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Self-Assembly of Supramolecular Nanocomposite in Thin Film: A Kinetic Study JOSEPH KAO, KARI THORKELSSON, PETER BAI, TING XU, University of California, Berkeley — The comprehensive studies on the thermodynamics in block copolymer-based nanocomposites have paved the way for hierarchically structured materials with unique collective properties. We extend the investigation to the assembly kinetics to gain further control over the 3D spatial organization of nanoparticles (NPs) in thin films of supramolecular nanocomposites. Our studies reveal that, by simply controlling the solvent fraction (f_s) in the film during solvent annealing, the thermodynamic driving force for defect elimination, the chain mobility, and the activation energy for interdomain diffusion can be modulated to tailor 3D NP assemblies in thin films. At a low f_s, the anisotropy in the local diffusion coefficient results in NP arrays normal to the surface. As f_s reaches an optimal value, the solvent and the small molecules effectively reduce the activation energy for interdomain diffusion and the T_g of the supramolecule. This leads to rapid formation of highly ordered 3D NP arrays in seconds. The nanocomposite eventually undergoes an order-disorder transition as f_s increases substantially. The fundamental insights gained from these studies lay the foundation for the rational design of functional nanocomposites with tunable macroscopic properties.

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