradiation with 130

mJ/cm^2 fluence on the surface of SIS+PS12k (initial film thickness = ~10 μm and final film

thickness = ~7 μm). Topographic and phase AFM images were the same.

Thermodynamic and Kinetic Stability of Block Copolymer Samples Used

In order to assess temperature-dependent phase behaviors of a block copolymer, first we have to find out an optimum reference annealing temperature at which the equilibrium morphology of the block copolymer is reliably produced. Such reference temperature should be well above the glass transition temperatures of PS block and blended PS homopolymers to exclude kinetically frozen block copolymer morphology, but at the same time, it should be thermodynamically favorable to a specific cylinder orientation (in our case, it should be low enough to maintain a perpendicular cylinder orientation). To determine optimum reference annealing temperature, we performed dynamic mechanical measurements on neat SIS and its homopolymer mixtures. Since the shear rate dependence of the steady-state viscosity η is equal to the angular frequency (ω) dependence of the linear viscoelastic viscosity $\eta*$,[S2] we can estimate the temperature-dependent relative molecular mobility of neat SIS and its homopolymer mixtures from the measurements of complex shear viscosity as a function of temperature at a fixed low ω. As shown in Figure S2, all samples showed sufficient molecular motions above ~130°C, and hence 130°C was selected as the lowest annealing temperature for the reference block copolymer morphologies, providing highest experimentally achievable incompatibility between the blocks without a significant kinetic constraint. Since the microdomain structures of neat SIS and its homopolymer blends did not vary notably with the increase of annealing time after 20 h at the annealing temperature of 130°C, the block copolymer microdomain structure achieved after the annealing process at 130°C for 50 h was considered as its nearly equilibrated morphology at 130°C.

In addition, we can also confirm the presence of a global PS pair interaction in SIS+PS12k and SIS+PS15k from the dynamic mechanical measurements. As shown in Figure S2, those two block copolymer mixtures maintain their viscoelasticity even in the high temperature

region, due to the strong intermolecular affinity between the homologous PS pair, which induces a global cylinder orientation perpendicular to the shear fields, and also due to strong segregation forces between the block domains.
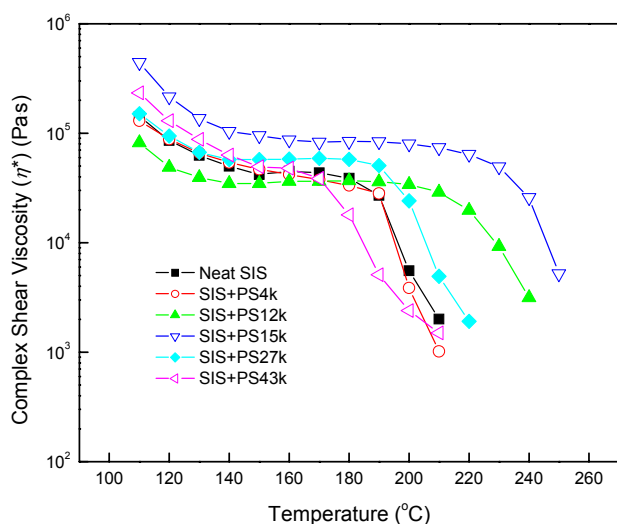

Figure S2. Complex shear viscosity of neat SIS and its PS homopolymer mixtures at different homopolymer molecular weights as a function of temperature at the fixed angular frequency of 0.05 rad/s.

References

S1. D. U. Ahn and E. Sancaktar, *Adv. Funct. Mater.*, 2006, **16**, 1950.

S2. S. Kwak and D. U. Ahn, *Macromolecules*, 2000, **33**, 7557.