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Polyolefins as homogeneous supports of ruthenium based olefin metathesis catalysts

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Olefin metathesis is a powerful tool in C-C double bond formation having numerous applications in polymer chemistry and material science. Ring-opening metathesis polymerization (ROMP) and ring-closing metathesis (RCM) in particular are versatile methods for the synthesis of functional materials. Ruthenium-based Grubbs and Hoveyda-Grubbs catalysts are certainly the most popular complexes in the field of olefin metathesis. Unfortunately, only a limited number of studies have been conducted where both recycling and ruthenium waste content are examined. Moreover, numerous papers do not report on the levels of contamination in the product, which clearly is a drawback when developing olefin metathesis for industrial procedures. The separation of the polymeric product and the catalyst is one of the major challenges facing metathesis polymerization. This process currently requires extra steps or additional chemical processes. Alternative processes that avoid a second process step, thus remain of interest. We will discuss our latest results using homogeneous polymer-supported ruthenium catalysts. These include different generations of the Grubbs and the Hoveyda-Grubbs complexes. Our approach uses a scheme in which the solubility of the Ru catalyst byproducts is differentiated from the solubility of the product polymer. This strategy employs soluble polymer-supported NHC-ligated Ru catalysts and a liquid/liquid biphasic separation of catalyst residues from the polymer products after a reaction. We will then discuss the activity of these catalysts in a series of ring opening metathesis polymerizations yielding high-molecular weight polymers with narrow polydispersities.

Recent publications

1. Hlil A R, Balogh J, Moncho S, Su H L, Tuba R, Brothers E N, Al Hashimi M and Bazzi H S (2017) Ring opening metathesis polymerization (ROMP) of five- to eight-membered cyclic olefins: Computational, thermodynamic, and experimental approach. Journal of Polymer Science Part A: Polymer Chemistry, 55:3137-3145.
2. Balogh J, Hlil A R, El Zoghbi I, Rafique M G, Choukhi D, Al Hashimi M and Bazzi H S (2017) Phase-separable polyisobutylene palladium-PEPPSi precatalysts: synthesis and application in Buchwald-Hartwig amination. Macromolecular Rapid Communications, DOI: 10.1002/marc.201700214.
3. Suriboot J, Hu Y, Malinski T J, Bazzi H S and Bergbreiter D E (2016) Controlled ring-opening metathesis polymerization with polyisobutylene-bound puridine-ligated Ru(II) catalysts. ACS Omega 1(4):714-721.
4. Hlil A R, Moncho S, Tuba R, Elsaid K, Szarka G, Brothers E N, Grubbs R H, Al Hashimi M and Bazzi H S (2016) Synthesis and catalytic activity of supported acenaphthoimidazolylidene N-heterocyclic carbene ruthenium complex for ring closing metathesis (RCM) and ring opening metathesis polymerization (ROMP). Journal of Catalysis 344:100-107.
5. Tuba R, Balogh J, Hlil A, Barlog M, Al Hashimi M and Bazzi H S (2016) Synthesis of recyclable tire additives via equilibrium ring-opening metathesis polymerization. ACS Sustainable Chemistry & Engineering, 4(11):6090-6094.

Biography

Hassan S Bazzi is the Associate Dean for Research and Professor of Chemistry at Texas A&M University at Qatar, a branch campus of Texas A&M University. He received his Bachelor's and Master's degrees in Chemistry and Organic Chemistry, respectively, from the American University of Beirut in 1996 and 1998 and his PhD in Polymer Chemistry with Dean's Honor List from McGill University in 2003. He worked briefly with the United Nations as a Chemical Weapons Inspector in Iraq before doing a Postdoctoral Research Fellowship at Université de Montréal. He joined Texas A&M at Qatar as Assistant Professor in 2004, was promoted to Associate Professor in 2009 and then to full Professor in 2014.

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