Acknowledgments

Firstly and the most importantly, I would like to thank God who have wonderful plans for me and have guided me to here at this moment. He has kept me strong and focused so that I would not go wrong. I praise the Lord who would continue to do so until the end day comes.

I must thank my family, my dad who supported me on every decisions I made, my mom who loved me unconditionally from the beginning, my older sister who was always proud of me and cared about me, and lastly my younger sister who sometimes behaves like a trouble maker and may appears to be inconsiderate to us but I know inside her, she cares about our family. Without the presence of my family, Caltech graduate school would be much harder.

I am very grateful to Bob, my advisor for taking me as his student. I got to learn the rich chemistry of olefin metathesis, and its importance, I got to realize only when I became the senior graduate student. He gave me freedom to work on any projects and he paid a great attention and gave great guidance so that I could get my degree. I would like to thank Prof. Brian Stoltz for allowing me to have him as the last committee member. Things got much easier.

Now it’s time to thank Grubbs’ group. I am fortunate to have talented students and post docs as my labmates, and they were just wonderful. The greatest thank goes to Dr. Arnab Chatterjee who introduced cross metathesis reaction to me. With this knowledge I was able to apply it to the synthesis of many different molecules. I would like to thank Dr. Mat Sholl and Dr. J. P. Morgan who helped me at the beginning of my career in Grubbs’ group. I would like to thank Dr. Steve Goldberg, Prof. Dean Toste, and

Prof. Justin Gallivan who created amazingly nice environment at 130 Church. I would like to thank successors of 130 Church, Andy, Jacob, Irina, and Diego for nice working environment.

I would like to thank Dr. Chris Bielawski, Oren, Dan, and Isaac for their helpful discussion about polymer chemistry. With their help, I learnt a lot about polymers from the synthesis to characterizations. I would like to thank all the Grubbs' group members for their helpful discussion and suggestion, especially those who have done painful job of proof-reading my papers, candidacy, proposal and the final thesis. It's pretty much every one of them.

I would like to thank Mona for MALDI, Dr. Chi for SEM, Dr. Hwang for solid-state NMR, Steve from Davies' groups for DLS, Dr. J. J. Lee for AFM, Carol for TEM and S. Y. Lee for XRD.

Special thanks go to our Korean chemists in the group, Dr. Choon Woo Lee, Dr. Hyunjin Kim, Dr. Jaesook Yun, and Soonhyuk Hong. Without them, I would be really bored, and lost, especially Choon Woo, who was like a counselor to me. We would talk about science, life, religion, sports and what not.

Lastly, I would like to thank Caltech Korean gangs whom I played sports, games and all source of other fun events. Especially, 'Be the Reds', the Korean softball team was awesome. I hope you guys beat 'Jerry's Kids' next time.

Well, there are too many people I have to thank, church people, KCCC friends and all those post docs who took care of me. That includes Prof. Sukbok Chang and Prof. Soyeob Han. Wow, just too many, I will stop here. Pasadena, I must leave you now. What a memory I have during the last 50 months of my staying at Caltech!

Abstract

In olefin metathesis, the designing of better catalysts has been the key to the success of its utility. Throughout the history of olefin metathesis research, the development of new and improved catalysts has brought new applications and new structures that are accessible by olefin metathesis routes. With the development of highly active catalyst containing an N-heterocyclic carbene, the field of olefin metathesis is currently in a period of renaissance opening up the versatile synthesis of both small organic molecules to macromolecules. Following four chapters describe recent applications toward the synthesis of molecules with various sizes.

Chapter 2 describes selective CM of various of α,β-unsaturated carbonyl compounds such as acrylic acid, acrylic amides, and vinyl phosphonate with terminal olefins and stryenes. For CM of acrylic amides, an interesting chelation effect which reduced the olefin metathesis activity of the catalyst containing an N-heterocyclic carbene was observed for electron rich amides. Also direct generation of enoic carbenes by catalyst was possible from acrylates, acrylic acid and vinyl ketones. Enoic carbenes were shown to catalytically ring-open cyclohexene for the first time. Chapter 2 also provides examples of challenging CM between Type II and Type III olefins.

Chapter 3 demonstrates facile tandem RCM strategies to rapidly synthesize complex small molecules by the catalyst containing an N-heterocyclic carbene. Tandem ring-opening/ring-closing metathesis and tandem enyne RCM provided bicyclic compounds with good yields. An example of bicyclic macrocycle is presented. Lastly tandem ring-opening/cross/ring-closing metathesis, also known as ring expansion metathesis (REM), provided a convenient route to various macrocycles from the smaller cycloalkenes.

Chapter 4 introduces a new concept of metathesis polymerization, multiple olefin metathesis polymerizations (MOMP). MOMP uses more than one olefin metathesis process to synthesize polymers with uniform polymer microstructures. Ring-opening insertion metathesis polymerization (ROIMP) combines ROMP and CM process to yield highly A,B-alternating copolymers. Also ring-opening/ring-closing polymerization and ring-opening/closing addition polymerization were demonstrated.

Final chapter explores living ROMP of norbornene and its derivatives with a new ultra-fast-initiating catalyst. The modified catalyst produced the polymers with very narrow PDI and the monomers which used to be problematic with the previous catalysts also underwent living ROMP. Also amphiphilic block copolymers were prepared and shown to undergo spontaneous self-assembly in the reaction solution to produce stable nanoparticles even without cross-linking. Nanoparticles of 10 to 50 nm in radius were characterized by GPC, DLS and SEM.

In summary, this thesis describes the versatility of ruthenium catalysts being able to produce small molecules, macrocyles, polymers, and even supramolecules. Molecules that are described in the thesis have molecular weights ranging from 100 to 2 million g/mol, and the reactions to prepare those molecules with various sizes are fundamentally and mechanistically one transformation, the exchange of C=C bonds. This is a success story of how interdisciplinary efforts from organic, organometallic, and polymer communities have brought the new concept to chemical synthesis.

Table of Contents