# CHAPTER 5

Metal-catalyzed Addition and Ring-opening Metathesis Polymers of Fluorinated Oxatricyclononenes for Advanced Lithographic Applications

Reproduced in part with permission from Sanders, D.P.; Osborn, B. P.; Willson, C.G.; Grubbs, R. H. *Macromolecules*, manuscript in preparation. Unpublished work copyright 2005 American Chemical Society.

# Metal-catalyzed Addition and Ring-opening Metathesis Polymers of

## Fluorinated Oxatricyclononenes for Advanced Lithographic Applications

Fluorinated 3-oxatricyclo[4.2.1.0<sup>2,5</sup>]non-7-enes serve as oxetane-functionalized Abstract norbornene monomers amenable to metal-catalyzed addition or ring-opening metathesis polymerization afford ultraviolet lithography. to new materials for deep 4-Oxatricvclo[4.3.0<sup>1,6</sup>.0<sup>3,7</sup>]non-8-enes, the Lewis acid-catalyzed rearrangement products of the 3oxatricyclononenes, exhibit high transparency and good etch resistance indicating their suitability for use in a number of advanced photolithographic applications. Most importantly, the rigid alicyclic structure of 3,3-bis(trifluoromethyl)-4-oxatricyclononene affords a ROMP polymer with a glass transition temperature (Tg) in excess of 230 °C, indicating its potential to provide greatly needed T<sub>g</sub> enhancement in ROMP-based photoresist copolymers for deep UV lithography. While residual unsaturation dramatically affects absorption at 193 nm, small amounts of unsaturation have little effect at 157 nm. Molecular weights of these fluorinated norbornene-like polymers can only be efficiently controlled kinetically with the terminal olefin chain transfer agents unlike polynorbornene. Finally, although oxatricyclononene addition polymers image poorly due to the high stability of the oxetane ring, low molecular weight oxatricyclononene ROMP copolymers bear promise as crosslinking agents in negative tone resist formulations. Ring-opening of the norbornene framework during polymerization allows for more facile nucleophilic attack on the oxetane ring and, therefore, higher crosslinking activity.

## Introduction

The unique combination of transparency,<sup>1</sup> acidity,<sup>2</sup> and excellent dissolution behavior<sup>3</sup> imparted by hexafluorocarbinols to photoresist polymers has made them the dominant design motif for 157 nm photoresists.<sup>4-8</sup> While originally investigated for 157 nm lithography, hexafluorocarbinols are being back-integrated into resists for 193 nm and 193 nm immersion

lithography. The vast majority of chemically-amplified positive tone photoresists being investigated for 193 nm, 193 nm immersion, and 157 nm lithography (such as the one shown in Figure 5.1) employ a latent acidic functionality with a photoacid-cleavable protecting group.<sup>9</sup> After exposure to deep ultraviolet (UV) radiation, the protecting group is cleaved catalytically by a photogenerated acid, releasing a number of volatile fragments which can outgas from the photoresist film and contaminate optical elements and produce distortions in the imaged features.<sup>10</sup> These issues have prompted the development of low-outgassing or mass-persistent photoresists based on the acid-catalyzed ring-opening of small and medium-sized lactones.<sup>11</sup>



Figure 5.1. 157 nm photoresist with outgassing products

Negative tone resists also have the potential to solve this outgassing problem, however, no negative tone resists based on fluorinated oxiranes or oxetanes suitable for 157nm lithography have been reported. 2,2-Bis(trifluoromethyl) oxetane has been shown to ring-open under acidic conditions in the presence of water or other nucleophiles to produce hexafluorocarbinol-functionalized compounds.<sup>12</sup> We imagined using the olefin-containing annulated oxetane **5.2** (shown in Figure 5.2) which would remain intact during metal-catalyzed addition or ring-opening metathesis polymerization, yet ring-open under the superacidic conditions of imaging to produce either crosslinked networks (negative tone resists) or possibly hexafluoroalcohol-functionalized polymers (positive tone resists).



Figure 5.2. Oxetane-functionalized monomer and polymers



Figure 5.3. Lewis acid-catalyzed rearrangement of 5.2

Previously, we have reported the synthesis of number of 3-oxa-tricyclo[4.2.1.0<sup>2,5</sup>]non-7enes via the cycloaddition of quadricyclane with activated carbonyl compounds.<sup>13</sup> The resultant norbornene-like annulated oxetanes are exclusively exo in configuration, which is ideal for metalcatalyzed polymerization. The 3-oxa-tricyclononenes undergo a Lewis acid-catalyzed Wagner-Meerwein rearrangement to cleanly produce 4-oxa-tricyclo[4.3.0<sup>1,6</sup>.0<sup>3,7</sup>]non-8-enes in high yield as shown in Figure 5.3.<sup>13</sup> These two classes of oxatricyclononene monomers exhibit high transparency in the deep ultraviolet spectral region, indicating their potential for use in advanced photolithographic applications. Here, we report the polymerization of the bis(trifluoromethyl) 3and 4-oxa-tricyclononene monomers (**5.2** and **5.3**, respectively) via metal-catalyzed addition and ring-opening metathesis pathways to produce new materials for deep ultraviolet lithography.

#### **Results and Discussion**

Addition Polymerization Of the large number of metal catalysts capable of performing addition polymerization of norbornenes, the cationic palladium allyl and neutral  $\eta^6$ -tolyl-bis(perfluorophenyl) nickel catalysts were chosen for their ability to efficiently polymerize

tricyclononene compounds.<sup>4b,14-17</sup> Given the propensity of **5.2** to undergo Lewis acid-catalyzed rerarrangement, the stability of 5.2 to a variety of metal complexes [Pd(COD)(Cl)]<sub>2</sub>, [Rh(cyclooctene)<sub>2</sub>(Cl)]<sub>2</sub>, and inorganic salts (NaBF<sub>4</sub>, NaSbF<sub>6</sub>, AgBF<sub>4</sub>, AgSbF<sub>6</sub>) in dichloromethane at 40 °C for 18 hours was examined. Oxetane 5.2 proved to be inert to all except AgSbF<sub>6</sub>, in which case, predominantly isomerization to **5.3** was observed. Despite these generally encouraging results, initial polymerization attempts resulted in failure. No reaction was observed with the neutral nickel catalyst and immediate gelation and precipitation was observed with the cationic palladium allyl hexafluoroantimonate catalyst. Fortunately, this side reaction of the oxetane could be avoided by switching to the tetrafluoroborate counteranion. With the cationic palladium allyl tetrafluoroborate catalyst, moderate yields of polymer 5.4 were achieved after a few days at room temperature (Figure 5.4). Examination of the resultant polymer by NMR indicated two prominent structures, both that of the 3-oxatricyclononene 5.2 ( $\leq 20\%$ ) and of the 4-oxatricyclononane 5.3 (> 80%). This was confirmed by spectral comparison of polymer 5.5 synthesized independently from 5.3. Following the polymerization via NMR allowed observation of the competing isomerization of monomer 5.2 to 5.3 during the polymerization. Therefore, it is reasoned that the resultant polymers have a gradient structure, initially being rich in oxetane and



Figure 5.4. Addition polymerization of oxatricyclononenes

ending in tetrahydrofuranyl-rich sequences.

Copolymerization of **5.2** with 2-bicyclo[2.2.1]hept-5-en-2-ylmethyl-1,1,1,3,3,3hexafluoro-propan-2-ol (NBHFA, **5.6**) afforded polymer **5.7** with a composition of 70% **5.6**, 20% **5.2**, and 10% **5.3**. While incorporation of the 4-oxatricyclononane structure offers the likely benefit of increased etch resistance, a random incorporation via copolymerization of **5.2** and **5.3** rather than the gradient incorporation would be advantageous. In addition to the evaluating neutral nickel-based addition catalysts, the use of bulky and electron-donating phosphines such as tricyclohexylphosphine to lower the cationic character of the palladium center<sup>17</sup> and slow/eliminate this isomerization side reaction is being explored.

*Optical Properties of Addition Polymers* Variable angle spectroscopic ellipsometry (VASE) spectra of polymers **5.4** and **5.5** are shown in Figure 5.5. Two features are readily apparent. First, the homopolymer **5.5** shows low absorption at 157 nm (1.46  $\mu$ m<sup>-1</sup>) and 193 nm



Figure 5.5. VASE spectra of oxatricyclononene addition polymers

(0.78  $\mu$ m<sup>-1</sup>). This is similar to the performance shown by the early batches of poly(NBHFA) **5.1**, which upon optimization afforded the spectrum shown in Figure 5.5. Secondly, the copolymer **5.4** has a surprisingly high absorbance at 157 and 193 nm (2.28 and 2.02  $\mu$ m<sup>-1</sup>, respectively). The cause of this high absorbance is being investigated; however, it is presumed that some nortricyclane structures are formed which can absorb in these regions.

To examine the potential etch resistance of these oxatricyclononene-based materials, polymer **5.5** was subjected to a standard silicon oxide etch process as shown in Figure 5.6. While the oxide etch process is the most demanding etch process experienced by the resist, polymer **5.5** exhibited promising etch resistance (2.3 times slower than the base silicon oxide etch rate), comparing favorably to the optimized commercial resists Shipley UV-210 and UV-6. Better performance is expected under the more mild polysilicon etch conditions. These results suggest the potential for **5.3** and its derivatives to be used as transparent, etch-resistant comonomers in



Figure 5.6. Oxide etch resistance of 5.5

conventional metal-catalyzed or radically polymerized norbornene-based resists or, if the olefin is hydrated, as pendant groups in fluorinated cyclopolymer and tetrafluoroethylene copolymer resists in place of norbornyl or isobornyl groups.

*Lithographic Performance of Oxatricyclononene Resists* Two oxatricyclononene addition polymers were examined for their lithographic performance at 157 nm. Polymer **5.4** was blended with the more transparent base polymer, poly(NBHFA) **5.1**, (5% **5.4**, 95% **5.1**) (93.7% total) and combined with a standard amount of 6% triphenylsulfonium nonaflate photoacid generator and 0.03% tetra-*n*-butyl ammonium hydroxide in PGMEA. Irradiation at 157nm using a binary mask afforded poor positive tone images (Figure 5.7). The terpolymer **5.7** (70% NBHFA **5.6**, 20% oxetane **5.2**, 10% **5.3**) also provided similar positive tone images. The norbornene framework and bulky electron-withdrawing trifluoromethyl groups in addition polymers of **5.2**, while imparting significant stability and transparency to the oxetane, prevents



**Imaging conditions:** 93.7% polymer (95% **5.1**, 5% **5.4**), 6% triphenylsulfonium nonaflate, 0.03% tetrabutyl ammonium hydroxide Dose: ~ 47 mJ/cm<sup>2</sup>; Focus: ~0.35; NA: 0.85;  $\sigma$ : 0.7; Binary mask.

