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Shear Alignment and Realignment of Block Copolymer Microdomains in Thin Films[1]

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Bulk block copolymers, like all liquid crystalline structures, are well-known to align under flow. In the past few years, we have shown that analogous flow alignment can be achieved in substrate-supported thin films (<100 nm thick) containing only one or a few layers of spherical or cylindrical nanodomains. Alignment can easily be imparted either by pulling a soft rubber pad in contact with the top surface of the film, or by flowing a nonsolvent fluid across the film. The latter geometry opens the possibility to "write" relatively complex patterns on the millimeter or submillimeter scale, where the nanodomain director follows the fluid streamline. Alignment can be achieved via either unidirectional or oscillatory shear, and is conveniently executed in a parallel-plate rheometer, where the substrate-supported film forms one "plate" and the "gap" is filled with the nonsolvent fluid. A threshold stress is required to achieve alignment of the microdomains, a stress which decreases steadily as the temperature is raised towards the polymer's order-disorder transition temperature. A simple melting-recrystallization model appears to capture the dynamics of overall alignment. Though no grain boundaries remain in well-aligned films, isolated dislocations persist. For sphere-formers, where two or more layers are required for alignment, the isolated dislocations are preferentially oriented in such a way as to facilitate sliding of the two layers of spheres past each other. Once a macroscopic orientation has been imparted to the film (over square-cm area), the microdomains can be reoriented by applying shear in a different direction, but a higher threshold stress is required than was needed for the initial alignment from the polygrain state. Recently, we have observed a sphere-to-cylinder transition in one particular block copolymer under shear, opening another possible mechanism for shear-induced alignment of the spheres which form when these cylinders relax.

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