DEVELOPMENT OF FLUORINATED MONOMERS AND POLYMERS FOR ADVANCED PHOTOLITHOGRAPHIC APPLICATIONS

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

2005

(Defended December 8, 2004)

ACKNOWLEDGEMENTS

While I disagree that the acknowledgements section is the only portion of a Ph.D. thesis that is ever read, I do feel that it is by far and away the most important. I will take a few pages here to thank those whom have made this work possible. Here is my best effort to do justice to all of those to whom I owe so much. I would first and foremost like to thank my parents who did everything in their power to advance, encourage, and facilitate my education. At times, I am sure they thought I would never graduate, but would continually wander the earth collecting degrees in perpetuity. Now that the journey is complete, I hope they feel as much pride in this accomplishment as I do.

I would like to thank Prof. Jerome B. Lando (Case Western Reserve University), Dr. Ram S. Narang (Xerox), Prof. Hatsuo Ishida (Case Western Reserve University), and Dr. Joy P. Dunkers (NIST) for their assistance and guidance over the years.

The highlight of my initial visit to Caltech was visiting with the Grubbs group, sitting in the hallway on the second floor of Church drinking beer from a keg, talking sports with Arnab Chatterjee, and meeting Helen Blackwell (whose father I had taken classes from while I was at Case), Todd Younkin, Melanie Sanford, and many other members of the group. Although I was not sure what a Schlenk line really was for and I did not really understand why such a big deal was made out of a bunch of dirty bomb-like solvent purification cylinders, I *was* sure that Caltech was the place for me and that the Grubbs labs (specifically 214 Church) were by far the *worst* labs I had ever seen. Well, little did I know that the lab bay that I was so repulsed by would one day become my own and five years later I would be fretting about the remodeling of those same labs!

I would like to thank Bob Grubbs for affording me the opportunity to work in his group. Having seen the hard lessons learned by others during my Master's degree, I took awhile to choose a group at Caltech. I chose wisely. Joining the Grubbs group is not like joining a lab;

it is like joining a family. I would like to thank Bob, Helen, and their family for welcoming me into the fold. I have learned many things while in Bob's group, but two important lessons will stay with me. First, sometimes you just have to throw some stuff at some stuff and see what happens. That is how serendipity - the most useful tool in the arsenal of chemical discovery - works. It is the ideas that should not work that afford true insight when they miraculously do. Finally, if you find good people, treat them with respect, and give them the freedom to work on what they do best, good things happen.

Many other members of the Caltech community have assisted me throughout the years. First, I would like to thank the members of my committee: Professors Dave Tirrell, Brian Stoltz, Jack Beauchamp, and Pat Collier for their assistance and encouragement during my time at Caltech. Other members of the department staff were invaluable over the years, including Linda Clark, Dian Buchness, Scott Ross, Larry Henling, Mona Shahgholi, John Leite, Anne Penny, Steve Gould, Joe Drew, Chris Smith, and Cora from the VWR stockroom.

I have met some great people during my time in the Grubbs group who have helped me grow as a scientist and more importantly, as a person. I need to thank Eric Connor and Todd Younkin who helped teach me air sensitive chemistry as a first year graduate student. Their infectious good humor made the first year of graduate school at Caltech a great one. After Eric left, Christie Morrill became my new bay-mate for the next four years. I really could not have asked for someone better to work next to; Christie has always been willing to offer advice, encouragement, and commiseration during those (all too frequent) periods when seemingly every reaction ended in failure. In our bay, there are lies, damned lies, and then there are Tetrahedron Letters preps!!

I would like to thank Arnab Chatterjee for our productive collaboration on the trisubstituted olefin cross-metathesis work described in Chapter 7. Arnab's good humor and quality sports conversations made many hours in lab fly by. I need to thank Emmanuelle Despagnet-Ayoub who worked briefly with me on the ADMET chemistry described in Chapter 6.

I am grateful for Soon Hong's collaboration on our efforts to prevent/understand olefin isomerization. Finally, special thanks go out to Jolene Lau, a summer undergraduate student, who worked on the oxetane acetal structures presented in Chapter 4. I wish her all the best in her graduate career at Scripps.

Oren Scherman, Diego Benitez, and Tae-Lim Choi were my fellow classmates. Oren and his wife Cora have been good friends throughout graduate school. Oren was invaluable in offering advice on polymer chemistry, instigating never-ending political discussions, and bailing out our intramural basketball team with his patented drive/scoop shot. J.P. Morgan was a fellow member of the late night crew. Our many late nights working in lab while listening to Adam and Dr. Drew on Love Lines were "good times" as Adam would say. Fellow polymer chemists in the group with whom I have interacted include Chris Bielawski, Andreas Kilbinger, and Isaac Rutenberg. Melanie Sanford, Jen Love, Tina Trnka, and Bill Ward all helped me with catalyst-related issues throughout the years. Whenever my project seemed to be going nowhere, Andrew Waltman, one of the last remaining members of Team Nickel, could always be counted on to cheer things up with a spirited game of lab ball or a timely appearance of Surgical Elvis. Special thanks go to the class of Andy Hejl, Tim Funk, Jacob Berlin, and Jason Jordan for all the good times in lab the last three years.

