# FUNCTIONALIZED POLYMERS FROM RING-OPENING METATHESIS POLYMERIZATION THROUGH MONOMER DESIGN

Thesis by

Ron Walker

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# Acknowledgments

Confucius: "*A journey of a thousand miles begins with a single step*"

Upon reading this quote, my first interpretation was that Confucius was merely commenting on the simplicity as to which a journey begins. However, the more I contemplated those words, the more I began to understand the true meaning of what Confusius was attempting to communicate. Now that I am at the end of this chapter of my life, I believe I have fully grasped what Confucius was trying to convey. He was not simply commenting on how effortless it is to begin a journey, but instead that you take the "first step".

As I sit here thinking about what to write and how exited I am to finally receive my PhD, I can't help but think about all the people who have helped and guided me into taking that "first step" and all those who have encouraged me along the way. Throughout this process, I have grown more than I ever would have imagined. I've also met a lot of loving and positive people, more than I could possibly thank in this acknowledgments section, but I will do my best to try, so here it goes.

My first acknowledgement goes to God, for without him I would not be where I am today. Graduate school has the uncanny ability to stress a person beyond belief and at the same time make you feel like you just won the lottery. It can also make you find religion. Throughout the many ups and down of earning my degree, my relationship with God has grown closer and stronger.

Next to God, is my lovely and beautiful wife Tammie. She has been the angel by my side throughout this journey, constantly pushing me forward and sometimes even leading the way. Although she did not make it easy winning her love and attention, I

could not have asked for a better wife and friend. No one understands me better and can cheer me up when I am down like she can. She is more than I ever wanted in someone to love and I am truly a lucky man to be her husband. She is my first, my last, my everything.

I would also like to thank my brother Don. We've been walking this parallel journey for a long time and now we must separate to move onto the next chapter of our lives. Also if it were not for my brother, I would have probably finished graduate school a year earlier. We spent a lot of time together working in the dim North Wilson parking garage swapping an engine into his AE86 Toyota Corolla and doing various other projects. Nonetheless it was all worth it.

My parents have done nothing but encourage me to do my best throughout life. It is with there unconditional love and support that I have become the man I am today. I'll never be able to repay or thank them enough for what they have given me. I can only promise that I will try my very best to continue to make them proud. Also I have to give a special thanks to my little sister. Although she is five years younger than me, she has always been there to lend an ear when needed. I know she has a bright future ahead of her and I hope to give her the same encouragement that she has given me throughout this time.

While we are on the subject of family, I must thank my wife's family The Londons: Ra and Glo, Ats and Shavara, Willie and Latrice, Shad and Scottie, Dedrick and Monique, Brit, Trey and Ronald. Even before I married their little sister, they have always accepted me as part of the family and they continue to do so. Their love and support during my time here at Caltech has meant a lot to me, and I will forever be

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Of course I cannot go on writing these acknowledgements without thanking my advisor Bob Grubbs. What can I say about Bob that hasn't already been said? I will be forever thankful to him for allowing me a place in his group and advising me like he has done so many. Bob has allowed me the freedom to work on a wide range of interesting problems while teaching me to put things into a bigger perspective. His unique and positive style of advisement, constant encouragement and optimism is what made the fun part of graduate school fun.

As a member of the Grubbs' group I have developed a number of long and fruitful relationships with current and past members. Almost everyone who has been a part of the Grubbs group during my stay here has helped or aided me during my graduate career. During my first tenure at Caltech as summer MURF student Oren Scherman was my co-advisor. He was the first to teach me about polymer chemistry and the power of olefin metathesis. Special thanks to Cheol Chung, George Vougioukalakis, Donde Anderson, Erin Guidry, Greg Beutner, Brian Connel, Dan Sanders and Isaac Rutenburg who all have mentored me in the ways of metathesis during my time as a graduate student. I would like to especially thank Jason Jordan, who was my lab mate for four years. He was always the first person I would go to with questions about chemistry and anime. Also polymer chemistry would not have been so much fun if it was not for the polymer brain trust: John Matson, Irina Gorodetskaya, Rosemary and Yan Xia. Our many discussions about

polymer chemistry and just life in general have helped to make my graduate experience all the more fun. I also have to give a very, very special thanks Professor Mike Page, his wife Kim and their two children Chris and Matthew. Although Professor Page decided to spend only one year with me, it was all that was needed to develop a lifelong friendship. There have been many more that have helped me along my graduate career and I thank them all.

