

Directing non-equilibrium assembly of bottle brush block copolymers during additive manufacturing

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Additive manufacturing of functional polymers remains limited by the challenge of precisely controlling multiscale hierarchical assembly during processing. In this work, we address this challenge by integrating nonequilibrium self-assembly of densely grafted bottle brush block copolymers with a highly versatile direct-write 3D printing approach. We demonstrate that programmatic variation of printing conditions enables control of peak reflected wavelength for bottlebrush photonic crystals across a range of 403 to 626 nm (blue to red) with a single ink material. We further demonstrate spatial and functional patterning of photonic crystals to achieve colorful prints of chameleon patterns through on-the-fly tuning of assembly kinetics during printing. Via scanning electron microscopy and synchrotron small-angle X-ray scattering analysis of printed films, we then clarify the microstructural underpinning of this phenomena as tuning of lamellar domain d-spacing (total thickness of A+B block) over a range of greater than 30 nm, which we attribute to modulation of polymer conformation during printing. Finally, we establish the role of kinetic trapping of metastable microstructures as the mechanism for domain size control based on *in situ* optical microscopy and solvent-vapor annealing experiments. Thus, we demonstrate a new method for tunable block copolymer photonics without synthetic variation. Furthermore, we present a hardware and software integrated 3D printing scheme that can serve as a test bed for functional property modulation for a variety of functional polymeric and material systems.

