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Hierarchically Ordered Polymer/Block Copolymer/Nanoparticle Systems Enabled via Holographic Photopolymerization

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Combining top-down and bottom-up methods in one process step creates novel hierarchical nanostructures with tailored properties. We demonstrate the ability to spatially pattern block copolymers or nanoparticles into periodic volume gratings using a one-step holographic patterning (HP) technique. The confinement of the second phase (e.g. block copolymer or nanoparticle) within the grating results in local preferential ordering of that phase, enabling single-step fabrication of complex hierarchical structures. As an example, this simple interfering photopolymer 'writing' technique was utilized to generate a layer-in-layer structure of poly(ethylene oxide-b-epsilon-caprolactone) confined between crosslinked resin. The period of the volume grating was 200 nm, with the BCP occupying 100 nm of the 1-D structure. The BCP crystallized/phase separated to produce a lamellar structure with a 21 nm periodicity. This system exhibits interesting thermo-optical behavior during heating/cooling cycles. Alternatively, a layered polymer/nanoparticle composite was created through a one-step two-beam interference lithographic exposure of a dispersion of silica nanoparticles within a photopolymerizable mixture at a wavelength of 532 nm. The effects of exposure time and power, nanoparticle size, and periodicity on the nanocomposite structure were measured with transmission electron microscopy. The optical properties of the formed gratings were probed in real-time during formation. Collaborators on this work include M. Birnkrant and C. Li from Drexel University, A. Juhl and P. Braun from UIUC, and L. Natarajan, V. Tondiglia, and R. Vaia from AFRL.