Figure 5.7. Imaging of oxatricyclononene addition polymers

reaction of the oxetane to form crosslinked networks. However, it is this same stability that makes the oxetane ring very difficult to open.<sup>18</sup> It is unclear whether the large exposure dose required to achieve clearing of the exposed regions is due to the slow ring-opening of the oxetane to form hexafluorocarbinol species or whether the image we see is a result of dissolution inhibition due to the large amount of PAG.

It is obvious from these results that any ring-opening is too slow to be useful. The norbornene framework forces attacking nucleophiles to approach from the hindered endo face of the structure, forcing any ring-opening reaction to proceed by a slow E1-type mechanism, which can also lead to isomerization rather than ring-opening. In order to increase the reactivity of these annulated oxetanes, a potential reduction in the steric hindrance around the oxetane could be realized by polymerizing **5.2** via ring-opening metathesis. The resultant ring-opened structure (see Figure 5.2) should be more accessible to attack by nucleophilic species.

**Ring-Opening Metathesis Polymerization** The high activity and low Lewis acidity of ruthenium-based olefin metathesis catalysts catalysts (Figure 5.8, **5.8-5.10**)<sup>19</sup> should allow for the efficient polymerization of **5.2** without the isomerization problems encountered in the synthesis of addition polymers. In addition, the number of efficient chain transfer methodologies<sup>20</sup> available to control the molecular weight of norbornene ROMP polymers offers the possibility of using much lower catalyst loadings relative to metal-catalyzed addition polymerizations while producing more controlled molecular weights and molecular weight distributions. This is a



Figure 5.8. Olefin metathesis catalysts

distinct advantage when it comes to catalyst removal, given the need for extremely low residual metal contamination in commercial resists.<sup>21</sup>

While ROMP-based resists have been previously explored for 193 nm lithography.<sup>22</sup> a number of shortcomings, including generally low glass transition temperatures, phase incompatibility with common photoacid generators (PAGs), poor dissolution behavior with standard developer concentrations, and swelling during development, have prevented them from being adopted commercially. The necessary hydrogenation of the unsaturated backbone of ROMP polymers unfortunately results in a significant lowering of the glass transition For example, the glass transition temperature of the hexafluorocarbinoltemperature. functionalized ROMP polymer 5.11 shown in Figure 5.9 – one of the first ROMP polymers explored for use at 157 nm – suffers a significant decrease from 115 °C to the less useful 85 °C after hydrogenation.<sup>23</sup> A common route to achieve higher glass transition temperatures is to use norbornene-like monomers with additional cyclic units. Unfortunately, the increase in glass transition temperature gained by the incorporation of additional simple annulated rings onto norbornene has been shown to be relatively independent of ring-size and shows only moderate effect.<sup>24</sup> The additional hydrocarbon units also make dissolution into an aqueous base developer more difficult.



Figure 5.9. Effect of structure on glass transition temperatures of ROMP polymers

Other approaches towards increasing the glass transition temperature include incorporation of hydrogen bonding carboxylic acid groups<sup>22</sup> or bulky polar functionalities such as esters  $(5.12)^{25}$  or maleimides (5.13).<sup>26</sup> Unfortunately, free carboxylic acid dramatically increases the background dissolution rate and the esters and maleimide functionalities are not transparent at 157nm. After several unsuccessful attempts to bulk up the ethylene linkages of the ROMP polymer backbone, we decided to investigate making the cyclopentane backbone unit more rigid and bulky via incorporation of a bridging group. Methyl tricyclo[4.3.0<sup>1.6</sup>.0<sup>3.7</sup>]non-8-ene-2-carboxylate (5.14), originally synthesized by our laboratory as part of the effort to synthesize the natural product ( $\pm$ )- $\Delta$ 9(12)-capnellene,<sup>27</sup> seemed to be an ideal model system (Figure 5.10). However, the presence of the nearly identical core structure in 5.3 prompted us to initially explore the ring-opening polymerization of 5.3 as a possible transparent, high Tg ROMP structure suitable for use in 193 nm and 157 nm photoresist polymers.



Figure 5.10. Potential routes to high T<sub>g</sub> ROMP polymers

**Ring-opening Metathesis Polymerization of 5.3** Surprisingly, after reaction of 100 equivalents of **5.3** with the highly active bispyridine catalyst **5.10** in dichloromethane at room temperature for 12 hours, no polymer formation was observed (Entry 1, Table 5.1). Given the high ring strain of norbornene monomers, these conditions [0.4 M] are well above the critical concentration and ring-opening metathesis should proceed to very high conversions.<sup>28</sup> However, NMR experiments indicated only  $\sim$ 3% conversion of **5.3**. No conversion was detected in NMR

Entry	Monomer	Catalyst	[M]/[C]	Conc. [M]	Time (h)	M <sub>n</sub> (kDa)	PDI	Isolated Yield (%)
1	5.3	5.10	100:1	0.4	12	-	-	~3
2	5.3	5.10	100:1	1.0	12	18.5	1.30	45
3	5.3	5.10	100:1	3.0	12	27.0	1.14	79
4	5.3	5.10	100:1	neat	12	70.2	1.29	66
5	5.3	5.9	100:1	3.2	12	193.6	1.32	99
6	5.3	5.8	100:1	3.2	12	38.2	1.14	91
6	5.3	5.8	100:1	3.2	12	38.2	1.14	91
7	5.3	5.10	100:1	3.2	12	24.5	1.09	80
$8^{a}$	5.3	5.10	100:1	3.2	6	20.5	1.05	59
9	5.2	5.10	100:1	0.2	6	32.4	1.04	99
10	<b>5.2 + 5.3</b> (1:1)	5.10	100:1	0.8	24	22.2	1.08	71

 Table 5.1. Ring-opening metathesis polymerization of 5.3

<sup>a</sup> Reaction performed at 0 °C

experiments with catalysts **5.8** or **5.9**. For low ring-strain olefins such as cyclopentane, neat conditions are generally required to achieve significant molecular weight polymer.<sup>28,29</sup> When the polymerization of **5.3** with the bispyridine catalyst **5.10** was performed neat, the reaction mixture gelled after 1-2 hours at room temperature (Entry 4, Table 5.1). The resultant polymer **5.16** was insoluble in dichloromethane or chloroform, but is readily soluble in more polar solvents such as tetrahydrofuran. Gel permeation chromatography indicated a surprisingly high molecular weight polymer, given the relatively slow polymerization and extremely rapid initiation rate of **5.10**.<sup>30</sup> This is most likely the result of the low solubility of **5.10** in neat **5.3** (i.e., only a small amount of catalyst is soluble, thereby artificially increasing the effective monomer to catalyst ratio). The addition of a small amount of dicholoromethane to pre-dissolve the catalyst before injecting the monomer afforded much narrower molecular weight distributions and more controlled molecular weights. Catalyst **5.9** (the slowest initiating catalyst) produces high molecular weight polymer with a PDI ~1.32 (Entry 6, Table 5.1) while catalyst **5.10** which initiates more than a million times faster<sup>30</sup> produces controlled molecular weight polymers with a narrow PDI of 1.09.<sup>31,32</sup>

*Effects of Bulky Alicyclic Framework* We were delighted to discover that the ROMP polymer **5.16** possessed extremely high glass transition temperatures (~233 °C). Comparison with the much lower  $T_g$  of ROMP polymer **5.17** (~128 °C) from monomer **5.2** illustrates the effectiveness of the additional bridging structure in increasing the glass transition temperature of norbornene-based ROMP polymers. Unfortunately, we were unable to achieve hydrogenation of more than 50% of the backbone olefins of **5.16**. The combination of poor solubility due to the high degree of fluorination and polymer rigidity coupled with the steric hindrance around the backbone olefins prevented high degrees of hydrogenation of polymer **5.16** despite our screening a number of solvents and reaction temperatures.

*Control of Molecular Weight via Chain Transfer* While catalyst control of molecular weight is effective in the case of rapidly initiating catalyst **5.10**, use of chain transfer to control molecular weight and lower the required catalyst loadings would be advantageous. We expected the use of chain transfer to control the ROMP of **5.3** to be more complicated than with highly reactive monomers such as norbornene. The hindered backbone olefins in ROMP polymer **5.16** are potentially more resistant towards the efficient secondary metathesis required in thermodynamic chain transfer processes<sup>20</sup>.

Initially, *trans*-3-hexene was selected as a chain transfer agent (CTA). Attempts to control the molecular weight kinetically (Entries 1-6, Table 5.2 and Figure 5.10) were moderately effective. Molecular weights were consistently higher than expected and the effectiveness of the CTA decreased as the [CTA]:[monomer] ratio increased. Production of molecular weights in the 5-10 kDa range was not possible. A more active chain-transfer agent, 1,4-diacetoxy-*cis*-2-butene (DACB), which was demonstrated as an effective CTA for the ROMP of norbornene,<sup>20b</sup> was even less effective than 3-hexene. The reduced yields at higher chain transfer agent loadings may be due to the increased formation of very low molecular weight, non-isolable oligomers via ring-opening cross-metathesis.

Given the failure of the kinetic chain transfer approach to produce good control of molecular weight, the thermodynamic chain transfer methodology was examined. Polymerization of norbornene with catalyst **5.9** in the presence of DCAB at 55 °C was demonstrated to afford polynorbornene with a molecular weight determined by the monomer to chain transfer agent ratio.<sup>20b</sup> High molecular weight polynorbornene can also be reduced to lower molecular weights via this approach. The more sterically hindered olefins of polynorbornene necessitate the use of second generation catalysts such as **5.9** and elevated temperatures to allow for the efficient secondary metathesis necessary to redistribute the chain ends and achieve the equilibrium distribution. Unfortunately, this approach (Entries 10-12 and 13-15, Table 5.1 and Figure 5.11) met with equal difficulty. Catalyst **5.9** afforded very low yields of polymer (< 10%). Use of the

Entry	CTA <sup>b</sup>	[M]/[CTA]	M <sub>n</sub> (theor.) (kDa)	M <sub>n</sub> (expt.) (kDa)	PDI	Isolated Yield (%)
1	-		258	304.1	1.80	71
2	А	100:1	23.5	118.6	1.56	67
3	А	50:1	12.3	83.7	1.53	65
4	А	25:1	6.3	56.3	1.54	67
5	А	12.5:1	3.2	35.6	1.50	56
6	А	6.25:1	1.6	25.6	1.39	37
7	В	50:1	12.3	141.2	1.51	71
8	В	12.5:1	3.2	81.8	1.60	64
9	В	6.25:1	1.6	51.3	1.74	56
$10^{\circ}$	В	50:1	12.3	79.0	1.33	28
11 <sup>c</sup>	В	12.5:1	3.2	50.8	1.64	22
12 <sup>c</sup>	В	6.25:1	1.6	21.0	1.38	8.0
13 <sup>d</sup>	-	100:1	23.5	63.3	1.58	5.5
14 <sup>d</sup>	В	50:1	12.3	46.1	1.72	6.9
15 <sup>d</sup>	В	25:1	6.3	38.3	1.80	6.3

**Table 5.2.** Effect of chain transfer agents on ROMP of  $5.3^{a}$ 

<sup>a</sup> All reactions performed using 0.1 mol% catalyst **5.10** in  $CH_2Cl_2$  [1.5 M] at room temperature for 12 h.

