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Block copolymer alignment by shear induced during solvent vapor annealing with a crosslinked elastomer capping layer

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The long range alignment of block copolymers (BCPs) is generally accomplished through application of a gradient shear force or by topographical or chemical cues patterned into the substrate. These techniques require lithographic patterning, specialty substrates or custom built equipment to achieve the alignment, which limits the broad academic application of aligned BCPs. One technique to improve the large range ordering of BCPs is solvent vapor annealing (SVA), which exposes the BCP film to a controlled atmosphere of solvent vapor to swell the BCP and provide significant enhancements in the chain mobility. Here, we discuss a minor modification of the SVA process; a thin piece of crosslinked poly(dimethyl siloxane) (PDMS) is placed on top of the BCP film before SVA. Exposure to organic solvent vapors causes the PDMS to swell, while the solvent also plasticizes the BCP film. Removal of the solvent induces a shear to the BCP film as the PDMS shrinks back to its initial dimensions. The shape of the PDMS cap determines the anisotropy in the stress applied on deswelling that aligns and orients the BCP domains. Polystyrene-block-polyisoprene-block-polystyrene (SIS) is utilized as a model system to illustrate how the processing parameters impact the orientation as determined by both grazing incidence small angle x-ray scattering (GISAXS) and atomic force microscopy (AFM). Quantification of the alignment by Herman's orientational parameter (S) illustrates high degree of alignment (S=0.95) is possible through appropriate selection of processing conditions. This SVA-based alignment method provides a relatively simple method to orient BCP films within general SVA processing protocols.