There area also a few entities I must acknowledge that have made my life in graduate school pass by smoothly by affording me the opportunity to relieve all the bottled up stress and aggression from failed experiments. Special thanks go to our flag football team TEAM JUSTICE, without this crazy group of guys I would have no way of releasing my inner desire to lay down the hammer of justice and also for giving me a nine day, all expense paid trip to Huntington Hospital so that I could heal my level four liver laceration. I would also like to thank Paul Clark for introducing me to the greatest sport in the world “Olympic Weightlifting”. I will miss our daily trips to the gym and our never-ending quest to become Ripped and Shredded. And last, but not least I must give a special thanks to Ironmind’s Captains of Crush grippers. Never will there be a bottle that cannot be opened or rock that cannot be crushed. Thanks to these awesome training tools I now have the combined crushing force of 390 lbs in my hands or lets just say I have the grip strength of ten thousands gorillas “Crushed to Dust”.

Now onto a more serious note, my time here in California as a graduate student has also been influenced by number people outside of graduate school. I do not know how my wife and I would have survived, here being so far away from family, if it were not for the Johnson Family. I hold them in a very special place in my heart. They are not

simply a family away from home for us, they are our family. Al and his wife Ramona, my wife's best friend, and their three children Jordan, Ashley, and Kennedy have been our closest family here in Pasadena as well as here three sisters and their families, Regina, Lorraine, and Lisa. We cannot count the many times and ways they've been there for us. Also I have to give special thanks to their very caring and loving parents Lorretta and Conrad Johnson. They have become more than just a second mother and father to my wife and I. It is because of the Johnson`s love and support that the hardest part about leaving California will not be leaving the weather but saying goodbye to all of them. We will always remember all the countless birthday parties and holidays we have spent with the Johnson's and I know that even though we are moving onto the next phase of our lives we will continue to visit our "family" and "home".

And with this, I end my acknowledgements section and I take this "first step" into the next chapter of my life. Enjoy.

# Abstract

The focus of the research presented in this thesis deals with the synthesis and development of functionalized polymers using ring-opening metathesis polymerization (ROMP). The approach taken in developing the polymers presented within, feature the careful design and synthesis of a number of functionalized and unique monomers. A basic history and overview of olefin metathesis and polymer science is given in Chapter 1.

Chapters 2 and 3 describe the development of controlled polymer architectures for use as barrier materials. This work was done in collaboration with Kuraray, Inc, which is a major manufacturer of commercial barrier materials. Also the structure-property relationships of these materials were studied to better understand how polymer architecture affects polymer properties.

Chapter 4 discusses the controlled living ROMP of highly strained *trans*-cyclooctene. The knowledge and understanding of solvent effects during ROMP was also explored as a means to attenuate the rate of propagation during ROMP. Block copolymers containing polynorbornene and PCO were also synthesized and hydrogenated to form block copolymers containing blocks of linear, narrowly dispersed polyethylene.

Chapter 5 describes the development of photodegradable polymer. By incorporating photodegradable links into a polymer chain, using ROMP, the polymer chain may be degraded upon irradiation with light.

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# Chapter 1

# Introduction

## 1.1. Introduction

The mechanism whereby atoms combine to form molecules is called the chemical bond. It is the molecular glue that holds our world together. Chemical bonds may be created and broken by various processes. These processes occur on a daily basis oblivious to the naked eye. Our own bodies' consistently form and break bonds for the purpose of life. The art in chemistry lies in the ability and understanding of how to break and form chemical bonds to create new molecules or modify existing ones. The understanding, development and application of these mechanisms have lead to the discovery of many of today's medicines and advanced technologies.

Olefin metathesis is one such bond-forming/breaking reaction that was discovered in the mid-1950s.[1,2] It is a powerful method by which carbon-carbon double bonds broken to form to carbon-carbon double bonds (olefins). The process of olefin metathesis occurs when an olefin coordinates to a metal carbene catalyst, upon which a metallocyclobutane is formed as shown in Figure 1.1.[3] The metallocyclobutane can either form a new olefin or revert to its original form. This reaction affords the possibility of a number of applications, such as cross metathesis (CM), ring-closing metathesis (RCM), and ring-opening cross metathesis (ROCM) as shown in Figure 1.1.[1,4,5]

