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Quasi-Two-Dimensional Assembly of Bottlebrush Block Copolymers with Nanoparticles in Ultrathin Films: Combined Effect of Graft Asymmetry and Nanoparticle Size

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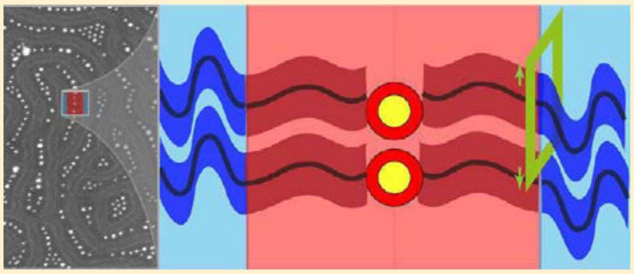
Supporting Information

ABSTRACT: Block copolymer guided assembly of nanoparticles leads to the formation of nanocomposites with periodic arrangement of nanoparticles, which are important for applications such as photonic devices and sensors. However, linear block copolymers offer limited control over the internal arrangement of nanoparticles inside their hosting domains. In contrast, bottlebrush block copolymers possess unique architectural attributes that enable additional ways to control the local organization of nanoparticles. In this work, we studied the coassembly of 8 and 13 nm gold nanoparticles with three bottlebrush block copolymers differing in the asymmetry of their graft lengths. Assembly was performed in ultraconfined films, where it occurs quasi-two-dimensionally. Our results indicate that graft asymmetry could be used as an additional tool to enhance nanoparticle ordering by forcing them to localize at the center of the domain regardless of their size. This behavior is analyzed in terms of the influence of the graft asymmetry on the average conformations of the blocks.



INTRODUCTION

Metal and semiconductor nanoparticles (NPs) possess unique physical properties, which derive from their chemical composition, size, and shape.[1,2] The collective properties of an ensemble of NPs are influenced by coupling interactions between adjacent NPs[3−6] and are also sensitive to the geometry of NP organization within the superstructure. For example, NPs organized in parallel layers exhibit enhanced light absorption,[7] behave as photonic crystals,[8,9] and display nonlinear optical properties,[10] whereas assembling NPs in a chainlike fashion enables tuning the wavelength[11,12] and creating plasmon waveguides.[13−17]

One of the most promising approaches for organizing NPs into ordered superstructures relies on the utilization of block copolymers (BCPs) as organizing matrixes. BCPs are composed of chemically distinct sequences (blocks) and form periodic, nanoscale structures because of microphase separation. The bulk periodicity of the block copolymer (typically in the range 10−100 nm) depends on the polymer molecular weight, and the bulk morphology is dictated by the volume fractions of the blocks. Mixing BCPs with NPs that have been modified with surface ligands that make them compatible with one of the BCP blocks leads to inherently ordered nanocomposites, in which the NPs are organized in alternating domains.[18,19]

Various parameters influence the organization of NPs in the BCP matrixes. Simulations performed by Balasz et al. have shown that large NPs segregate to the center of the domains whereas small NPs are more evenly distributed throughout the domain.[20] This result was explained by the large entropic penalty associated with the need of the block to circumvent a large NP compared to circumventing a small NP. Experimental findings corroborate these conclusions.[21−24] Kramer et al. have demonstrated that the distribution of the NPs across the domains becomes narrower at high filling fractions; this distribution was explained based on similar arguments.[25] Tuning the chemistry of the ligands protecting the nanoparticles provides a more controllable way to influence NP location.[2,26−29] For example, covering the NPs with a polymeric ligand that is identical in chemical composition to one of the blocks makes these NPs compatible with that block and thus directing them to the corresponding domains; functionalizing NPs with a mixed monolayer can be used to direct the NPs to the interface between the domains.[26,27]

The inclusion of NPs influences the nanocomposite periodicity by swelling the hosting domains. Ausserré et al. have shown that the lamellar periodicity increases linearly with NP filling fraction.[30] At high filling fractions, it may also alter the nanocomposite morphology.[29,31−33] In thin films, the inclusion of NPs often leads to perpendicular orientation of the

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