Fully Stretched to Collapsed: Bottlebrush Polymer Grafted Nanoparticle Materials

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Abstract: Hybrid materials composed of polymers and inorganic nanoparticles have been utilized for their unique ability to marry the differing properties and functionalities of each component into one system. Material design of these hybrids has featured polymer grafted nanoparticles (PGNs) due to their ability to control nanoparticle assembly, which is vital to material performance. However, work on PGNs has been primarily limited to linear chains from glassy polymers, which narrows the scope of potential applications. This work diversifies both the polymer architecture and chemistry using surface-initiated ring opening metathesis polymerization (SI-ROMP) to produce bottlebrush polymer grafted nanoparticles. Bottlebrush polymers present unique properties from linear chains due to the high density of side chains causing extended conformations that result in high entanglement molecular weight and super soft materials. Through an array of characterization, the polymer brush confirmations on the particle surface were found to have extreme differences dependent on the sample conditions. For PGN's in solvent, the brushes were highly extended with lengths that scale with increasing polymer molecular weight. Meanwhile, in the melt, the PGN brushes collapse onto the particle surface. These findings offer valuable insight on potential bottlebrush PGN materials as brush height and polymer chain conformation effect final material properties and applications. Potential bottlebrush PGN materials of interest feature diblock polymer chains for potential uses in thermoplastic elastomers. Sequential SI-ROMP produced a bottlebrush poly(dimethyl siloxane)-block-bottlebrush poly(ethylene oxide) grafted silica nanoparticle which resulted in a single-component PGN system with chewing gum-like mechanical properties. Ultimately, our methods afford tunability of chemistries and bottlebrush parameters, creating new avenues to realize modular hybrid materials with specialized properties for consumer and industrial applications.