Dewetting Kinetics in Polymer Grafted Nanoparticle Thin Films: Impact of Architecture and Viscosity on Thermal Stability

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— Rapid formation of ordered monolayers of polymer grafted nanoparticles (PGN) directly onto solid surfaces has spurred interest in using these materials for additive manufacturing of optical devices and energy storage. Herein, we discuss dewetting of polystyrene grafted Au nanoparticles (PS@Au) with an increased thermal (10-25°C) and energetic (5-15 mN/m) stability relative to linear polymer films of comparable thickness. Analogous to star macromolecules, the enhanced stability is related to the conformations of chains in the grafted canopy. Mechanistically, dewetting of PS@Au is similar to linear PS, however, the thickness transition from spinodal to heterogeneous nucleation is at least 5-6x larger. Time resolved optical microscopy during dewetting at 160°C revealed that the zero shear viscosity for linear PS scaled as \( \eta_0 \sim M_n^{3.3} \), consistent with reptation of entangled polymers. In contrast, PS@Au showed \( \eta_0 \sim M_n^{2.2} \) where \( M_n \) reflects the molecular weight of the grafted chains. Overall, PS@Au exhibited significantly slower dewetting rates, consistent with a ~100x increase in viscosity relative to the linear chain analogues. Quantification of the relationship between PGN architecture (e.g. nanoparticle size, graft density, polymer molecular weight) and dewetting processes is crucial to optimize the order of these assemblies via post-processing, as well as design the PGN canopy to maximize stability for devices.

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