<sup>b</sup> Chain transfer agents: (A) trans-3-hexene and (B) 1,4-diacetoxy-cis-2-butene

<sup>c</sup> Reaction performed in 1,2-dichloroethane at 55 °C for 16 h

<sup>d</sup> Reaction performed with 0.1 mol% catalyst **5.9** in 1,2-dichloroethane at 55 °C for 16 h



Figure 5.11. Effect of chain transfer on ROMP of 5.3

more rapidly initiating catalyst **5.10** which can effectively polymerize **5.3** at this concentration, afforded higher yields (<30%) of polymer, but exhibited less molecular weight control than **5.9**, probably due to its lower stability. However, molecular weight control was increased relative to the same reaction performed at 40 °C.

*Optimization of Chain Transfer Conditions* In order to determine optimal conditions to control the molecular weight of these polymers, the effects of chain transfer agent, temperature, and catalyst choice on molecular weight must be evaluated; however, no direct comparison of chain transfer performance of a number of first and second-generation ruthenium metathesis catalysts has been reported in the literature. Second-generation ruthenium metathesis catalysts have been shown to perform secondary metathesis reactions on the olefinic backbone of poly(norbornene), affording thermodynamic control of molecular weight via the use of chain transfer agents.<sup>20</sup> The molecular weights of a number of polynorbornenes synthesized using three

	5.9		5.18		5.10	
1,4-diacetoxy- <i>cis</i> -2-butene	M <sub>n</sub> (kDa)	PDI	M <sub>n</sub> (kDa)	PDI	M <sub>n</sub> (kDa)	PDI
Undistilled	176.1	2.25	16.6	1.46	20.1	2.95
Distilled	24.9	7.90*	15.9	1.46	9.4	1.51

Table 5.3. Effects of CTA purity and catalyst on molecular weight of polynorbornene

Conditions: 1.25M in 1,2-dichloroethane, 55 °C, 12 h. [M]/[C]= 1000:1, [M]/[CTA] = 25:1 (\* Bimodal distribution)

second-generation catalysts and 1,4-diacetoxy-cis-2-butene chain transfer agent are shown in Table 5.3. Catalyst **5.9** afforded extremely high molecular weight insoluble material immediately upon addition of monomer. Even after 12 hours, insoluble material remained. The phosphinefree catalyst 5.18 ((H<sub>2</sub>Imes)(Cl)<sub>2</sub>Ru (=CHC<sub>6</sub>H<sub>4</sub>(o-O-i-Pr)), which initiates faster than 5.9, did not form insoluble material and afforded polynorbornene with a molecular weight about 7 times higher than the monomer to catalyst ratio should afford. While catalysts 5.9 and 5.18 have significantly more stability than the bispyridine catalyst 5.10, the very high initiation rate of 5.10 afforded reasonable control of the molecular weight. However, the molecular weight distribution was much broader than expected. Subsequent inspection of the 1.4-diacetoxy-cis-2-butene chain transfer agent revealed it to contain a number of olefinic and aldehyde impurities. The presence of these impurities would likely have a large impact on the performance of the bispyridine catalyst. Distillation of the CTA from calcium hydride afforded a reduction in the contaminants; however, a number of impurities were still present. The use of the distilled chain transfer agent afforded a dramatic improvement in molecular weight control for catalysts 5.9 and 5.10. The performance of catalyst 5.18 was unaffected by purity of the chain transfer agent. Catalyst 5.10 afforded the best control of the molecular weight. Since the initial molecular weights are controlled kinetically, the use of a rapidly initiating catalyst is beneficial to prevent the formation of insoluble material. In addition, despite the lower stability of **5.10**, its polymerization of a highstrain monomer like norbornene is faster than decomposition reactions; therefore, its higher rate

of initiation<sup>30</sup> results in better control of the molecular weight than the more stable, slower initiating **5.9**. The molecular weight distributions are narrower than previous reports (PDI=2.0)<sup>20</sup> due to the shorter reaction times; however, these reaction times are perhaps more representative of common usage of these catalysts.

Previous polymerizations of **5.2** with *trans*-3-hexene resulted in poor molecular weight control ( $M_n(expt'l) = 69.9 \text{ kDa}$ , PDI = 1.77,  $M_n(theor.) = 5.2 \text{ kDa}$ ). Subjection of the isolated polymer to metathesis conditions with the undistilled 1,4-diacetoxy-*cis*-2-butene ([monomer equiv.]/[CTA] = 20:1) CTA for 24 hours at 55 °C afforded no reduction in molecular weight ( $M_n$ = 5.2 kDa, PDI = 1.71). Despite the presence of impurities, the good performance of this olefin in cross-metathesis reactions makes the total lack of reactivity in this case raise serious question marks about the ability of second-generation catalysts to perform secondary metathesis reactions on the more hindered olefins in these poly(2-oxatricyclonononene)s. All previous reported attempts to control the molecular weights of polynorbornene via this thermodynamic approach were performed on unsubstituted norbornene. The additional steric hindrance and the different solution conformations induced by the presence of the fluorinated substituents would be expected to influence the reactivity of the backbone olefins.

In order to examine the effects of fluorinated substituents on the molecular weight control using chain transfer agents, polymerizations of the hexafluorocarbinol-functional norbornene **5.6** with several catalysts and chain transfer agents were performed, the results of which are



Figure 5.12. Molecular weight control during polymerization of 5.6

Catalyst	Temp. (°C), solvent	[M]/ [CTA]	M <sub>n</sub> (calc.)	1,4-Diacetoxy- <i>cis</i> -2-butene		Allyl Acetate	
			rel. to PS <sup>a</sup>	M (Da)	рлі	M (Da)	PDI
	rt, CH <sub>2</sub> Cl <sub>2</sub>	10:1	4960	20560 <sup>*</sup>	1.48	6990 <sup>b</sup>	1.61
5.8	rt, CH <sub>2</sub> Cl <sub>2</sub>	5:1	2480			4000 <sup>b</sup>	1.53
	rt, CH <sub>2</sub> Cl <sub>2</sub>	1:1	495			1310*	1.46
	rt, CH <sub>2</sub> Cl <sub>2</sub>	10:1	4960			20650	1.66
5.9	rt, CH <sub>2</sub> Cl <sub>2</sub>	5:1	2480			17110 <sup>b</sup>	1.84
	rt, CH <sub>2</sub> Cl <sub>2</sub>	1:1	495			4840 <sup>b</sup>	1.85
	rt, CH <sub>2</sub> Cl <sub>2</sub>	10:1	4960			28200 <sup>b</sup>	1.50
	rt, CH <sub>2</sub> Cl <sub>2</sub>	5:1	2480			24800	1.65
5.10	rt, CH <sub>2</sub> Cl <sub>2</sub>	1:1	496			7900 <sup>b</sup>	2.12
	55, 1,2 <b>-</b> DCE	10:1	4960	10240	1.47	13900	1.68
	55, 1, <b>2-D</b> CE	1:1	495	13270	1.64		
	rt, 1,2-DCE	10:1	4960			13980	1.72
5.18	55, 1, <b>2-D</b> CE	10:1	4960	33300	1.59	12660	1.70
	55, 1, <b>2-D</b> CE	1:1	495	16130	1.94		

 Table 5.4. Control of molecular weight of polymer 5.1 via chain transfer

<sup>a</sup> Calculated molecular weight corrected to reflect value vs. polystyrene (see text)

 $M_n(calc.) = M_0 \times [M]/[C] \times 1.81$ . Does not include endgroups

<sup>b</sup> Monomer and CTA mixed with catalyst solution at -40 °C and allowed to warm to rt All molecular weights are reported relative to polystyrene

presented in Table 5.4 and Figure 5.12. Under thermodynamic conditions (55 °C, 1,2dichloroethane), catalyst **5.10** exhibited identical performance with both CTAs; however, catalyst **5.18** showed slightly better molecular weight control with allyl acetate. Unfortunately, the molecular weights are much larger than the theoretical values (without correction). Under kinetic control with the bisphosphine catalyst **5.8**, the use of the terminal olefin chain transfer agent (allyl acetate) afforded significantly better molecular weight control. These results indicate that the molecular weight of polymer **5.1** appears to be primarily controlled kinetically. Since terminal olefins are more reactive than internal olefins, allyl acetate is the preferred CTA in these

polymerizations. Allyl acetate also has none of the purity concerns of 1,4-diacetoxy-cis-2-butene. Room temperature polymerizations with second generation catalysts 5.9 and 5.10 were unable to produce low molecular weight material (M<sub>n</sub> < 5 kDa), even with stoichiometric loadings of chain transfer agent. The first-generation, bisphosphine catalyst 5.8 was able to control the molecular weight down to the oligomer level. GPC analysis clearly shows the production of monomeric, dimeric, and other oligomeric species. The apparent molecular weight difference between the successive oligomeric fractions was ~495 g/mol relative to polystyrene. The calculated theoretical molecular weights in Table 5.4 are corrected by a factor of 1.81 (495/274) to account for the relative molecular weight values determined by gel permeation chromatography. The ability of the first generation catalysts to kinetically control molecular weight more efficiently is somewhat surprising, given the higher activity of the bispyridine catalyst 5.10. However, these molecular weight results reflect not the initiation rates, but more likely, the relative reaction rates of the respective catalysts with high-strain, bulky norbornenes and terminal olefins. This relative rate of reaction appears to be more competitive with the first generation catalyst. It should be noted that these results are also highly monomer dependent. Polymerization of 5.2 with the second-generation bispyridine catalyst 5.10 and allyl acetate affords good molecular weight control below 5000 Da. Therefore, it must be reiterated that selection of the most active catalyst or fastest initiating catalyst will not always produce the best results and each system should be evaluated independently.