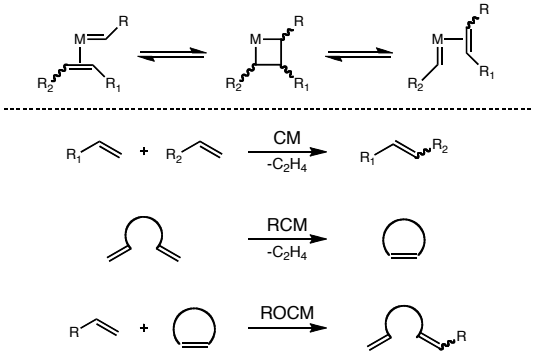
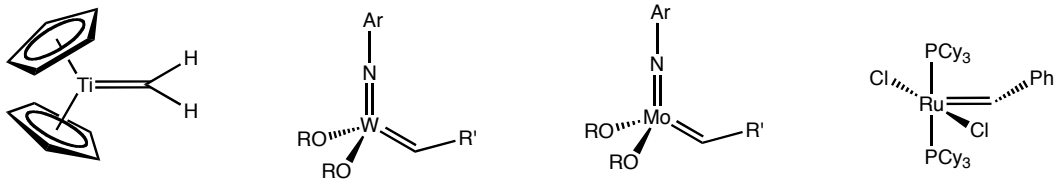



**Figure 1.1.** Olefin metathesis mechanism and applications.

Since olefin metathesis is a metal mediated process, there have been numerous studies and developments of olefin metathesis catalysts. Early research focused on the development of homogenous well-defined early transition metal catalysts based on titanium, tungsten, and molybdenum Figure 1.2. Although these catalysts exhibited high activity, their selectivity for reactions with olefins is poor and they exhibit functional group intolerance. Furthermore, they required rigorous handling conditions due to their instability towards air. Catalysts based on late transistion metals are more tolerant of functional and are more reactive towards olefins. In the mid 1990s, Grubbs et al. reported a family of well-defined ruthenium-carbene olefin metathesis catalyst.[6] These catalyst showed remarkable reactivity with olefins and possessed high functional group tolerance with a number of substrates. Since, then a wide range of ruthenium-based catalysts has been developed.




| Titanium | Tungsten | Molybdenum | Ruthenium |
|---|---|---|---|
| Acids | Acids | Acids | **Olefins** |
| Alcohols, Water | Alcohols, Water | Alcohols, Water | Acids |
| Aldehydes | Aldehydes | Aldehydes | Alcohols, Water |
| Ketones | Ketones | **Olefins** | Aldehydes |
| Esters, Amides | **Olefins** | Ketones | Ketones |
| **Olefins** | Esters, Amides | Esters, Amides | Esters, Amides |

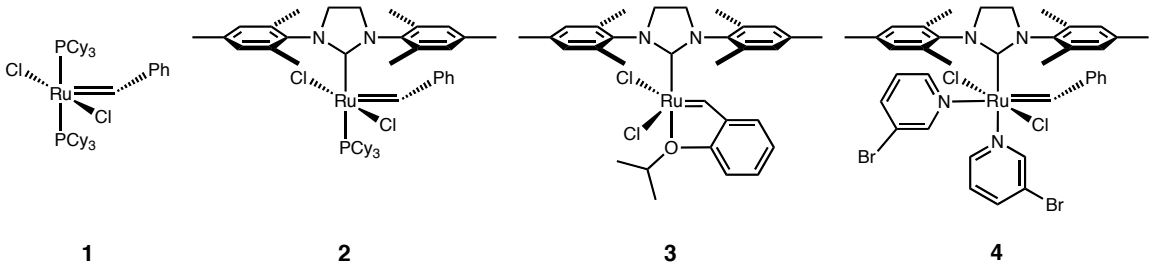
*reactivity* ↑

*functional group tolerance* →

← *catalyst activity*

**Figure 1.2.** Reactivities of olefin metathesis catalysts.

Although the ruthenium catalysts are very functional group tolerant, their activities are much lower than that of early transition metal catalysts.[2,7-9] Replacement of the phosphine ligand with an N-heterocyclic carbene to form **2**[10], greatly increases catalyst activity while maintaining functional group tolerance as shown in Figure 1.3. Since this development a number of catalysts have been developed and used extensively due to their high activities and functional group tolerance.




