Non Equilibrium Block Copolymer Directed Self Assembly. Multiblocks, Solvents, and Thick Films.

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Past research on directed self-assembly (DSA) of copolymers for lithographic processes has generally relied on equilibrium thermodynamic considerations to interpret the morphologies that arise in thin films on patterned substrates. Whether such substrates rely on chemistry or topographic constraints to guide the assembly of a polymeric material, a general assumption has been that the end morphology of the copolymer corresponds to an equilibrium state. Recent experiments and calculations, however, have revealed that this is not always the case. Experiments with triblock copolymers on patterned substrates, for example, show that the wider processing window offered by these materials is due to the emergence of non-equilibrium, metastable morphologies. Similarly, experiments conducted under a solvent atmosphere have shown that the structure adopted by the copolymer can be manipulated by control of the pressure of the solvent and the length of time that the polymer is exposed to it.

Non-equilibrium, metastable morphologies can only be identified through a coupled experimental and theoretical approach. At the University of Chicago we have developed a new formalism capable of describing structure and dynamics of assembly during block copolymer DSA, both with and without solvents, in systems where film thickness, composition, and morphology are allowed to evolve as a function of time. This presentation will provide an overview of that approach, along with comparisons to experimental data for directed assembly of diblock copolymers, triblock copolymers, and solvent-containing copolymers, that serve to emphasize its advantages and limitations.