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

Thesis by

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Acknowledgments

Without a doubt, the person that has had the biggest impact on how I lived for the last several years is my advisor, Professor Bob Grubbs. Early on, I realized that I don't think there is an environment where I could have enjoyed learning and doing chemistry among other things any more than with Bob. Through the years, he has managed to create a self-sufficient system, where highly creative individuals thrive in what could be described as a rich growing medium of ideas. I got to experience the 'Grubbs group' at a fabulous time since I pretty much arrived at the same time as the "Sheng Ding" catalyst.

Realistically, this has all been possible thanks to Professor Jack Roberts which led me across the hall from his office to talk to Bob for the first time. I will always be grateful to 'Big John' for opening the doors to Caltech just after finishing the first term as a junior undergraduate. I am also thankful to the SURF program since without it, I wouldn't be where I am now. Way back, as I started my undergraduate studies in Mexico, I knew of 'Grubbs metathesis' as a magic reaction that could do things never before thought possible. Given my interest in elementary particle physics and quantum field theory, I applied for a SURF at Caltech with Jack Roberts. A week before the end of the SURF program and only a few weeks before the first day of classes at UCLA as an exchange visitor, I applied to graduate school (Jack Roberts idea) and got accepted in about three days. Since I was pretty sure of the type of chemistry that I wanted to pursue, Jack walked me across the hall to meet Bob for the first time. Bob suggested talking to "Chris" since I said I was interested in polymers and this was the beginning of a very fruitful friendship.

Even though the closest member of my family lived 2500 miles away, I always had any kind of support I needed. They often visited or invited me on short trips wherever they went on vacation. In a special place is my dear cousin Sergio Echeverria with whom I traveled often and was a regular at Bob's parties.

I have been fortunate to interact with Bob, not only in a professional way, but also at a personal level. I considered them as my "host family" since I had great times out especially when Brendan, Barney and Katy were around. Helen is a wonderful person that cared for me a lot and I will always be grateful with. I enjoyed being the self-proclaimed "Grubbs high-quality tequila provider" and every time I brought in a new and sometimes different bottle, Helen and Bob would tell me what people had to say about the last bottle. I would then relay notes to my mother, who was serving as the Sommelier and source.

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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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