

Photoredox mediated cross metathesis for molecular weight control in ring-opening metathesis polymerization

Rachel Tritt¹, Victoria Kensy², Fariyah Haque³, Daniel Knorr⁴, Scott Grayson³, and A. J. Boydston¹

1. University of Wisconsin-Madison, Middleton, Wisconsin, United States
2. University of Washington, Seattle, Washington, United States
3. Tulane University, New Orleans, Louisiana, United States
4. US Army Research Laboratory, Aberdeen, Maryland, United States

We have explored and established conditions for the synthesis of targeted, low molecular weight polymers in metal-free ring-opening metathesis polymerization (MF-ROMP) by utilizing the ability of terminal alkenes to do cross metathesis with the radical cation chain end. This method using alkenes as chain transfer agents has facilitated the synthesis of norbornene polymers with average molecular weights between 30 and 1 kDa. Set up and execution of the reaction are both simple and prediction of molecular weights is straightforward. The structures of final polymer end groups were successfully identified using MALDI-TOF MS and NMR spectroscopy and were shown to be consistent with efficient chain transfer and reinitiation. Furthermore, mechanistic investigations revealed high regioselectivity of the chain transfer event. This procedure has also been successfully used on multi-gram scales, as well as with functionalized norbornene copolymers for materials applications.