A great number of post-docs have been helpful during my graduate career including (in chronological order): Adam Matzger, Mike Koscho, Janis Louie, John Seiders, Steve Goldberg, Justin Gallivan, Dean Toste, Jon Efskind, Eric Marinez, Brian Connell, Anatoly Chlenov, Paula Diaconescu, Anna Wenzel, Greg Beutner, and Al Nelson. A great benefit of working in the Grubbs lab is the opportunity to work with post-docs from all around the world. A few of them not mentioned previously include (in chronological order): Choon-Woo Lee, Hyun-Jin Kim, Jaesook Yun, James Tsai, Stu Cantrill, Sebastian Smidt, and Christiane Marti-Meyers. Thank you all for broadening my intellectual and cultural horizons. To the many post-docs and senior graduate students who have assisted me, I hope that I have repaid my debt in part by trying to help the younger members of the lab as much as you helped me. I wish Donde Anderson, Erin Guidry, Irina Gorodetskaya, Ron Walker, Kevin Kuhn, and Michelle Robbins all the best.

Much of my work has been conducted in collaboration with a number other groups and industrial sponsors. The majority of this work has been done in collaboration with Professor C. Grant Willson's group at the University of Texas, Austin. The pervasive enthusiasm and energy of Prof. Willson is truly amazing. I consider myself truly blessed to have been able to work with not one, but two of the greatest professors and people in all of chemistry.

My primary collaborator in the Willson group was Brian Osborn. Brian is directly responsible for all the vacuum UV, VASE, and imaging measurements shown in this work. There is no way I can give him enough credit here. I also need to thank many of the other chemists in Dr. Willson's group for welcoming me into their group. I worked with Ray Hung and Shintaro Yamada on the norbornene addition polymers presented in Chapter 3. Matt Pinnow and I worked on mass-persistent resist platforms and I thank him for many excellent conversations. Other members of the group with whom I had great interaction include: Brian Trinque, Takashi Chiba, H. V. Tran, Charles Chambers, and Ryan Callahan.

My collaboration with UT-Austin was part of the Universities Resist Project (LITJ 102) funded by International SEMATECH and its member companies. I thank them for their generous funding of this work. I am grateful to Will "Hamburgers for Polymers" Conley and Paul Zimmerman, the SEMATECH academic liaisons for this project, and Gene Feit, the director of SEMATECH, for facilitating my involvement in this project. I also need to thank SEMATECH employees Danny Miller, Shashikant Patel, Vicky Graffenberg, and Georgia Rich, without whom all of the 157 nm imaging, vacuum UV, and VASE measurements would not have been possible. Finally, I would like to acknowledge the participating members of the Frechet group (UC-Berkeley), the DesMarteau group (Clemson), and the industrial members of SEMATECH for their helpful comments and advice, particularly Ralph Dammel of AZ-Clariant and Bob Allen of IBM. Special thanks go out to Dick Pederson, Yann Schrodi, Sharad Hajela, and Materia, Inc. for their generous supply of various catalysts and assistance with patent-related issues. Paul Cahill, Exciton, Inc. and the U.S. Air Force are acknowledged for their generous supply of quadricyclane.

During my time at Caltech, a large number of people have helped me keep my sanity. Shawn Briglin (of the Lewis group) was my roommate for 3 years. Thanks to Shawn and his partner-in-arms, Dave Michalak, I made my first film appearance (providing a true LA experience!) when our living room was frequently turned into a production set and pre-production assembly area. After Shawn graduated, Andy Hejl became my roommate for the next 2+ years. Andy was responsible for introducing me to some of the finer things in life. Most notably, these include the George Foreman grill and TiVo - two truly life-changing technological developments without which I could not have made it through graduate school! Events like Andy and Tim Funk's Thanksgiving Extravaganza have made being so far away from home that much easier. Andy was also responsible for bringing Hodge the cat into our apartment. Hodge would always keep me company as I relaxed after late nights in the lab, although that usually resulted in me being covered with cat hair and cat drool. Thanks, Shawn, Andy, and Hodge for making the Catalinas a great home for the last five years.

Intramural sports have served as a greatly needed outlet for stress and aggression. Jacob Berlin deserves special recognition for tireless efforts to assemble various softball and basketball teams over the years. Thanks to all of those who competed alongside me through various seasons of softball, basketball, and soccer. A great part of intramurals was the chance to meet and befriend many members of other research groups over the years; a few of these include: Ryan Julian, Nick Graham, James Peterson, Jeremy Heidel, Steve Spronk, Rob Moncure, Ian Mangion, Jeremy May, Darren Beene, and the many members of the MacMillian group soccer team.

