

## Development of advanced hybrid polymer/inorganic nanoparticles using surface-initiated ring-opening metathesis polymerization

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Polymer/inorganic nanoparticle hybrids are potential candidates for designing advanced materials due to the nanoparticle's ability to reinforce or add inorganic functionality to the polymer matrix. However, thermodynamics of mixing will govern the nanoparticle dispersion state within the matrix, and can effectively dictate the degree of material performance and processability. As a solution, an effective method for tuning dispersion in hybrid materials is to graft polymer chains from the particle surface to desirably interact with the polymer matrix. Several successful surface-initiated polymerization techniques are commonly used, but their chemistries typically yield linear styrene or acrylate-based grafts that are limited in miscibility and reactivity within commercial grade materials and processes. To assess the potential of polymer-grafted nanoparticle (PGNP) components within polyolefin and other semi-crystalline materials, the synthetic toolbox of surface-initiated polymerizations needs to be expanded. The work here presents a surface-initiated ring-opening metathesis polymerization (SI-ROMP) technique that was developed to graft unsaturated backbones from silica nanoparticle surfaces. The versatility of ROMP and the resulting polyolefin grafts enable new opportunities for functionality in PGNP components. Through the use of size exclusion chromatography, dynamic light scattering, thermal analysis and transmission electron microscopy, structural and thermal properties of poly(norbornene)- and poly(cyclooctadiene)-grafted nanoparticles can be quantified. The technique can also be implemented to produce PGNPs with chemistries that can be used in in situ polymerizations, hydrogenated to achieve semi-crystalline poly(ethylene)-grafted nanoparticles, or functionalized to create non-linear bottlebrush architectures. These new graft properties present desirable chemical, thermal and structural properties in PGNPs that cannot be easily replicated with traditional methods and are useful for fundamental investigations in novel hybrid systems.

