

Studies of Dispersion and Self-assembly of Grafted Nanoparticles in Polymeric Systems

Supriya Gupta

Abstract

Incorporation of small amount of nanoparticles in polymers results into phenomenal improvement in material properties when at least one dimension of the particles is smaller than the size of polymeric chains. The nano-scale of particles ensures that large fraction of polymer segments is in contact with the particles to bring out the synergistic interaction between the constituents leading to dramatic enhancement in material properties. The dispersion of nanoparticles in polymer matrix is achieved by inducing steric repulsion realized by grafting polymeric chains on particles. The first part of the present study addresses the dispersion of clay nano-sheets grafted with polymeric chains in a matrix of varying architecture. With the help of self-consistent field theory, we construct the distance dependent inter-particle interaction potential between a pair of nano-sheets grafted with polymeric chains dissimilar to the matrix polymer with respect to either chain size, chain architecture or chemical structure. Upon replacing linear polymeric chains of the matrix polymer with multi-armed star polymer of same degree of polymerization, the strength of attraction is found to be weakened and is completely eliminated for high degree of branching. The compactness of star molecule overcomes the entropy driven depletion between nano-sheets leading to wetting of brush with purely repulsive potential, an indicative of exfoliated dispersion. Thus, the clay sheets can be better dispersed in a star polymer compared to linear polymer matrix.

Beyond dispersion, the controlled self-assembly of nanoparticles in a polymer matrix offers a great potential to produce highly ordered nanostructures with far superior opto-electronic properties. The templated ordering of nanoparticles is increasingly gaining attention to produce advanced nano-materials with wide ranging technological applications. Block copolymers, by virtue of their fascinating ability to self-organize to yield plethora of interesting ordered phases, provide ideal templates to achieve particle ordering. Using self-consistent field theory, we examine the self-assembly of polymer grafted spherical nanoparticles in lamellar mesophase of symmetric ABA triblock copolymer. The localization behaviour of B-grafted nanoparticles is found to be qualitatively different from that of the A-grafted particles. In particular, the absence of free ends and the bridge conformation of mid-block tend to reduce the spatial segregation of B-grafted particles at the center of B-domain and promote segregation of particles at the domain interface, a behavior in contrast to AB diblock copolymer. The spatial localization of particles, governed by the interplay of enthalpic and entropic contributions to the free energy, is found to be strongly influenced by particle size, selectivity, volume fraction, and number & size of grafted chains.

Physical confinement of block copolymers plays an important role in generating a rich variety of novel ordered phases not seen in bulk systems. These novel ordered microstructures, arising mainly out of structural frustration and confinement-induced entropy loss, are ideal templates to self-assemble nanoparticles. For a mixture of diblock copolymer and grafted nanoparticles, the morphology under cylindrical pore confinement and ensuing particle ordering are studied in both two and three dimensions. Various equilibrium morphologies are observed depending upon the degree of confinement, particle loading, density of grafted segments and selectivity

of particle core to the polymeric species. The curvature of the circular pore strongly influences the localization behaviour of particles. Further, the physical confinement produces, apart from concentric lamellar and cylindrical phases, some interesting 3-d structures like helical ordering. Incorporation of spherical nanoparticles grafted with polymer chains chemically identical to the helical block leads to helical ordering of nanoparticles. Such chiral structural motifs generated from achiral polymeric molecules are fascinating due to superior performance in sophisticated optical functions. The roles of confinement size, particle load and grafting density in self-assembly behaviour of nanoparticles and ensuing microstructure are examined.

In order to generate novel multicomponent helical structures, block copolymers with topologically complex architectures, like three-armed ABC star polymer and four-armed ABCD star polymer are also investigated for their equilibrium states under cylindrical nanopore confinement. ABCD star tetrablock copolymer exhibits rich self-assembly behaviour with myriads of three-dimensional ordered phases ranging from one, two and three components helices to honeycomb structures depending upon the block fractions and the size of cylindrical nanopore. The comprehensive understanding of the self-assembly behaviour enables one to design novel nanostructured materials with desired material properties.