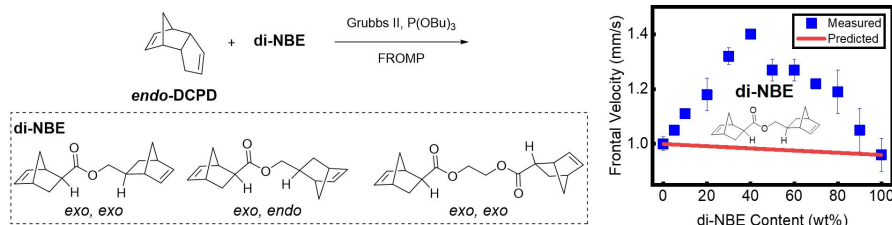


Confronting Rule of Mixtures in Frontal Ring-Opening Metathesis Polymerization

Huiying Liu and Jeffrey S. Moore

Frontal ring-opening metathesis polymerization (FROMP) is a class of autocatalytic reaction that rapidly transform monomer to polymer upon a small thermal stimulus. Dicyclopentadiene (DCPD) and norbornene (NBE) are excellent candidates for FROMP because of their high ring strain. While copolymerization of two monomers generates a material with properties predicted by the rule of mixtures, we find that copolymerization with di-NBE compounds does not conform to the rule. Instead, as di-NBE cross-linker content increases, the reaction shows a non-monotonic increase in frontal velocity. We hypothesize that the proximity of two reactive norbonenyl rings results in this unusual behavior. This study not only provides mechanistic insight into bulk polymerization at high temperatures, but also guides new monomer design in FROMP.



Lewis Base Catalyzed, Enantioselective, Intermolecular Sulfenoamination of Olefins

Aaron Roth and Scott E. Denmark

A method for the catalytic, enantioselective, intermolecular sulfenoamination of various olefins has been developed using a chiral BINAM-based Lewis base catalyst. Styrenes and *trans*-disubstituted alkenes afford the corresponding vicinal disubstituted products in high yields and high enantiomeric ratios via enantioselective formation and subsequent stereospecific capture of a thiiranium intermediate with anilines and benzylamines. The use of hexafluoroisopropyl alcohol as solvent allows for broad functional group tolerance.

