

Abstract for an Invited Paper
for the MAR07 Meeting of
The American Physical Society

Polymer brushes on nanoparticles: their positioning in and influence on block copolymer morphology.

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Polymers brushes grafted to the nanoparticle surface enable the precise positioning of particles within a block copolymer matrix by determining the compatibility of nanoparticles within a polymeric matrix and modifying the interfacial properties between polymers and inorganic nanoparticle. Short thiol terminated polystyrene (PS-SH), poly(2-vinylpyridine) (P2VP-SH) and PS-*r*-P2VP with the molecular weight (M_n) of 3 kg/mol were used to control the location of Au nanoparticles over PS-*b*-P2VP diblock copolymer template. We will discuss further the approach of varying the areal chain density (Σ) of PS-SH brushes on the PS coated particles, which utilizes the preferential wetting of one block of a copolymer (P2VP) on the Au substrate. Such favorable interaction provides the strong binding of Au particles to the PS/P2VP interface as Σ of PS chains on the Au particle decreases. We find that at Σ above a certain value, the nanoparticles are segregated to the center of the PS domains while below this value they are segregated to the interface. The transition Σ for PS-SH chains ($M_n = 3.4$ kg/mol) is 1.3 chains/nm² but unexpectedly scales as $M_n^{-0.55}$ as M_n is varied from 1.5 to 13 kg/mol. In addition, we will discuss changes in block copolymer morphology that occur as the nanoparticle volume fraction (ϕ) is increased for nanoparticles that segregate to the domain center as well as those that segregate to the interface, the latter behaving as nanoparticle surfactants. Small ϕ of such surfactants added to lamellar diblock copolymers lead initially to a decrease in lamellar thickness, a consequence of decreasing interfacial tension, up to a critical value of ϕ beyond which the block copolymer adopts a bicontinuous morphology. I thank my collaborators G. H. Fredrickson, J. Bang, C. J. Hawker, and E. J. Kramer as well as funding by the MRL as UCSB from the NSF-MRSEC-Program Award DMR05-20418.