**Copolymerization of 5.3** While the high glass transition temperature was extremely desirable, the high concentrations required for significant monomer conversion and the inability to fully hydrogenate these polymers posed significant challenges. Given the norbornene-like structure of 5.3, its reluctance to polymerize was puzzling. ROMP of 5.3 with an excess of acyclic olefin such as *t*-butyl acrylate or *trans*-3-hexene revealed only low to moderate conversions to ring-opened product, whereas under the same conditions, 5.2 ring-opened quantitatively. These results indicated that the primary issue was not ring strain, but coordination

to, and reaction of **5.3** with the catalyst, especially if the catalyst had already initiated to form a very bulky alkylidene. If this was indeed the case, a less sterically bulky comonomer should be able to coordinate and undergo metathesis to form a more accessible ruthenium alkylidene capable of coordinating and reacting with another monomer of **5.3**. Similar rationales have been used to explain the alternating ROMP copolymerizations of norbornenes in certain systems.<sup>33</sup> Indeed, when a less bulky monomer such as cyclooctene or norbornene was introduced with **5.3** to a dichloromethane solution of **5.10** at concentrations where **5.3** by itself would not homopolymerize [0.4 M], significant conversions of **5.3** were observed via <sup>19</sup>F NMR (55% and 20%, respectively). This provided evidence that monomers such as **5.3** could be copolymerized at reasonable concentrations and opened up the possibility of synthesizing alternating copolymer structures.

*Copolymerization of Oxatricyclononenes* The ring-opening polymerization of 5.2 (Entry 9, Table 5.1) provides good yields of the oxetane-functionalized polymer 5.18 (Figure 5.13).
ROMP polymer 5.17 was hydrogenated under standard conditions to produce the saturated



Figure 5.13. ROMP of oxatricyclononenes

polymer **5.19**. No evidence of ring-opening or oxetane isomerization after either polymerization or hydrogenation was observed via <sup>19</sup>F NMR. Unfortunately, as expected, the glass transition temperature of polymer **5.17** (128 °C) was reduced to ~99 °C after hydrogenation. However, it is sufficiently high that incorporation of 30-50% of **5.3** via copolymerization should boost the  $T_g$  into a useful range of 120 °C.

Given the inability to adequately hydrogenate polymer 5.16, copolymerization incorporation ratios of 5.3 lower than 50% seemed desirable to avoid the formation of sequences of 5.3 which would be difficult to hydrogenate. Copolymerization of a 1:1 mixture of 5.2 and 5.3 resulted in copolymer **5.20** with an incorporation ratio of 66:34 (Figure 5.12 and Entry 10, Table 5.1). This is highly reproducible within experimental error and reflects the lower reactivity of 5.3 relative to 5.2. The second-generation catalyst 5.10 was used exclusively in these polymerizations due to the ease of separation of catalyst from the polymer via precipitation into methanol. Unlike the other catalysts investigated, catalyst 5.10 and its Fischer carbene (the product of quenching the polymerization) are highly soluble in methanol. In addition, their brilliant green color affords simple visual determination of the number of precipitations required to remove the catalyst. Trace metals analysis of a hydrogenated copolymer **5.21** prepared initially using 1 mol% 5.10 via inductively coupled plasma mass spectroscopy revealed the initial metal content (3804 ppm) had been reduced to 130 ppm. While this level is significantly higher than would be acceptable to the semiconductor industry, it is important to note that the initial catalyst concentration used in this example was 2-3 orders of magnitude larger than would be required for a process using chain transfer to control molecular weight. In addition, this removal of 96.6% of the ruthenium was achieved without the use of any special metal scavenging techniques.

Unlike the partial hydrogenation of the ROMP homopolymer **5.16**, hydrogenation of the less hindered backbone in copolymer **5.20** proceeded to significantly higher conversions. However, the polymers **5.21a** and **5.21b** still contain roughly 5-10% residual unsaturation.<sup>34</sup>

Nevertheless, polymer **5.21a** exhibits a  $T_g$  of 120 °C in good agreement with the expected value calculated from via the Flory-Fox equation. This result confirms the ability of **5.3** to serve as glass transition temperature enchancing comonomers in ROMP polymerizations.

*Transparency of Oxatricyclononene ROMP Polymers* The deep UV spectra of hydrogenated 4-oxatricyclononene copolymers **5.21a** and **5.21b** were measured by variable angle spectroscopic ellipsometry (VASE) and are shown in Figure 5.14. Copolymer **5.21b**, despite showing a fairly strong absorption at 193 nm due to the residual unsaturation (~ 8%), exhibits promisingly low absorbance (1.34  $\mu$ m<sup>-1</sup>) at 157 nm. While the effect of the higher degree of hydrogenation of the 3-oxatricyclononene polymer **5.19** (~ 98%) on the absorbance at 193 nm is substantial, the transparency at 157 nm is barely affected. The olefinic absorption band centered at 190 nm, therefore, appears to be a larger concern for applications in 193 nm and 193 nm immersion lithography. However, when extremely large amounts of unsaturation are left in the



Figure 5.14. VASE of oxatricyclononene ROMP polymers

polymer such as in the case of the non-hydrogenated polymer **5.17**, the absorbance at 157 nm becomes unacceptably high.

These initial fluorinated ring-opening metathesis polymers already offer similar transparency to one of the most transparent norbornene addition polymers. Optimization of the polymer hydrogenation and purification conditions is expected to produce further gains in transparency. For example, although copolymer **5.21a** appears to have more residual unsaturation than **5.21b** (9.1% v. 7.7%) via <sup>1</sup>H NMR, it is significantly less absorbing at 193 nm (Figure 5.15). It seems unlikely that a 2% compositional difference would account for this. The major difference between these copolymers is that **5.21a** underwent a second hydrogenation using hydrogen and palladium on carbon. Although the palladium-catalyzed hydrogenation was unable to reduce the degree of unsaturation by more than 1%, apparently, the hydrogenation conditions were effective in removing some highly absorbing species that are not readily identifiable by NMR.



Figure 5.15. VASE of oxatricyclononene ROMP polymers

Computational studies have suggested that cylcopentane structures are more transparent than norbornane structures and much more transparent than tricylcododecane structures.<sup>35</sup> All of our efforts to prepare ROMP polymers of hexafluorocarbinol-functionalized tetracyclododecenes resulted in polymers with absorbances of ~ 3  $\mu$ m<sup>-1</sup> or greater, indicating there is a significant absorbance penalty for adding the additional cyclic unit. However, by comparing the addition polymer **5.1** with polymers **5.19** and **5.21**, it can be seen that there is very little difference in the transparency of these vastly different frameworks. Although polymer **5.1** has an additional CH<sub>2</sub> per repeat unit, it is the longer runs of adjacent methylenes (such as the ethylene unit in the ROMP polymers) that are predicted to absorb at 157 nm.<sup>35</sup> Therefore, the transparency at 157 nm for these polymers is dictated more by the overall levels and distribution of fluorination (i.e. two CF<sub>3</sub> groups) than the alicyclic backbone structure. In the end, higher levels of fluorination are required to achieve the transparencies required for 157 nm photoresists (~ 0.7  $\mu$ m<sup>-1</sup>).

Lithographic Performance of ROMP-based Oxatricyclononene Resists: In order to evaluate their potential as negative tone photoresists, polymer 5.21a was imaged under standard lithographic conditions; however, the polymer did not clear in the unexposed areas. No clearing was observed in the exposed regions either, even at an extremely high exposure dose ( $\sim 100$  $mJ/cm^2$ ). The oxetane is not opening in the presence of the photoacid to produce hexafluorocarbinol groups which would render the polymer soluble in the exposed regions. Meanwhile, the base polymer is too hydrophobic to dissolve in the aqueous developer in the unexposed regions. Polymer 5.21a was subsequently blended with polyNBHFA 5.1 (10:90, respectively) to afford a more base soluble composition. Here, the oxetane polymer 5.21a is intended to act as a crosslinking agent to react with the hexafluorocarbinols of 5.1 in the exposed regions. Initial exposure results without a mask show clear negative tone behavior at ~32 mJ/cm<sup>2</sup> Figure 5.16).



Figure 5.16. Negative tone behavior of blend of 5.1/5.21a (90:10) as a function of exposure dose

However, when a mask was used, no discernable pattern was formed, only swelling and cracking. The solubility of **5.21** is clearly not high enough to afford development of fine features. Therefore, to resolve this hydophobicity concern, the oxetane monomer **5.2** was copolymerized with **5.6** to afford oligomeric copolymers using the terminal olefin chain transfer strategy mentioned above. Previous attempts to copolymerize **5.2** with hexafluorocarbinol-functional tetracyclododecenes resulted in polymers which crosslinked enough during storage to form insoluble gels when attempted to be redissolved. This problem can be mediated by reducing the molecular weight of the material by more than an order of magnitude. Lower molecular weight materials require a larger number of crosslinking reactions to generate insoluble material. However, when blended into a base-stabilized resist formulation with polyNBHFA (**5.1**), only a few crosslinks are required to form an insoluble, crosslinked material.

Copolymerization of **5.2** with **5.6** using allyl acetate as a CTA with the bisphosphine catalyst **6.1** afforded near quantitative yields of low molecular weight copolymers **5.22a/b**( $M_n < 5$  kDa). The incorporation ratio is identical to the feed ratio within experimental error. Initial

155



Figure 5.17. Low-molecular weight copolymers for crosslinking agents

imaging experiments are underway to evaluate the lithographic utility of these oligomeric crosslinking agents. Incorporation of a more nucleophilic alcohol to the base polymer (such the primary alcohol of norborn-5-en-2-yl methanol) is expected to improve crosslinking considerably.

## Conclusions

Fluorinated oxatricyclononenes offer good transparency at 193 nm and 157 nm and may be employed in either metal-catalyzed addition or ring-opening metathesis polymerizations. Palladium-catalyzed addition polymerization of 3-oxatricyclonene proceeded with a simultaneous isomerization reaction to produce gradient copolymers. Oxatricyclononene-based addition polymer resists showed positive-tone behavior rather than negative tone behavior due to the stability of the norbornene-annulated framework. The 4-oxatricyclononene **5.2** provides transparent addition polymers with high etch-resistance and ROMP polymers with high glass transition temperatures. Such structures could be used in conventional photoresists in place of norbornene to impart transparency and etch resistance or in ROMP polymers as a valuable comonomer to increase glass transition temperatures. Polymer molecular weights were most readily controlled using kinetic molecular weight control using terminal olefin chain transfer agents such as allyl acetate. Secondary metathesis on the hindered backbone olefins of these functionalized norbornenes occurs too slowly (if at all) to afford useful molecular weight control. The second-generation ruthenium bispyridine catalyst **5.10** affords the best combination of activity, molecular weight control, and ease of removal. While ROMP copolymers of 3-oxatricyclononenes proved too hydrophobic to dissolve in common aqueous developers, they have been shown to exhibit negative tone behavior when blended with polyNBHFA **5.1**. The reduction in steric hindrance around the oxetane ring via opening the norbornene framework during metathesis affords higher crosslinking activity. Work is continuing to explore alternative approaches towards utilizing these promising functionalities in deep ultraviolet resist materials, including low molecular weight copolymers with NBHFA **5.1** for transparent crosslinking agents in negative tone resist formulations.

