# Syntheses of Polymers with Diverse Architectures via Metathesis Polymerization and Investigation of Their Structure-Property Relationships

Thesis by

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In Partial Fulfillment of the Requirements for the

Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

2010

(Defended on April 19, 2010)

For Mom, Dad, and my Wife

## Acknowledgements

Many people asked me “what do you like about Caltech best?” After nearly five years, I give my short answer without hesitation: “The People!” It is all the wonderful people at Caltech that make it the world’s best place to explore science and made my time here truly unforgettable.

My advisor, Bob Grubbs, has been giving me the total freedom to pursue my interests on some projects that are quite nontraditional in the Grubbs group, yet providing his complete support whenever it is needed. I have been constantly impressed by his broad interest, deep knowledge, and repetitive enthusiasm. (As he said, when you get older and more forgetful, you can get excited about the same thing many times.) His often brief yet insightful and encouraging advice has taught me to think with the big perspective, and the much longer stories almost always following his scientific advice (often about the history of certain chemistry or about his outdoor adventure) have definitely been the best delightful reliefs when I was stressed with not-going-well projects. Outside the lab, the Grubbs camping trips have allowed me to enjoy more American culture; the Christmas dinners with his family have always made me feel I have a home away from home.

“Thank you, Bob!” for providing all these to shape me into an independent researcher and to give me the confidence to challenge myself in the future.

Julie Kornfield has been my coadvisor, and she has a completely different character from Bob. She is definitely the smartest and the most critical lady I have ever seen. Being both means that she will NEVER let it go if I try not to be meticulous in

research. With her training, I will not be afraid of any scientific criticism in the future. On the other hand, she is also a very caring person, always putting others' personal needs/feelings first. From her, I have learned to consider things from the angles of others.

I have also been blessed by an excellent committee: Dave Tirrell, Mark Davis, and Jim Heath. They are all wonderful scientists as well as mentors, and their knowledge pretty much covers the full range of chemistry and materials science, which is sometimes scary as I talk to them about my prop ideas and my research. I have also used certain equipment from all three labs for free at some point of my graduate research (sometimes it can be as long as over a year) and they never seemed to mind. Many members from these groups have also provided me with generous help on training and discussions about my need.

In the Grubbs group, I have had the privilege to work with AJ Boydston for three years on the tough yet enjoyable journey of making cyclic polymers. Since day one, I have been impressed with his outside-the-box thinking, vast chemistry knowledge, and incredible efficiency in everything, ranging from finishing up a reaction to writing up a proposal to setting up a science party for his lovely kids. I also owed him half a tooth on the basketball court. Being an absolutely outstanding scientist and such a fun person to work with, he has become my best friend and a role model for doing research. I am sure he will have a stellar career at the University of Washington soon.

I also had the fortune to work with many other members in the polymer sub-group: Masao Yanagawa and Ron Walker first taught me how to ROMP, although Ron seemed to be more interested in Louisiana and Chinese culture, and he also helped me buy a nice car with his good knowledge of cars (although I had to get the transmission fixed two

months after I bought it). John Matson, “beef”, has been the most polymer person in the group during my time in the Grubbs group, and our basketball coach for a while. John and Ron have also been fixing the clogged GPC tirelessly during the time I had to work with multimillion molecular weight polymers. I really appreciate the effort from both of you! Paul Clark, a professional fisherman and a chemist, is in my year. He has a truly selfless heart and neat skills for kilogram-scale reactions. I look forward to working with him again in a few months. Erin Guidry was the rotaxane master in the group; Mike Page is the happiest person I have seen; Irina Gorodetskaya introduced the cyclic polymer project to me; Rose Conrad is great sources for synthetic chemistry; Jeremiah Johnson is the most hipster chemist I have met with lots of wild ideas. I am happy that Benjamin Sveinbjornsson is going to carry the torch of brush polymers.

The Grubbs group is never short of talents. I have had interactions with other excellent fellow students Jason Jordan, Soon Hong, Donde Anderson, Matt Whited, Kevin Kuhn, Jean Li, Chris Daeffler, Keith Keitz (Thank you for taking good care of the vulnerable “Flory”!), Matt Van Wingerden, Renee Thomas, and Myles Herbert; as well as fabulous postdocs with diverse backgrounds: Cheol Chung, Georgios Vougioukalakis J. B. Bourg, Koji Endo, Vince Lavallo, Peili Teo, and Guangbin Dong. I would like to thank them for all their friendship and help!

Rafael Verduzco was a senior grad student when I worked in Julie’s lab in my first year. He introduced me to basic polymer physics, especially liquid crystal polymers and rheology, and never hesitated to offer his help to get me started. More importantly, he taught me how to communicate with chemical engineers. I look forward to his future

success. I also had many happy chats with Matt Mattson, Ameri David, Zuli Kurji, and Jeremy Wei in Julie's lab.

Brad Olsen was a joint postdoc in three (!) groups at Caltech, but we got to know each other quite a while before he came to Caltech. He is an excellent scientist, mentor, and coworker. He offered tremendous help on the characterization of the brush copolymers, and taught me about almost all aspects of the physics of block copolymers. Without him, Chapter 5 of this thesis would not be complete. I am sure he will have an outstanding independent career and become a rising star in the field of polymer science.

There are so many more wonderful people that I cannot list all their names with the fear that I will forget some. Thank you all of you!

Outside Caltech, I would like to acknowledge our long-time collaborator, Professor Greg McKenna and his student Miao Hu at Texas Tech University, for all their teaching about rheology and patience to bear with my samples; as well as Professor Hans Spiess and his former student Yefeng Yao at Max-Plank Institute for their generous help on the melt state $^{13}C$ NMR experiments.

Last but not least, I would like to take this time to memorialize my grandma, who taught me to be a genuine person but did not wait to see me finish my study. May you rest peacefully. No words can really describe my gratitude to my parents and to my wife for always putting me first and always being willing to sacrifice everything.

## Abstract

Metathesis polymerization using highly active, functional-group-tolerant catalysts is a powerful and versatile method for polymer synthesis. This thesis focuses on the preparation of a variety of advanced polymer architectures using well-defined ruthenium-based metathesis catalysts and the study of materials properties dictated by those unique macromolecular structures.

Chapter 1 introduces olefin metathesis, metathesis polymerization, and recent developments in living/controlled polymerization and polymer functionalization. The goal is to provide a summary of the current toolbox of polymer chemists. The second part of Chapter 1 describes using these tools to synthesize different macromolecular architectures.

Chapters 2 and 3 describe ring-expansion metathesis polymerization (REMP) using cyclic catalysts. Chapter 2 focuses on catalyst development, while Chapter 3 focuses on the REMP mechanism and cyclic polymer characterization.

Chapters 4 and 5 focus on brush polymers. Chapter 4 describes the syntheses of linear and cyclic brush polymers using ring-opening metathesis polymerization (ROMP) and REMP of macromonomers (MMs), respectively. Chapter 5 describes the efficient synthesis of brush copolymers and the study of their melt state self-assembly into highly ordered nanostructures.

Chapter 6 describes the synthesis and electro-optic response of well-defined liquid crystalline (LC) gels that were made from controlled end-linking of telechelic LC

polymers. These gels possessed very fast, reversible electro-optic switching; the degree of response was closely related to network structure.

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