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USING POLYMER BRUSHES TO TUNE THE STRUCTURE-PLASMONIC RELATIONSHIP IN POLYMER NANOCOMPOSITES CONTAINING NANORODS

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The thermodynamic factors that affect the dispersion of polymer-brush grafted gold nanorods (NRs) added to polymer matrix films have been studied by experiment and theory. When the brush (degree of polymerization N) and matrix (degree of polymerization P) have a favorable interaction (enthalpy driven), NRs uniformly disperse in the matrix, independent of P/N. When the brush and matrix are chemically similar, NRs randomly disperse for P/N < 2 (i.e., wet brush), but align side-by-side for P/N > 2. UV-visible spectroscopy is used to investigate the structure-optical property relationship as function of P/N. For P/N > 2, self-consistent field theory (SCFT) and density functional theory (DFT) indicate that NR aggregation correlates with rod-rod interactions greater than -5kT. As NR aspect ratio (AR) increases, dry and wet brush behavior is observed for ARs from 2.5 to 6.3. For P/N < 2, long NRs exhibit much longer range local order than short NRs and corresponding strong blue shift in the longitudinal surface plasmon resonance (LSPR). Chemically mixed brushes on NR surfaces provide another means to tune NR dispersion. To induce end-to-end linking, Au NRs are selectively functionalized with dithols and peptides to create permanent and revisable linking as well as a red shift in the LSPR.