However, the longest running extracurricular activity in my graduate career has been flag football. Our feeble Eight Year Plan evolved into the Team Justice juggernaut and yearlong weekend football with a large number of friends/fanatics: Chad Schmutzer, Jake Wiener and his brother Dave, Brian Johnson, Brian McKay, Dave Anderson, Randy, Christine, Jim Falsey, Sean

Brown, Matt Pohlman, Ted Betley, Steve Brown, Brian Leigh, Mark Cappucci, Justin Romberg, Anand Vahedra, Andrew Mollner, Ron and Don Walker and many, many others. Thanks to all of you for helping me hold onto my youth just a little bit longer. It has been a great five years!

Well, I have probably forgotten many people in this acknowledgements section and for that, I apologize. To make up for it…and most importantly, I would like to thank (*insert name here*) for their (*insert contribution here*), without which none of this would have been possible.

Now if for some reason you still feel like you need to read this thesis, please either go lie down or have a few beers until that feeling goes away…..

ABSTRACT

The incorporation of fluorine into photoresist materials imparts a variety of highly desirable properties for deep ultraviolet lithography at 193 nm and 157 nm. Chief amongst these benefits are the high optical transparency of partially fluorinated materials and the high acidity of fluoroalcohols. While metal-catalyzed polymerizations historically have received less attention than radical polymerizations for photoresist synthesis due to concerns over residual metal contamination, the high deep UV transparency and etch-resistance of alicyclic norbornene monomers have revived interest in metal-catalyzed polymerizations for the development of advanced lithographic materials. Yet, significant challenges remain to incorporate sufficient fluorine for high transparency without adversely affecting the polymerization process or dissolution behavior.

Chapters 2 details the synthesis and characterization of a series of partially fluorinated tricyclo[4.2.1.$0^{2,5}$]non-7-ene (TCN) monomers. The fused cyclobutane ring serves as an additional scaffold onto which additional fluorinated groups can be substituted without adversely affecting the polymerization behavior of the monomer. Specifically, this allows the transparent α-trifluoromethyl carboxylic acid ester moiety to be incorporated into a polymerizable norbornene-like framework. The ability to incorporate additional fluorine allows for the synthesis of metal-catalyzed addition polymers with greatly enhanced transparency relative to their less-fluorinated norbornene analogues. The synthesis and imaging of TCN-based photoresist polymers are explored in Chapter 3.

Chapter 4 introduces a series of 3-oxa-tricyclonon-7-ene monomers synthesized from quadricyclane and fluorinated ketones. These oxetane-containing monomers undergo a facile Lewis acid-catalyzed isomerization to form the polycyclic 4-oxa-tricyclonon-8-enes. While the oxetane ring in oxatricyclononane structures was found to be largely unreactive, the similar high transparencies of addition and ring-opening metathesis polymers of fluorinated oxatricyclononenes detailed in chapter 5 reveal the effect of the alicyclic backbone structure on

transparency at 157 nm. 4-Oxatricyclononenes are valuable comonomers for the elevation of glass transition temperatures in ROMP polymers, while low molecular weight ROMP copolymers of 3-oxatricyclonene are being evaluated as crosslinking agents in negative tone resist formulations.

Chapter 6 details the use of cross-metathesis and ring-opening cross-metathesis in the synthesis of multifunctional monomers and oligomers for 193 nm immersion and 157 nm lithography. Cross-metathesis with unsaturated hexafluorocarbinols is a facile method to generate functionalized olefins without using toxic hexafluoroacetone gas. In certain instances, cross-metathesis reactions with these acidic alcohols were shown to proceed with unusual stereoselectivity. While investigating the nature of this stereoselectivity, simple carboxylic acids were found to eliminate problematic ruthenium-catalyzed olefin migration in specific substrates. These developments culminate in the synthesis of difunctional norbornenes containing both ester and hexafluorocarbinol functionalities. These ester-containing structures display dramatically increased transparency at 157 nm and will potentially afford unique dissolution behavior.

Finally, chapter 7 explores the synthesis of trisubstituted olefins via ruthenium-catalyzed cross-metathesis. Mechanistic investigations into the reaction pathways of isobutylene cross-metathesis revealed 2-methyl-2-butene to be a convenient isobutylene surrogate in the formation of prenyl groups via cross-metathesis. With less reactive olefins, a mechanistic reversal occurs which affords only 1,2-disubstituted products. Understanding of the reactivity of second-generation metathesis catalysts with 1,1-disubstituted and trisubstituted olefins has prompted the exploration of ring-opening cross-metathesis of low strain cyclic olefins and three component cross-metathesis reactions with high product selectivity.

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