

School of Materials Seminar

Tailoring 'Hairy' Nanoparticle Surfaces to Control Positioning in Block Copolymers

Edward Kramer

Professor, Materials & Chemical Engineering
University of California-Santa Barbara

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End-functional polymers grafted to form brushes on inorganic nanoparticles, the “hairy” nanoparticles of the title, provide useful fundamental test systems for block copolymer/nanoparticle self-assembly. Short thiol terminated polystyrene (PS-SH), poly(2-vinylpyridine) (P2VP-SH) and PS-*r*-P2VP-SH ($M \sim 3$ kg/mol) were synthesized to allow Au nanoparticles (~ 1.5 nm radius Au core) coated with polymer brushes to be prepared. The polymer brush coating enabled these nanoparticles to be incorporated at low volume fractions into PS-*b*-P2VP diblock copolymers with precise control over nanoparticle location, namely wholly within the PS or P2VP domains or segregated either strongly or weakly to the PS-*b*-P2VP interface. Such control is achieved with three different types of brushes on the Au nanoparticles: a.) High areal chain density (> 1.5 chains/nm²) mixed brushes of PS-SH and P2VP-SH with fractions $f_{\text{PS-SH}}$ of PS-SH ranging from 0 to 1; b.) High areal chain density brushes of PS-*r*-P2VP-_x-SH random copolymer with different x values; c.) Variable areal chain density brushes of PS-SH. For mixed brushes we find that the nanoparticles are segregated to the interface over a wide range (0.90 to 0.10) in $f_{\text{PS-SH}}$ while for the PS-*r*-P2VP-_x-SH random copolymer brushes x must be close to 0.5 before these segregate to the block copolymer interface. These results strongly suggest that the PS-SH and P2VP-SH ligands are mobile on the nanoparticle surface and phase separate in the 2D brush to form “Janus” particles that bind more strongly to the interface than those coated with random copolymer brushes. For the variable areal chain density brushes of PS-SH we find that at areal chain density above a certain value that increases with decreasing molecular weight M of the brush, the nanoparticles are segregated to the center of the PS domains while below this value they are segregated to the interface. The preferential interaction between the P2VP block of the PS-*b*-P2VP and the imperfectly shielded Au surface is responsible for the segregation of the nanoparticles with a low areal chain density brush to the interface. The transition areal chain density is $\sim 4/R_g^2$ for $M \sim 3$ kg/mol PS-SH where R_g is the radius of gyration of chains of $M = 3.4$ kg/mol but unexpectedly scales as $M^{-0.55}$ when M is varied. Along with suggesting an explanation for this scaling law, I will discuss the 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.

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² B.J. Kim, J. Bang, C.J. Hawker and E.J. Kramer, *Macromolecules*, **39**, 4108-4114 (2006)

³ B.J. Kim, J.J. Chiu, G.-R. Yi, D.J. Pine, and E.J. Kramer, *Adv. Materials*, **17**, 2618-2622 (2005).

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⁶ B.J. Kim, G.H. Fredrickson, and E.J. Kramer, *Macromolecules*, **41**, 436-447 (2008).

⁷ B. J. Kim, S. Given-Beck, J. Bang, C.J. Hawker, E.J. Kramer, *Macromolecules*, **40** 1796-1798 (2007).

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