

## Supporting Information

# **Kinetics of Domain Alignment in Block Polymer Thin Films during Solvent Vapor Annealing with Soft Shear: An *in Situ* Small-Angle Neutron Scattering Investigation**

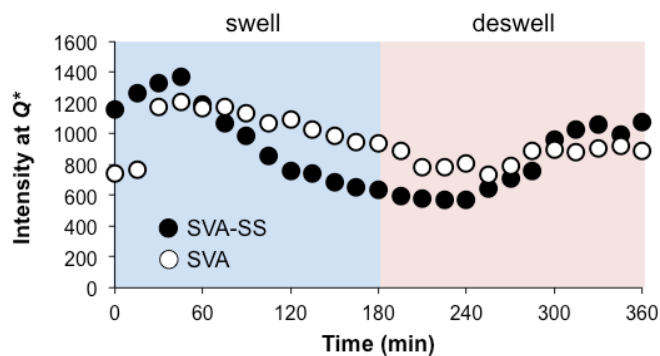
Cameron K. Shelton,<sup>a</sup> Ronald L. Jones,<sup>b</sup> and Thomas H. Epps, III<sup>a,c,\*</sup>

<sup>a</sup>Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States

<sup>b</sup>Materials Science and Engineering Division, National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899, United States

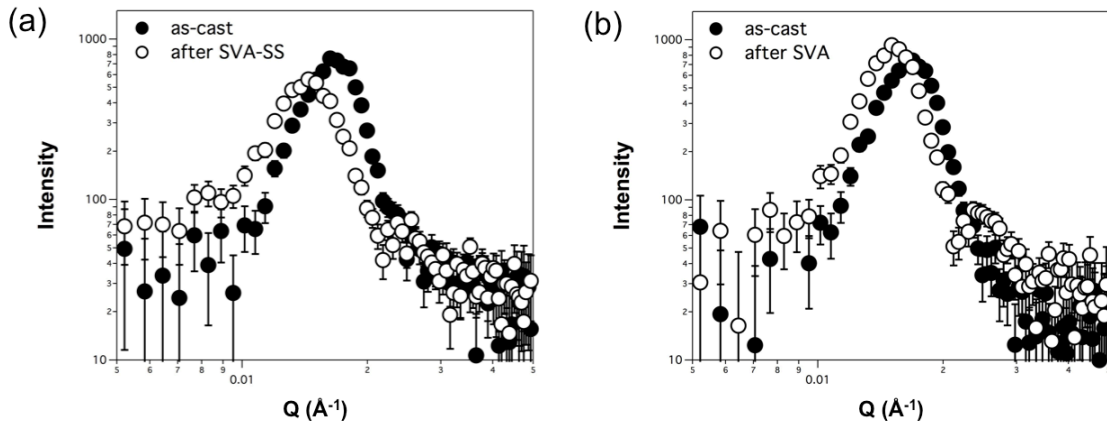
<sup>c</sup>Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716, United States

\*To whom correspondence should be addressed. Email: [thepps@udel.edu](mailto:thepps@udel.edu)



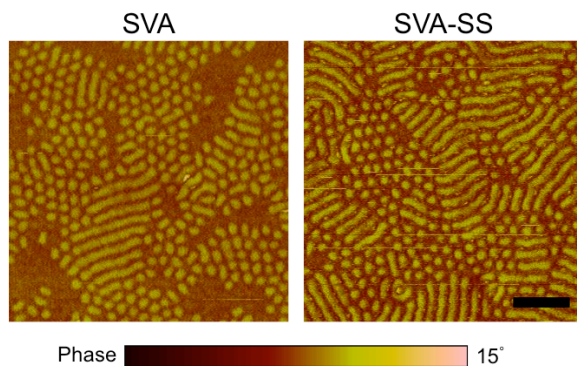
**Figure S1:** Temporal plot of small-angle neutron scattering (SANS) intensity of the primary peak ( $Q^*$ ) during toluene solvent vapor annealing with soft shear (SVA-SS; black data points) or solvent vapor annealing (SVA; white data points) of poly(deuterated styrene-*b*-isoprene-*b*-deuterated styrene) (*dSIIdS*) thin films.

SVA-SS was implemented through the placement of a polydimethylsiloxane (PDMS) pad on a film to induce shear forces as the pad swelled and deswelled while in contact with the film. In Figure S1, SVA-SS or SVA was conducted with a 3 h swelling time and 10 mL/min toluene-rich nitrogen flow rate during swelling and 3 mL/min diluent nitrogen flow rate during film deswelling. An initial increase in the scattering intensity was followed by a decrease in intensity as the film swelled and then an increase in scattering intensity as the film deswelled. SVA-SS resulted in a larger degree of scattering loss and recovery in comparison to SVA, which suggested the change in scattering intensity during SVA-SS was caused by more than solvent swelling. The most likely cause of the pronounced changes in scattering intensity during SVA-SS was nanostructure disordering (during swelling) and ordering (during deswelling) caused by shear forces. The loss of scattering intensity during SVA likely was caused by the appearance of parallel lamellae (*i.e.*, featureless areas in atomic force microscopy [AFM] images), as suggested in Figure S3.