#### Experimental

*Materials:* All air sensitive manipulations and polymerizations were carried out in an N<sub>2</sub>-filled drybox or using standard Schlenk techniques. All solvents were rigorously degassed in 18 L reservoirs and passed through two sequential purification columns consisting of activated alumina.<sup>36</sup> All starting materials were procured from Aldrich except quadricyclane (Exciton, Inc.), 3-(bicyclo[2.2.1]hept-5-en-2-yl)-1,1,1-trifluoro-2-(trifluoromethyl)propan-2-ol (NBHFA, **5.6**) and polyNBHFA (**5.1**) (courtesy of the Willson Lab, University of Texas, Austin). Quadricyclane was a gift from Exciton, Inc., Dayton, Ohio, and was made available through a Phase II SBIR project that has been sponsored by the Propulsion Directorate of the U.S. Air Force Research Laboratory, AFRL/PR. (WARNING: Quadricyclane has extraordinary toxicity for a hydrocarbon.)<sup>37</sup> Just as with the fluorinated ketones used in this paper, standard chemical safety precautions should be taken to avoid inhalation of quadricyclane vapors. Ruthenium olefin metathesis catalysts **5.8**, **5.9**, and **5.18** were obtained from Materia, Inc. Catalyst **5.10** was synthesized according to the literature.<sup>38</sup>

*Methods:* Nuclear magnetic resonance (NMR) spectra were obtained using either a Bruker AMX300, Varian *Unity Plus 300*, or a Varian *Gemini 300*, or Varian *Mercury 300* spectrometer (<sup>1</sup>H: 300 MHz, <sup>13</sup>C: 75 MHz, <sup>19</sup>F: 282 MHz). Shifts for NMR spectra are reported in ppm relative

to TMS (for <sup>19</sup>F, internal C<sub>6</sub>F<sub>6</sub> (~ 0.5 %) at -162.2 ppm) or to the chemical shift of the residual proteo solvent. Molecular weights (M<sub>n</sub>) and polydispersity indices (PDI) were measured from THF solutions by size exclusion chromatography (SEC) using a GPC apparatus equipped with two PLgel 5  $\mu$ m mixed-C columns (Polymer Labs) connected in series with a DAWN EOS multiangle laser light scattering (MALLS) detector and an Optilab DSP digital refractometer (both from Wyatt Technology). All molecular weight values are given relative to polystyrene standards. When no calibration standards were used, *dn/dc* values were obtained for each injection by assuming 100% mass elution from the columns. Differential scanning calorimetry (DSC) measurements were performed on either a Perkin Elmer *Series-7* or *Pyris* thermal analysis system. Trace metals analysis via inductively coupled plasma mass spectroscopy (ICP-MS) was performed by Desert Analytics, Tucson, Az.

*Vacuum UV Spectroscopy:* VUV spectra of polymer films were calculated from measurements made with a J. A. Woollam *VU301* variable angle spectroscopic ellipsometer (VASE) and/or measured with the Acton *CAMS-507* spectrophotometer. The films were cast on either silicon wafers (VASE) or calcium fluoride disks (Acton) from solutions in propylene glycol methyl ether acetate (PGMEA) or cyclohexanone and baked at 100-130°C for at least 5 minutes prior to analysis. All absorbance data reported are in base 10.

*Silicon oxide etch:* Reactive ion etching (RIE) experiments were performed using a Tel Unity2 DRM. The polymer sample was spin-coated on a hexamethyldisilazane-primed silicon substrate and baked at 90 °C for 90 seconds to afford a polymer coating with final thickness of approximately 150 nm. The blanket etch rate for the material was determined by pre- and post-etch thickness measurements using a non-polymerizing Ar/C4F8 oxide etch process. Tool conditions used for the experiment are as follows: 1500 W / 40 mT / 200 sccm Ar / 50 sccm C0 / 10 sccm C4F8 / 5 sccm O2 / 40 C

*Lithographic Imaging:* All imaging work was performed on an Exitech 157 nm small field (1.5 x 1.5 mm<sup>2</sup>) mini-stepper (0.6 NA) using either a binary mask ( $\sigma$  0.7) or phase-shift mask ( $\sigma$  0.3) at International SEMATECH in Austin, TX. Scanning electron micrographs were collected on a JEOL *JWS-7550*, and cross-sectional data were collected on a Hitachi *4500* microscope. Coating, baking, and development of resist films were performed using an FSI *Polaris 2000* track. Thickness measurements were made on a Prometrix interferometer. A typical resist formulation was prepared by mixing the polymer with 6 wt% (relative to polymer) photoacid generator (triphenylsulfonium nonaflate) and 0.3 wt% tetrabutylammonium hydroxide (TBAH) as the base to control acid diffusion and reduce T-topping. Dissolution inhibitors were mixed with the polymer to the desired ratio. The entire mixture was diluted in PGMEA to provide a viscosity that provides resist thicknesses of approximately 100-200 nm after spinning the resist at 2500 rpm onto a silicon wafer that had been previously coated with ~80 nm BARC (bottom anti-reflective coating, Shipley AR19). The post-apply bake was 140°C for 60 seconds and the post-exposure bake was 130°C for 90 seconds, unless stated otherwise. The exposed resists were developed in the industry-standard 0.26 *N* tetramethylammonium hydroxide (TMAH) developer.

## Synthesis and Compounds:

Poly(2-bicyclo[2.2.1]hept-5-en-2-ylmethyl-1,1,1,3,3,3-hexafluoro-propan-2-ol)<sup>4b</sup> (5.1).  $M_n = 3.86 \text{ kDa}$ . PDI = 2.11.  $\alpha_{10}^{157\text{nm}} = 1.15 \text{ }\mu\text{m}^{-1}$ .  $\alpha_{10}^{193\text{nm}} = 0.27 \text{ }\mu\text{m}^{-1}$ .  $\alpha_{10}^{248\text{nm}} = 0.20 \text{ }\mu\text{m}^{-1}$ .

**4,4-Bis(trifluoromethyl)-3-oxa-tricyclo[4.2.1.0<sup>2,5</sup>]non-7-ene (5.2).**<sup>13</sup> Quadricyclane<sup>39</sup>(10.2 mL, 10.0 g, 109 mmol) was added to an oven-dried 100 mL Fisher-Porter bottle and degassed via 3 sequential freeze-pump-thaw cycles. After cooling the reaction vessel to 0 °C, the system was exposed to 20 psi of hexafluoroacetone under rapid stirring. After the hexafluoroacetone was consumed over the course of a few minutes, the system was repressurized with hexafluoroacetone. This was repeated until the no observable pressure decrease was observed after 20 minutes. Excess hexafluoroacetone was carefully vented through concentrated sodium

hydroxide solution. The colorless liquid was purified via silica gel flash column chromatography (20:1 pentane/ether) to produce a colorless liquid. Alternatively, hexafluorocarbinol-containing impurities may be washed away with saturated potassium carbonate solution followed by vacuum distillation (79 °C, 30 Torr). Yield: 71%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm):  $\delta$  6.31 (dd, *J* = 5.7, 3.3 Hz), 5.91 (dd, *J* = 5.7, 3.3 Hz), 4.74 (d, *J* = 3.6 Hz), 3.23 (s), 3.20 (s), 2.59 (d, *J* = 4.8 Hz), 2.40 (d, *J* = 9.6 Hz), 1.59 (d, *J* = 9.6 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz, ppm):  $\delta$  -69.09 (q), -78.68 (q). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, ppm): 140.84, 132.56, 123.87 (q, *J* = 286 Hz), 121.94 (q, *J* = 286 Hz), 84.33, 80.40 (m), 45.32, 42.24, 42.00, 41.69 (q, *J* = 4.60 Hz). HRMS-[GC-EI+] (m/z): [M•]+ calc'd for C<sub>10</sub>H<sub>8</sub>F<sub>6</sub>O, 258.0479; found, 258.0481.

**5,5-Bis(trifluoromethyl)-4-oxa-tricyclo[4.3.0<sup>1.6</sup>.0**<sup>3,7</sup>]**non-8-ene (5.3).**<sup>13</sup> 3-Oxa-tricyclo[4.2.1.0<sup>2,5</sup>]non-7-ene (5.1) (9.68 g, 37.5 mmol) was added to a flame dried 100 mL round bottom flask with 50 mL anhydrous dichloromethane [0.2M]. Boron trifluoride diethyl etherate (3.75 mmol, 0.1 eq.) was added via syringe at 0 °C and the reaction was slowly warmed to room temperature and stirred for 12 hours. The boron trifluoride was quenched with excess anhydrous triethylamine. The dichloromethane was stripped and the crude reaction mixture was purified via silica gel flash column chromatography (20:1 pentane/ether) to afford 9.42 g (97%) of 5.2 as a colorless liquid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm):  $\delta$  6.45 (dd, *J* = 6.0, 3.3 Hz), 5.84 (dd, *J* = 5.4, 3.3 Hz), 4.48 (s), 3.56 9(s), 2.99 (m), 2.93 (s), 2.16 (dd, *J* = 12.6, 4.8 Hz), 1.09 (dm, *J* = 12.6 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz, ppm):  $\delta$  -69.72 (q, *J* = 12.6 Hz), -74.97 (q, *J* = 12.16 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, ppm):  $\delta$  124.51, 127.72, 123.24 (q, *J* = 288 Hz), 122.73 (q, *J* = 288 Hz), 81.140 (m), 78.13, 64.99, 52.58 (m), 41.93, 36.29 (m). HRMS-[EI+GC] (m/z): [M•]+ calc'd for C<sub>10</sub>H<sub>8</sub>F<sub>6</sub>O, 258.0479; found, 258.0487.

*General Addition Polymerization Procedure:* To a 20ml vial equipped with a stir bar were added allyl palladium chloride dimer (49.6 mg, 0.136 mmol) and silver tetrafluoroborate (52.8 mg, 0.271 mmol) in a dry box. Dichloromethane (5 mL) was added and the mixture was stirred

at room temperature for 20 minutes. The mixture was filtered through a 0.45  $\mu$ m PTFE syringe filter into a 25 mL round-bottom flask containing a solution of oxatricyclononene monomer (0.70 g, 2.71 mmol, [M]/[C]=10:1) in dichloromethane (10 mL). The reaction mixture was stirred at room temperature for 96 hours then filtered through a 0. 45  $\mu$ m PTFE syringe filter to remove the polymer-bound base, concentrated *in vacuo*, and precipitated into methanol (100 mL). The crude polymer was dissolved in ethyl acetate (50 mL) and stirred vigorously under a hydrogen atmosphere overnight. The solution was then allowed to sit for another hour to allow the palladium(0) to coagulate and precipitate. The black solid was removed by filtration through celite. The filtrate was concentrated and precipitated into methanol. Filtration provided the product as a white powder.

