

**Theoretical Study of the Mechanism of Olefin Metathesis and Synthesis  
of Cyclic Polymers**

Thesis by  
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## Abstract

The research presented in this thesis focuses on the study of the metathesis reaction and applications to synthetic polymeric structures. More specifically, how targeted changes in the polymerization reactants and catalyst provide very unique and useful macromolecular architectures.

Chapter 1 describes the synthesis of acetoxy end-functionalized polynorbornenes. By introducing 1,4-bis(acetoxy)-2-butene as chain transfer agent (CTA) during a Ruthenium mediated ring opening metathesis polymerization (ROMP) of norbornene (NBE), the respective end-functionalized polymers with molecular weights controllable up to 30 kDa could be obtained in high yield.

Chapter 2 describes a new synthetic route to cyclic polymers and their characterization. In this approach, the ends of growing polymer chains remain attached to a cyclic Ru catalyst throughout the entire polymerization process. This effectively excludes all types of linear intermediates, which were a major drawback of previous approaches to cyclic polymers.

Chapter 3 describes the synthesis of cyclic poly-butadiene and the importance of the monomer purity. Techniques for characterizing and determining the purity of cyclic polymers are also discussed.

Chapter 4 describes a quantum mechanical (QM) study of the mechanism of chloride isomerization of a ruthenium metathesis catalyst with density functional theory (DFT) with the B3LYP hybrid functional. This isomerization is relevant to the mechanism of metathesis and it serves as validation to further studies of the mechanism with the same method.

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