

**DEVELOPMENT OF FLUORINATED MONOMERS AND
POLYMERS FOR ADVANCED PHOTOLITHOGRAPHIC
APPLICATIONS**

Thesis by

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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.

Chapter 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 hexafluorocarbinals 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 hexafluorocarbinal 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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