

Redox-switchable catalysts for the controlled polymerization of cyclic esters

Alicia Doerr¹, Lauren Brown¹, Justin Burroughs¹, Nicholas Legaux¹, and Brian Long¹

1. University of Tennessee Knoxville, Knoxville, Tennessee, United States

The field of redox-switchable catalysis has gained considerable interest in recent years, enabling catalytic reactivity/selectivity to be oscillated based on the redox-state of the ligand or active metal center. Unfortunately, though a myriad of redox-switchable catalysts have been developed for the ring opening polymerization of cyclic esters, very few fundamental structure-catalytic performance studies have been conducted that ascertain how systematic changes in ligand structure affect the catalytic performance. Herein, we will describe our studies to determine how changes in the placement and number of redox-active moieties, ligand denticity, and active metal center identity impacts the catalytic performance. We will compare group IV metal centered catalysts bearing symmetric, tetradentate [ONNO] ligands with two redox-active moieties distal to the active metal center to related catalysts bearing either symmetric, tetradentate [ONNO] ligands with one redox-active moiety in close proximity to the active metal center or asymmetric, tridentate [ONN] ligands featuring a single redox-active moiety distal to the active metal center. The results of these studies reveal that the proximity of the redox-active moiety to the active metal center may influence both catalyst activity and redox-switchability. Conversely, the number of redox-active moieties present within the ligand scaffold may not play a crucial role in the catalysts' switchability. Lastly, when Ti-/ Zr-centered analogues of these catalysts were compared it was revealed that the choice of metal center may dramatically influence both catalyst activity and redox-switchable.

