

Polymer-grafted Nanocrystal Superlattice with Long-range Order Mediated by Melt Additions

Boyce Chang^{†§}, Vittoria Tommasini[†], Pricilla Pieters, Derrick Ong[†], Bryan Kim[†], Whitney Loo[‡], Scott Dhuey[†], Eric Dailing[†], Yi Liu[†], A. Paul Alivisatos[#], Paul Nealey[‡], Ricardo Ruiz^{†*}

[†] Molecular Foundry, Lawrence Berkeley National Lab, Berkeley, CA, USA 94720

[§] Department of Materials Science and Engineering, Iowa State University, Ames, IA, 50014

[‡] Pritzker School of Molecular Engineering, University of Chicago, Chicago, IL, USA, 60637

[#] Department of Chemistry, University of Chicago, Chicago, IL, USA, 60637

Abstract

Polymer grafted nanocrystals are an attractive class of materials for fabricating superlattices due to the increased level of structural control brought forth by the polymer brush. The periodicity of superlattices can be tuned independent from particle size. However, PGNCs retain characteristics from its colloidal roots during assembly despite their surface interactions screened by the polymer brush. Here, we demonstrate that systematically applying chemically identical polymer melt additions into a PGNCs superlattice improves long-range order. We infer that the melts act as “solvents” that plasticize the PGNC superlattice, lowering the barrier towards grain growth. Controlling the relative molecular weight between the melt, P and polymer brush, N was found to be critical in managing phase stability of the composite. At $P/N < 1$, an ordered superlattice is maintained up to 50 vol% melt addition whereas at $P/N > 1$, order-disorder transition is shifted asymptotically to 10 vol%. This was attributed to autophobic dewetting between high molecular weight melt and brush chains. We demonstrate directed self-assembly of the PGNC composite using templated substrates. The composite showed tolerance to incommensurate patterns and adopts a noncanonical lattice structure at low particle density.