## Poly[(4,4-bis(trifluoromethyl)-3-oxa-tricyclo[4.2.1.0<sup>2,5</sup>]non-7-ene)-co-(5,5-

**bis(trifluoromethyl)-4-oxa-tricyclo[4.3.0.0**<sup>3,7</sup>**]non-8-ene)]** (5.4). Catalyst: Allyl palladium chloride dimer/AgBF<sub>4</sub>. [M]/[C] = 20:1. Conditions: dichloromethane, rt, 5 d. Polymer composition: 18% 5.2. 82% 5.3. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, ppm): δ 6.6-5.4 (0.25H), 5.3-4.0 (1.0 H), 3.6-0.6 (6.7H). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 282 MHz, ppm): δ -68- -69 (0.9F), -69 - -72 (12.7F), -72 - -73 (1F), -73 - -77 (11.37), -79 - -81 (m, 3F).  $\alpha_{10}^{157nm} = 2.28 \ \mu m^{-1}$ .  $\alpha_{10}^{193nm} = 2.02 \ \mu m^{-1}$ .

Poly(5,5-bis(trifluoromethyl)-4-oxa-tricyclo[4.3.0<sup>1,6</sup>.0<sup>3,7</sup>]non-8-ene) (5.5). Catalyst: Allyl palladium chloride dimer/AgBF<sub>4</sub>. [M]/[C] = 20:1. Conditions: dichloromethane, rt, 8 d. <sup>1</sup>H NMR (Acetone-d<sub>6</sub>, 300 MHz, ppm): δ 4.9-4.3 (m. aliphatic), 3.6-1.0 (m, aliphatic). <sup>19</sup>F NMR (Acetone-d<sub>6</sub>, 282 MHz, ppm): δ -67.62 (m, 3F),-72.66 (m, 3F). M<sub>n</sub> = 1.75 kDa. PDI = 1.23.  $\alpha_{10}^{157nm} = 1.46 \mu m^{-1}$ .  $\alpha_{10}^{193nm} = 0.78 \mu m^{-1}$ .  $\alpha_{10}^{248nm} = 0.37 \mu m^{-1}$ .

Poly[2-bicyclo[2.2.1]hept-5-en-2-ylmethyl-1,1,1,3,3,3-hexafluoro-propan-2-ol)-co-(4,4bis(trifluoromethyl)-3-oxa-tricyclo[4.2.1.0<sup>2,5</sup>]non-7-ene)-co-(5,5-bis(trifluoromethyl)-4-oxatricyclo[4.3.0.0<sup>3,7</sup>]non-8-ene)] (5.7). Reaction performed by Brian Osborn, Willson research group, University of Texas, Austin. Catalyst: allyl palladium chloride dimer/NaSbF<sub>6</sub>. [M]/[C] =
9:1. 1 eq. polymer-bound 2,6-di-*t*-butyl pyridine per eq. catalyst. Conditions: dichloromethane, rt,
3 d. Feed ratio: 66:33 5.2:5:6. Polymer composition: 70:20:10 5.6:5.2:5.3. Yield: 24 %.
Polymer composition: 70% NBHFA (5.6), 20% 5.2, 10% 5.3.

*General Ring-Opening Metathesis Polymerization Procedure*: To a 50 mL round-bottom flask with Teflon stirbar and teflon-coated septa cap was added the ruthenium catalyst (56 mg, .077 mmol, 0.01 eq.). The flask was purged with argon and anhydrous dichloromethane was injected. Upon dissolution of the catalyst, monomer (3.86 mmol) was injected and allowed to stir at room temperature. The reaction was quenched by the addition of more than 50 equivalents (relative to catalyst) of ethyl vinyl ether and allowed to stir at room temperature for 1 hour. The dichloromethane was removed *in vacuo* and the crude polymer dissolved in a minimal amount of ethyl acetate. The polymer was precipitated into methanol, centrifuged, and rinsed with methanol. After 2-3 precipitation cycles, the colorless polymer was dried under vacuum (10 mTorr) to afford a white polymeric solid. Note in all copolymers there is  $\sim 1\%$  of an unknown fluorinated structure. It is assumed that this is the result of a ruthenium-catalyzed olefin isomerization.

For screening of chain transfer conditions, the scale was significantly reduced with 100-200 mg of monomer and the reactions were performed in 5 dram vials with teflon septa caps.

Poly(5,5-bis(trifluoromethyl)-4-oxa-tricyclo[4.3.0.0<sup>3,7</sup>]non-8-ene) (5.16). Catalyst: 5.10 (1 mol%). CTA: 1,4-diacetoxy-*cis*-2-butene [M]/[CTA] = 50:1. Conditions: Dichloromethane, rt, 24 h. Yield: 71%. <sup>1</sup>H NMR (Acetone-d<sub>6</sub>, 300 MHz, ppm): δ 6.0-5.5 (m, 2H), 4.61 (m, 1H), 3.31 (m, 1H), 2.89 (m, 2H), 2.25 (m, 1H), 2.00 (m, 1 H). <sup>19</sup>F NMR (Acetone-d<sub>6</sub>, 282 MHz, ppm): δ - 66.80 (s, 3F), -71.06 (s, 3F).  $M_n = 83.0$  kDa. PDI = 1.07.  $T_g = 233$ °C.

Poly(4,4-bis(trifluoromethyl)-3-oxa-tricyclo[4.2.1.0<sup>2,5</sup>]non-7-ene) (5.17). Catalyst: 5.10 (0.2 mol%). CTA: allyl acetate [M]/[CTA] = 5:1. Conditions: dichloromethane, rt, 12 h. Yield: 67%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm): δ 5.8-5.4.9 (m, 2H), 4.8-4.55 (m, 0.1H), 4.52 (m, 0.1H), 3.62

(m, 0.4H), 3.45-2.9 (m, 1.4H), 2.42 (m, 0.6H), 1.44 (m, 0.6H). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz, ppm):  $\delta$  -72.0 - -73.5 (m, 3F), -79.55 (m, 3F). M<sub>n</sub> = 3.1k kDa. PDI = 1.38.

For thermal analysis:  $M_n = 91.6 \text{ kDa}$ , PDI = 1.43,  $T_g = 128 \text{ °C}$ .

## Poly[(4,4-bis(trifluoromethyl)-3-oxa-tricyclo[4.2.1.0<sup>2,5</sup>]non-7-ene)-co-(5,5-

#### bis(trifluoromethyl)-4-oxa-tricyclo[4.3.0.0<sup>3,7</sup>]non-8-ene)] (5.20).

(5.20a). Catalyst: 5.10 (1 mol%). Conditions: 1,2-dichloroethane, 55 °C, 24 h. Feed ratio: 50:50 5.2:5:3. Polymer composition: 66:34 5.2:5.3. Yield: 71%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm):  $\delta$ . <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz, ppm):  $\delta$  -68.23 (m, 1.74F), -69.76 (m, 0.06F), -72- -73.2 (m, 2.94), -73.53 (m, 1.86F), -75.08 (m, 0.09F), -79.81 (m, 3F). M<sub>n</sub> = 22.2 kDa. PDI = 1.08. T<sub>g</sub> = 154 °C.

(5.20b). Catalyst: 5.10 (2 mol%). Conditions: dichloromethane, rt, 16h. Feed ratio: 50:50 5.2:5:3. Polymer composition: 65:35 5.2:5.3. Yield: 72%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm):  $\delta$ . 6.0-5.3 (3H), 5.3-5.0 (1H), 4.8-4.55 (0.64H), 3.8-3.57 (0.60H), 3.55-3.3 (2.44H), 3.2-2.8 (1.7H), 2.6-2.2 (1.6H), 2.2-1.8 (1H), 1.8-1.5 (1.1H). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz, ppm):  $\delta$  -68.15 (m, 1.74F), -69.70 (m, 0.06F), -72.4- -73.2 (m, 2.94F), -73.38 (m, 1.86F), -75.01 (m, 0.09F), -79.69 (m, 3F). M<sub>n</sub> = 12.1 kDa. PDI = 1.10.

# Poly[(4,4-bis(trifluoromethyl)-3-oxa-tricyclo[4.2.1.0<sup>2,5</sup>]non-7-ene)-co-(2-bicyclo[2.2.1]hept-5en-2-ylmethyl-1,1,1,3,3,3-hexafluoro-propan-2-ol) (5.22).

(5.22a). Catalyst: 5.8 (0.8 mol%). Conditions: CH<sub>2</sub>Cl<sub>2</sub>, rt, 24 h. CTA: allyl acetate ([M]/[C] = 7:1). Feed ratio: 50:50 5.2:5:6. Polymer composition: 55:45 5.2:5.6. Yield: 99%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm):  $\delta$  6.6-6.4 (m, 1H), 6.0-5.7 (m, 0.7H), 5.7-5.3 (m, 6H), 5.3-4.9 (m, 3H), 4.7-4.4 (m, 1H), 3.8-3.5 (m, 0.4H), 3.5-3.2 (m, 3.4H), 3.2-1.0 (25H). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz, ppm):  $\delta$  -72.24 (m, 2.6F), --76 - -79 (m, 4.7H), -79.56 (m, 3F). M<sub>n</sub> = 4.2 kDa. PDI = 1.35. (5.22b). Catalyst: 5.8 (0.8 mol%). Conditions: CH<sub>2</sub>Cl<sub>2</sub>, rt, 24 h. CTA: allyl acetate ([M]/[C] = 7:1). Feed ratio: 33:66 5.2:5:6. Polymer composition: 33:66 5.2:5.6. Yield: 99%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm):  $\delta$  6.6-6.4 (m, 1H), 6.0-4.9 (m, 6H), 4.7-4.4 (m, 0.7H), 3.8-3.5 (m, 0.7H).

0.4H), 3.5-3.2 (m, 1.5H), 3.2-1.0 (18H). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz, ppm): δ -72.32 (m, 2.3F), --76 - -79 (m, 8.6H), -79.56 (m, 3F). M<sub>n</sub> = 4.2 kDa. PDI = 1.35.

*General Hydrogenation Procedure for Ring-Opening Metathesis Polymers:* In a flame-dried, 100 mL 2-neck round bottom flask equipped with a Teflon stirbar and reflux condenser, p-tosylhydrazide (5 eq.) was added. ROMP polymer was dissolved in 25 mL of propylene glycol methyl ether acetate (PGMEA) and added to the flask, followed by tri-n-propylamine (7 eq.). The mixture was degassed via 3 freeze-pump-thaw cycles. The reaction was heated to 130 °C under argon at which point, gas evolution began. After 4 hours, a second portion of p-tosylhydrazide was added and the reaction allowed to stir for 6 hours. Upon completion, the reaction was cooled to room temperature, taken up in ethyl acetate, washed with 0.1 N HCl solution, NaHCO<sub>3</sub> solution, and brine. The organic layer was dried over sodium sulfate, filtered, and concentrated. Repeated precipitation into methanol, centrifugation, and washing with methanol produced colorless polymer which was dried overnight to produce a white polymeric solid.

