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Polymer Nanocomposite Films: Dispersion of Polymer Grafted Nanorods and Optical Properties[1]

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The thermodynamic factors that affect the dispersion of polymer-brush grafted gold nanorods (NR) in polymer matrix films have been studied by experiment and theory. When brush and matrix have a favorable interaction, such as poly(ethylene oxide) (PEO)-NR/ poly(methyl methacrylate) (PMMA) and polystyrene (PS)-NR / poly(2,6-dimethyl-p-phenylene oxide) (PPO), nanorods are uniformly dispersed. For PEO-NRs in PMMA, the NRs are regularly spaced and well dispersed, independent of the ratio of the degree of polymerization of the matrix (P) to that of the brush (N), namely P/N. As the NR volume fraction increases, the local orientation of the nanorods increases, whereas the macroscopic orientation remains isotropic. When the brush and matrix are similar (i.e., PS-NR / PS and PEO-NR / PEO), the nanorods randomly disperse for $P/N < 2$ (i.e., wet brush), but align side-by-side in aggregates for $P/N > 2$. UV-visible spectroscopy and discrete dipole approximation (DDA) calculations demonstrate that surface plasmon coupling leads to a blue shift in the longitudinal surface plasmon resonance (LSPR) as P/N increases. For $P/N > 2$, self-consistent field theory (SCFT) calculations and Monte Carlo (MC) simulations indicate that nanorod aggregation is caused by depletion-attraction forces. Starting with a dry brush system, namely, a PS matrix where $P/N = 30$, these attractive forces can be mediated by adding a compatibilizing agent (e.g., PPO) that drives the NRs to disperse. Finally, dry and wet brush behavior is observed for NR aspect ratios varying from 2.5 to 7. However, compared at the same volume fraction, long rods for the dry case exhibit much better local order than lower aspect ratio nanorods, suggesting that long rods may exhibit nematic-like ordering at higher loadings.