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Nanoparticle Order through Entropic Confinement REN ZHANG, Univ of Akron, BONGJOON LEE, Carnegie Mellon University, CHRISTOPHER STAFFORD, JACK DOUGLAS, NIST, MICHAEL BOCKSTALLER, Carnegie Mellon University, ALAMGIR KARIM, Univ of Akron — As has been addressed in colloidal science, visual order transitions can be achieved with entropy contributions alone. Herein, entropy-driven ordering of nanoparticle (NP) structures is generated where entropy increase and visual order are achieved simultaneously. We study an “athermal” NP-polymer blends where NPs are densely grafted with polymer brush of the same chemical composition as the polymer matrix. Visual order of the NPs is induced by geometrically confining the thin film blends with meso-scale topographic patterns. When the residual layer thickness of the patterned blend films approaches the nanoparticle dimension, exclusive segregation of NPs to less confining imprinted mesa region occurs. This preferential segregation of NPs, defined by partition coefficient $K = 0$, is attributed to purely entropic penalty, where K denotes the particle density ratio at highly confined residual layer to that at mesa region. We further demonstrate K is fully tunable and even invertible with increasing matrix chain dimension. The associated entropic free energy change ($\Delta F = -\ln K$) is calculated to explain NP segregation preference. Accordingly, variation of residual layer thickness and polymer matrix molecule size can both affect NP distribution among patterned thick and thin regions.

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