Poly(4,4-bis(trifluoromethyl)-3-oxa-tricyclo[4.2.1.0<sup>2,5</sup>]non-7-ene) (5.19). Starting polymer: M<sub>n</sub> = 20.2k, PDI = 1.25. Conditions: Hydrogenated according to general procedure. 86% hydrogenation, 79% yield. Second hydrogenation: 98% hydrogenation, 79% yield. Yield: 62%. Yield: 53 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm): δ. 5.39 (m, 0.03H), 5.03 (1H), 4.1-4.0 (0.2H), 3.75-3.5 (0.04H), 3.4-3.2 (1H), 2.75-2.5 (1H), 2.5-2.2 (2H), 1.6-1.4 (4H), 1.4-1.2 (1H) <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz, ppm): -72.54 (m, 3 F), -79.73 (m, 3F). M<sub>n</sub> = 20.2 kDa. PDI = 1.25.  $\alpha_{10}^{157nm}$  = 1.22 μm<sup>-1</sup>  $\alpha_{10}^{193nm}$  = 0.57 μm<sup>-1</sup>.  $\alpha_{10}^{248nm}$  = 0.07μm<sup>-1</sup>.

For thermal analysis:  $M_n = 208.3 \text{ kDa}$ . PDI = 1.52.  $T_g = 99 \text{ °C}$ .

Poly[(4,4-bis(trifluoromethyl)-3-oxa-tricyclo[4.2.1.0<sup>2,5</sup>]non-7-ene)-co-(5,5-

bis(trifluoromethyl)-4-oxa-tricyclo[4.3.0.0<sup>3,7</sup>]non-8-ene)] (5.21).

(5.21a). Conditions: Hydrogenated according to general procedure. 90% hydrogenation, 72% yield. Second hydrogenation H<sub>2</sub> (1 atm), Pd/C (10 wt % Pd), rt, 9h: 90.8% hydrogenation, 84% yield. Yield: 60%. Polymer composition: 65:35 5.2:5.3. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm): δ 6.0-5.3 (0.44H), 5.2-5.0 (1H), 4.8-4.4 (0.54H), 3.8-3.10 (1.5H), 3.1-2.75 (1H), 2.75-2.5 (1.4H), 2.5-2.3 (2H), 2.2-2.0 (1.7H), 1.95-1.3 (6H). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz, ppm): -68.02 (m, 1.68F), -70.4 (m, 0.03F), -72 - -74.0 (m, 4.8F), -75.1m, 0.02F), -79.98 (m, 3F). M<sub>n</sub> = 25.0 kDa. PDI = 1.08. T<sub>g</sub> = 120 °C.  $\alpha_{10}^{157nm}$  = 1.27 μm<sup>-1</sup>  $\alpha_{10}^{193nm}$  = 1.20 μm<sup>-1</sup>.  $\alpha_{10}^{248nm}$  < 0.01 μm<sup>-1</sup>.

(5.21b). Conditions: Hydrogenated according to general procedure. 78% hydrogenation, 59% yield. Second hydrogenation: 92.3% hydrogenation, 81% yield. Total yield: 48%. Polymer composition: 63:37 5.2:5.3. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm):  $\delta$  6.0-5.3 (0.19H), 5.15-5.0 (1H), 4.8-4.4 (0.66H), 3.4-3.2 (1H), 3.0-2.8 (1H), 2.8-2.55 (1.5H), 2.5-2.3 (2H), 2.2-2.0 (2H), 2-1.35 (7 H), 1.35-1.0 (1.5H) <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz, ppm):  $\delta$  -67.90 (m, 1.83F), -70.34 (m, 0.03F), -72- -74 (m, 4.95F), -74.94 (m, 0.06F), -79.79 (m, 3F). M<sub>n</sub> = 14.2 kDa. PDI = 1.09.  $\alpha_{10}^{157nm} = 1.34 \ \mu m^{-1} \ \alpha_{10}^{193nm} = 1.60 \ \mu m^{-1}. \ \alpha_{10}^{248nm} = 0.09 \ \mu m^{-1}.$ 

Trace metals analysis: Polymer composition: 68:33 **5.2:5.3**.  $M_n = 19.9 \text{ kDa}$ , PDI = 1.11. %Ru (ICP-MS) = 0.013%.

#### **References and Notes**

- (a). Patterson, K.; Yamachika, M.; Hung, R. J.; Brodsky, C. J.; Yamada, S.; Somervell, M. H.; Osborn, B.; Hall, D.; Dukovic, G.; Byers, J.; Conley, W.; Willson, C. G. *Proc. SPIE* 2000, *3999*, 365-374.
   (b). Brodsky, C.; Byers, J.; Conley, W.; Hung, R.; Yamada, S.; Patterson, K.; Somervell, M.; Trinque, B.; Tran, H. V.; Cho, S.; Chiba, T.; Lin, S-H.; Jamieson, A.; Johnson, H.; Vander Heyden, T.; Willson, C. G. *J. Vac. Sci. Technol.* B 2000, *18*, 3396-3401.
- (2) Gandler, J. R.; Jencks, W. P. J. Am. Chem. Soc. 1982, 104, 1937-1951.

- (3) (a). Ito, H. *IBM J. Res. Dev.* 2001, 45, 683-695. (b). Hoskins, T.; Chung, W. J.; Agrawal,
  A.; Ludovice, P. J.; Henderson, C. L.; Seger, L. D.; Rhodes, L. F.; Schick, R. A. *Macromolecules* 2004, 37, 4512-4518.
- (4) (a). Trinque, B. C.; Chambers, C. R.; Osborn, B. P.; Callahan, R. P.; Lee, G. S.; Kusumoto, S.; Sanders, D. P.; Grubbs, R. H.; Conley, W. E.; Willson, C. G. *J. Fluor. Chem.* 2003, *122*, 17-26. (b). Tran, H. V.; Hung, R. J.; Chiba, T.; Yamada, S.; Mrozek, T.; Hsieh, Y-T.; Chambers, C. R.; Osborn, B. P.; Trinque, B. C.; Pinnow, M. J.; MacDonald, S. A.; Willson, C. G.; Sanders, D. P.; Connor, E. F.; Grubbs, R. H.; Conley, W. *Macromolecules* 2002, *35*, 6539-6549. (c). Willson, C. G.; Trinque, B. C.; Osborn, B. P.; Chambers, C. R.; Hsieh, Y-T.; Chiba, T.; Zimmerman, P.; Miller, D.; Conley, W. *J. Photopolym. Sci. Technol.* 2002, *15*, 583-590. (d). Tran, H. V.; Hung, R. J.; Chiba, T.; Yamada, S.; Mrozek, T.; Hsieh, Y-T.; Chambers, C. R.; Osborn, B. P.; Trinque, B. C.; Pinnow, M. J.; Sanders, D. P.; Connor, E. F.; Grubbs, R. H.; Conley, W. *J. Photopolym. Sci. Technol.* 2002, *15*, 583-590. (d). Tran, H. V.; Hung, R. J.; Chiba, T.; Yamada, S.; Mrozek, T.; Hsieh, Y-T.; Chambers, C. R.; Osborn, B. P.; Trinque, B. C.; Pinnow, M. J.; Sanders, D. P.; Connor, E. F.; Grubbs, R. H.; Conley, W.; MacDonald, S. A.; Willson, C. G. *J. Photopolym. Sci. Technol.* 2001, *14*, 669-674. (e). Chiba, T.; Hung, R. J.; Yamada, S.; Trinque, B.; Yamachika, M.; Brodsky, C.; Patterson, K.; Vander Heyden, A.; Jamison, A.; Lin, S-H.; Somervell, M.; Byers, J.; Conley, W; Willson, C. G. *J. Photopolym. Sci. Technol.* 2000, *13*, 657-664.
- (5) (a). Ito, H.; Wallraff, G. M.; Brock, P. J.; Fender, N.; T., Hoa D.; Breyta, G.; Miller, D. C.; Sherwood, M. H.; Allen, R. D. *Proc. SPIE* 2001, *4345*, 273-284. (b). Trinque, B. C.; Chiba, T.; Hung, R. J.; Chambers, C. R.; Pinnow, M. J.; Osborn, B. P.; Tran, H. V.; Wunderlich, J.; Hsieh, Y-T.; Thomas, B. H.; Shafer, G.; DesMarteau, D. D.; Conley, W.; Willson, C. G. *J. Vac. Sci. & Technol. B.* 2002, *20*, 531-536. (c). Trinque, B. C.; Osborn, B. P.; Chambers, C. R.; Hsieh, Y-T.; Corry, S. B.; Chiba, T.; Hung, Raymond J-P.; Tran, H. V.; Zimmerman, P.; Miller, D.; Conley, W.; Willson, C. G. *Proc. SPIE* 2002, *4690*, 58-68.

- (6) (a). Kodama, S.; Kaneko, I.; Takebe, Y.; Okada, S.; Kawaguchi, Y.; Shida, N.; Ishikawa, S.; Toriumi, M.; Itani, T. *Proc. SPIE* 2002, 4690, 76-83. (b). Irie, S.; Ishikawa, S.; Hagiwara, T.; Yamazaki, T.; Furukawa, T.; Itani, T.; Kawaguchi, Y.; Kodama, S.; Yokokoji, O.; Kaneko, I.; Takebe, Y.; Okada, S. *Jap. J. Appl. Phys. Pt. 1.* 2003, 42(6B), 3743-3747.
- (7) (a). Feiring, A. E.; Crawford, M.; Feldman, J.; Farnham, W. B.; Feldman, J.; French, R. H.; Leffew, K. W.; Petrov, V. A.; Schadt, F. L., III; Wheland, R.C.; Zumsteg, F. C. *J. Fluorine Chem.* 2003, *122*, 11-16. (b). Toriumi, M.; Ishikawa, T.; Kodani, T.; Koh, M.; Moriya, T.; Araki, T.; Aoyama, H.; Yamashita, T.; Yamazaki, T.; Itani, T.; *J. Photopolym. Sci. Technol.* 2003, *16*, 607-614. (c). Sharif, I.; DesMarteau, D.; Ford, L.; Shafer, G. J.; Thomas, B.; Conley, W.; Zimmerman, P.; Miller, D.; Lee, G. S.; Chambers, C. R.; Trinque, B. C.; Chiba, T.; Osborn, B. P.; Willson, C. G. *Proc. SPIE* 2003, *5039*, 33-42.
- (8) (a). Bae, Y. C.; Douki, K.; Yu, T.; Dai, J.; Schmaljohann, D.; Koerner, H.; Ober, C. K.; Conley, W. *Chem. Mater.* 2002, *14*, 1306-1313. (b). Schmaljohann, D.; Young, C. B.; Dai, J.; Weibel, G. L.; Hamad, A. H.; Ober, C. K. *J. Photopolym. Sci. Technol.* 2000, *13*, 451-458.
- (9) (a). Stewart, M. D.; Patterson, K.; Sommervell, M. H.; Willson, C. G. J. Phys. Org. Chem.
  2000, 13, 767-774. (b). Ito, H. IBM J. Res. Dev. 2000, 44, 119-130. (b). MacDonald, S. A.;
  Willson, C. G.; Frechet, J. M. J. Acc. Chem. Res. 1994, 27, 151-158.
- (10) (a). Bloomstein, T. M.; Sedlacek, Jan H. C.; Palmacci, Stephen T.; Hardy, D. E.; Liberman, V.; Rothschild, M. Proc. SPIE 2003, 5040, 650-661. (b). Rothschild, M.; Bloomstein, T. M.; Fedynyshyn, T. H.; Liberman, V.; Mowers, W.; Sinta, R.; Switkes, M.; Grenville, A.; Orvek, K. J. Fluorine Chem. 2003, 122, 3-10. (c). Matsui, Y.; Umeda, S.; Seki, S.; Tagawa, S.; Ishikawa, S.; Itani, T. Jap. J. Appl. Phys., Pt. 1. 2003, 42(6B), 3894-3899. (d). Hien, S.; Angood, S.; Ashworth, D.; Basset, S.; Bloomstein, T. M.; Dean, K. R.; Kunz, R. R.; Miller, D. A.; Patel, S.; Rich, G. Proc. SPIE 2001, 4345, 439-447. (e). Fedynyshyn,

