

IRG-2: Shearing Progressively Aligns Block Copolymer Films (DMR-1420541)

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Nanostructured block copolymer thin films align in response to an applied shear stress, yielding highly aligned patterns which can be used as nanofabrication or nanopatterning templates. For example, polymers forming in-plane cylinders can be sheared into an array of parallel stripes covering a macroscopic (cm²) area, with a periodicity from 10-100 nm, controlled via molecular weight. But the mechanism by which this alignment occurs has remained obscure, meaning that the required stresses and shear times to achieve a particular quality of alignment are unknown. PCCM researchers recently tackled this problem, by synthesizing a range of block copolymers varying in composition and molecular weight, and applying a gradient of shear stress to rapidly map out the quality of alignment. A melting-recrystallization model provided an excellent fit to the data, allowing predictions of the quality of alignment for shearing conditions or polymer compositions outside the ranges investigated.



(a) Schematic of the experimental setup for imparting a gradient of shear stress to a polymer film using a parallel plate rheometer. (b) Topdown view of the applied stress gradient. (c-f) Representative atomic force microscopy (AFM) images from a monolayer of PS-PHMA 21-77, sheared at 150 °C for 30 mins, showing the progressive increase in alignment quality as the applied stress is increased: (c) 0 Pa (order parameter $\psi_2 = 0.09$, computed over the entire 2 μ m × 2 μ m area of the full image), (d) 800 Pa ($\psi_2 = 0.51$), (e) 1200 Pa ($\psi_2 = 0.82$), (f) 2000 Pa ($\psi_2 = 0.98$). Scale bar = 500 nm. (g) Alignment *vs.* stress for PS-PHMA 48-88 for varying shear times; The symbols display the experimental results from AFM, while the lines show the predictions of the melting-recrystallization model.

Reference: R.L. Davis, B.T. Michal, P.M. Chaikin, and R.A. Register, "Progression of Alignment in Thin Films of Cylinder-Forming Block Copolymers upon Shearing", *Macromolecules*, **48**, 5339-5347 (2015).