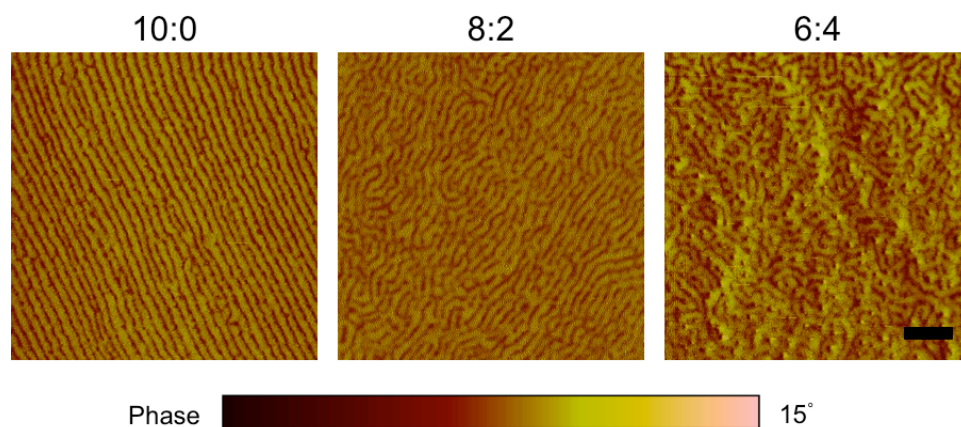
**Figure S2:** Azimuthally averaged SANS data for *dSI/dS* films subjected to toluene SVA (a) with or (b) without soft shear. As-cast and after SVA-SS profiles in (a) were recorded without PDMS. For both SVA-SS and SVA, the location of the primary peak shifted from  $Q = 0.017 \text{ \AA}^{-1}$  to  $Q = 0.015 \text{ \AA}^{-1}$ , which was indicative of an increase in domain spacing ( $L_0$ ) from 37 nm to 42 nm. Also, there was a difference in intensity of the primary peak for SVA-SS *vs.* SVA; the primary peak intensity decreased for samples treated by SVA-SS and increased slightly for samples treated *via* SVA.

In Figure S2, the increase in  $L_0$  likely was caused by polymer-solvent interactions that effectively swelled the domains. The higher scattering intensity after SVA was generated as domains likely coalesced into larger grains that produced more scattering in the detector direction relative to smaller domains. Although larger grains formed during SVA-SS, the final scattering intensity decreased because some film damage was incurred (mostly at the edges where the film was sheared off the substrate) when the PDMS was removed from the BP.



**Figure S3:** AFM images of *dSIIdS* films after SVA or SVA-SS with the same swelling (10 mL/min toluene-rich nitrogen flow rate for 3 h) and deswelling (3 mL/min diluent nitrogen flow rate) conditions. The SVA-SS image was obtained from a portion of the film that the PDMS pad did not shear. Both micrographs indicate a mixture of parallel and perpendicular cylinders and featureless areas. The scale bar represents 250 nm and applies to both images.

The similar structures in the two micrographs indicated that the presence of the PDMS pad did not significantly alter the solvent vapor swelling of samples treated *via* SVA-SS *vs.* SVA. Therefore, the alignment of domains in the SVA-SS film was a primary result of the shear force produced by the PDMS, rather than a change in the swelling conditions between samples. The featureless areas in the film likely are kinetically trapped lamellae domains that formed during solvent swelling of the *dSIIdS* as has been reported for these polymers in previous solvent annealing studies using a different solvent (chloroform).<sup>1</sup>



**Figure S4:** AFM images of *dSIIdS* films exposed to different toluene-rich to diluent stream flow rate ratios (10:0, 8:2, or 6:4) during SVA-SS swelling. Shear forces from the swelling of the PDMS pad resulted led to well-ordered and aligned nanostructures across the film in the 10:0 sample. At the 8:2 ratio (reduced PDMS swelling relative to 10:0), the shear fields appear to be sufficient to align domains but not large enough to generate either a high degree of ordering or defect removal. At the 6:4 ratio, shear-alignment was not readily apparent. The scale bar represents 250 nm and applies to all images.

Increases in the solvent concentration led to greater PDMS swelling and larger shear forces that induced chain mixing and facilitated domain break-up. These effects helped overcome entropic penalties for the coalescence of grains in a single direction and prevented defects from becoming kinetically trapped. Minimal alignment and domain ordering was noted at the lowest solvent concentration (6:4 ratio) likely because the film and PDMS did not swell enough to plasticize the polymer chains and promote restructuring nor permit sufficient time for shear alignment prior to deswelling.

**References:**

1. Albert, J. N. L.; Young, W.-S.; Lewis, R. L.; Bogart, T. D.; Smith, J. R.; Epps, T. H., III. Systematic Study on the Effect of Solvent Removal Rate on the Morphology of Solvent Vapor Annealed ABA Triblock Copolymer Thin Films. *ACS Nano* **2012**, 6, 459-466.