T. H.; Kunz, R. R.; Sinta, R. F.; Goodman, R. B.; Doran, S. P. J. Vac. Sci. Technol. B 2000, 18, 3332-3339. (f). Cefalas, A. C.; Sarantopoulou, E.; Gogolides, E.; Argitis, P. Microelectronic Eng. 2000, 53, 123-126.

- (11) (a). Pinnow, M. J.; Noyes, B. F., III; Tran, H. V.; Tattersall, P. I.; Cho, S.; Klopp, J. M.; Bensel, N.; Frechet, J. M. J.; Sanders, D. P.; Grubbs, R. H.; Willson, C. Grant. *PMSE Prepr.* 2002, *87*, 403-404. (b). Klopp, J. M.; Bensel, N.; Fresco, Z. M.; Frechet, J. M. J. *Chem. Comm.* 2002, *24*, 2956-2957. (c). Kim, J-B.; Lee, J-J. *Polymer* 2002, *43*, 1963-1967.
- (12) Tarrant, P.; Bull, R. N. J. Fluorine Chem. 1988, 40, 201-215.
- (13) (a). Sanders, D. P. *Chapter 4 Ph. D. Thesis*, California Institute of Technology, 2004. (b).
  Sanders, D. P.; Osborn, B. P.; Willson, C. G.; Grubbs, R.H. Manuscript in preparation, 2004.
- (14) Sanders, D. P.; Connor, E. F.; Grubbs, R. H.; Hung, R. J.; Osborn, B. P.; Chiba, T.;
   MacDonald, S. A.; Willson, C. G.; Conley, W. *Macromolecules* 2003, *36*, 1534-1542.
- (15) Mathew, J. P.; Reinmuth, A.; Melia, J.; Swords, N.; Risse, W. Macromolecules 1996, 29, 2755-2763.
- Barnes, D. A.; Benedikt, G. M.; Goodall, B. L.; Huang, S. S.; Kalamarides, H. A.; Lenhard, S.; McIntosh, L. H., III; Selvy, K. T.; Schick, R. A.; Rhodes, L. F. *Macromolecules* 2003, 36, 2623-2632.
- (17) (a). Lipian, J.; Mimna, R. A.; Fondran, J. C.; Yandulov, D.; Shick, R. A.; Goodall, B. L.; Rhodes, L. F.; Huffman, J. C. *Macromolecules* 2002, *35*, 8969-8977. (b). Hennis, A. D.; Polley, J. D.; Long, G. S.; Sen, A.; Yandulov, D.; Lipian, J.; Benedikt, G. M.; Rhodes, L. F.; Huffman, J. *Organometallics* 2001, *20*, 2802-2812.
- (18) Sulfuric acid-catalyzed methanolysis of oxetane 5.2 proceeded in 69% of ring-opened compounds after 22 hours. Ring-opening of the saturated version was significantly slower (14% after 2.5 days). Depending upon reaction conditions, reaction of saturated 5.2 with

triflic acid in benzene resulted in either stoichiometric ring-opening or catalytic isomerization to saturated version of **5.3**.

- (19) (a). Nguyen, S. T.; Trnka, T. M. In *Handbook of Olefin Metathesis*, vol. 1: Wiley-VCH: Weinheim, 2003; pp. 61- 85. (b). Frenzel, U.; Nuyken, O. *J. Polym. Sci. A. Polym. Chem.* 2002, 40, 2895-2916. (c). Trnka, T. M.; Grubbs, R. H. Acc. Chem. Res. 2001, 34, 18-29. (d). Buchmeiser, M. R. Chem. Rev. 2000, 100, 1565-1604. (e). Bielawski, C. W.; Grubbs, R. H. Angew. Chem. Int. Ed. 2000, 39, 2903-2906.
- (20) (a). Bielawski, C. W.; Hillmyer, M. A. In *Handbook of Olefin Metathesis*, vol. 3: Wiley-VCH: Weinheim, 2003; pp. 255- 282. (b). Bielawski, C. W.; Benitez, D.; Morita, T.; Grubbs, R. H. *Macromolecules* 2001, *34*, 8610-8618. (c). Katayama, H.; Fukuse, Y.; Nobuto, Y.; Akamatsu, K.; Ozawa, F. *Macromolecules* 2003, *36*, 7020-7026.
- (21) Reichmanis, E.; Nalamasu, O.; Houlihan, F. M. Acc. Chem. Res. 1999, 32, 659-667.
- (22) (a). Okoroanyanwu, U.; Shimokawa, T.; Byers, J.; Willson, C. G. *Chem. Mat.* 1998, *10*, 3319-3327. (b). Patterson, K. W. *Ph.D. Dissertation*, University of Texas-Austin, **2000**.
  (c). Suwa, M.; Iwasawa, H.; Kajita, T.; Yamamoto, M.; Iwanaga, S-I. *Proc. SPIE* **1998**, *3333*, 26-31. (d). Meyer, U.; Kern, W.; Hummel, K.; Stelzer, F. *Eur. Polym. J.* **1999**, *35*, 69-76.
- (23) Sanders, D. P.; Osborn, B. P. Unpublished results.
- (24) Preishuber-Pflugl, P.; Eder, E.; Stelzer, F.; Reisiniger, H.; Mulhaupt, R.; Forsyth, J.;
   Perena, J. M. *Macromol. Chem. Phys.* 2001, 202, 1130-1137.
- (25) Otsuki, T.; Goto, K.; Komiya, Z. J. Polymer Sci. A Polym. Chem. 2000, 38, 4661-4668.
- (26) Contreras, A. P.; Cerda, A. M.; Tlenkopatchev, M. A. Macromol. Chem. Phys. 2002, 203, 1811-1818.
- (27) (a). Stille, J. R.; Grubbs, R. H. J. Org. Chem. 1989, 54, 434-444. (b). Stille, J. R.; Grubbs, R. H. J. Org. Chem. 1990, 55, 843-862.
- (28) Ivin, K. J. Makromol. Chem., Macrmol. Symp. 1991, 42/43, 1-14.

- (29) Hejl, A.; Scherman, O. A.; Grubbs, R. H. Macromolecules 2005, accepted.
- (30) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. Angew. Chem. Int. Ed. 2002, 41, 4035-4037.
- (31) (a). Slugovc, C.; Demel, S.; Stelzer, F. Chem. Commun. 2002, 2572-2573. (b). Choi, T. L.;
  Grubbs, R. H. Angew. Chem Int. Ed. 2003, 42, 1743-1746. (c). Slugovc, C.; Riegler, S.;
  Haynn, G.; Saf, R.; Stelzer, F. Macromol. Rapid Commun. 2003, 24, 435-439.
- (32) It should be noted that these PDIs are significantly narrower that those of norbornene polymerized at room temperature with these catalysts.<sup>31b</sup> The inability of the ruthenium catalyst to readily react with the more hindered backbone olefins of **5.16** at these temperatures limits chain transfer and provides for a more controlled polymerization. Even lower PDIs (1.05) can be achieved with catalyst **5.10** by lowering the reaction temperature to 0 °C (see Entry 8, Table 3).
- (33) (a). Ilker, M. F.; Coughlin, E. B. *Macromolecules* 2002, *35*, 54-58. (b). Al Samak, B.;
  Carvill, A. G.; Hamilton, J. G.; Rooney, J. J.; Thompson, J. M. *Chem. Commun.* 1997, 2057-2058.
- (34) It is unknown whether this reluctance to hydrogenate is due to adjacent units of 5.2 or olefin isomerization to very sterically hindered trisubstituted olefins which may be occurring during either polymerization or hydrogenation. In certain cases, copolymers polymerized at a lower temperature (room temperature) in order to limit any rutheniumcatalyzed olefin isomerization proved to hydrogenate more completely (>98%). Additional work is ongoing to understand and resolve this difficulty.
- (35) Dixon, D. A.; Matsuzawa, N. N.; Ishitani, A.; Uda, T. *Phys. Stat. Sol B* 2001, *226*, 69-77.
  (b). Matsuzawa, N. N.; Ishitani, A.; Dixon, D. A.; Uda, T. *Proc. SPIE* 2001, *4345*, 396-405.
  (c). Yamazaki, T.; Itani, T. *Jpn. J. Appl. Phys.* 2003, *42*, 3881-3884.
- (36) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K. Trimmers, F. J. Organometallics 1996, 15, 1518-1520.

- (37) Kinkead, E. R.; Wolfe, R. E.; Salins, S. A.; Grabau, J. H. Report (1993), (Order No. AD-A272694). CAN 123:190700.
- (38) Sanford, M. S.; Love, J. A.; Grubbs, R. H. Organometallics 2001, 20, 5314-5318.
- (39) Quadricyclane (tetracyclo[3.2.0.0<sup>2,7</sup>.0<sup>4,6</sup>]heptane) can be synthesized photochemically from norbornadiene. (a). Hammond, G. S.; Turro, N. J.; Fischer, A. J. Am. Chem. Soc. 1961, 83, 4674-4675. (b). Hammond, G. S.; Wyatt, P.; DeBoer, C. D.; Turro, N. J. J. Am. Chem. Soc. 1964, 86, 2532-2533. (c). Smith, C. D.; Taggi, A. J.; Meinwald, J. Org. Synth. 1971, 51, 133-138. (d). Alberici, F.; Cassar, L.; Monti, F.; Neri, C.; Nodarai, N. US Pat. 5076813, 1991.