**1** **2** **3** **4**

**Figure 1.3.** Olefin metathesis catalysts.

## 1.2. Ring-Opening Metathesis Polymerization

Polymers science is field of chemistry in which these chemical bonds are linked together to form large molecules, consisting of repeated units.[11] One can envision a polymer as a long chain and each link is a repeat unit. The chemical bonds in this chain are the physical loops created by the interlocking of the links. There unique properties have lead to their implementation in almost all aspects of our daily lives. From simple plastic grocery bags to the materials used in the Space shuttle, polymers are everywhere.

As stated previously, the formation of polymers consist of the formation of repeated chemical bonds to form a large chain. By utilizing different olefin geometries, polymers may be formed using the olefin metathesis reaction as shown in Figure 1.4. At low concentrations $\alpha,\omega$-dienes can be used in RCM. However at high concentration the same substrates may be used in acyclic diene metathesis (ADMET). Furthermore, by

using an olefin with a strained cyclic configuration ring-opening metathesis polymerization (ROMP) may take place.

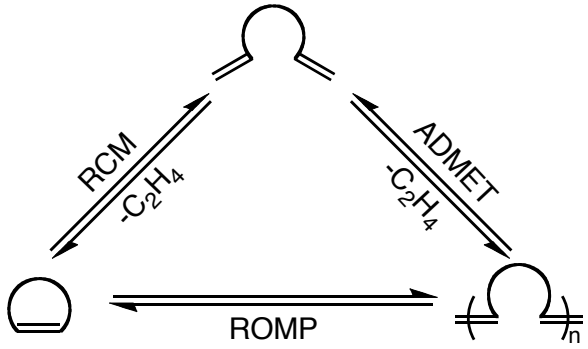



**Figure 1.4.** Olefin metathesis transformations.

The basis for much of the work reported in this thesis based on the understanding and application of ROMP. One key factor that drives ROMP is the release of ring strain. This ring strain is inherent in typical cyclic olefins used from ROMP (figure). Additionally, since metathesis is a reversible process, it is controlled by a thermodynamic equilibrium.[1]

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# Chapter 2

# Synthesis and Characterization of Regioregular Ethylene-Vinyl Alcohol Copolymers made by Ring-Opening Metathesis Polymerization from 3,5-Cycloheptene-1,3-diol.

# Abstract

The syntheses of regioregular as well as stereoregular ethylene vinyl alcohol (EVOH) copolymers by ring-opening metathesis polymerization (ROMP) with ruthenium catalysts are reported. Symmetric cycloheptene-diol monomers were protected as acetates and benzoates to impart solubility to the monomer. Polymer molecular weights could be easily controlled by either varying the monomer-to-catalyst ratio or by the addition of a chain transfer agent. Hydrogenation and subsequent deprotection of the ROMP polymers afforded the EVOH materials in good yields and the structures were confirmed by $^{1}H$ NMR and $^{13}C$ NMR spectroscopies.

## 2.1. Introduction

Ethylene-vinyl alcohol copolymers (EVOH) exhibit excellent barrier properties towards gases and hydrocarbons.[1-6] Due their robust barrier properties, they have found utility in the food packaging, biomedical, and pharmaceutical industries.[3] They are typically synthesized through the free radical polymerization of ethylene and vinyl acetate, followed by saponificiation.[7] While free-radical polymerization is effective, it does not allow for absolute control of the polymer architecture. These polymers usually contain some degree of branching, along with a random distribution of alcohol functionality along the polymer backbone.[3,8] Consequently free radical polymerization only allows the ratio of the monomers may be controlled, which is key for understanding the structure-property relationships of these materials.

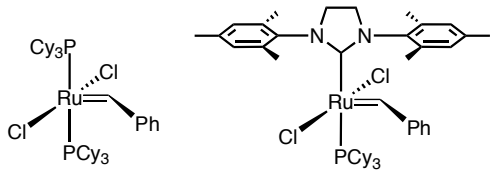



**Figure 2.1.** Ruthenium olefin metathesis catalysts (Cy=cyclohexyl).

The Grubbs group has developed functional-group tolerant ruthenium alkylidene catalysts for use in a variety of olefin metathesis reactions including ring-opening metathesis polymerization (ROMP), shown in **Figure 2.1**.[9,10] ROMP of substituted cyclic-olefins has been shown to produce linear polymers that incorporate polar functional groups along the polymer backbone. Hillmyer et al. reported the ROMP of several polar substituted cyclooctenes.[11] However the asymmetry of the cyclooctenes prevents regioregular placement of functional groups. By utilizing $C_2$-symmetric

monomers, regioregular placement of alcohols along the polymer backbone can be maintained along with their stereochemistry.

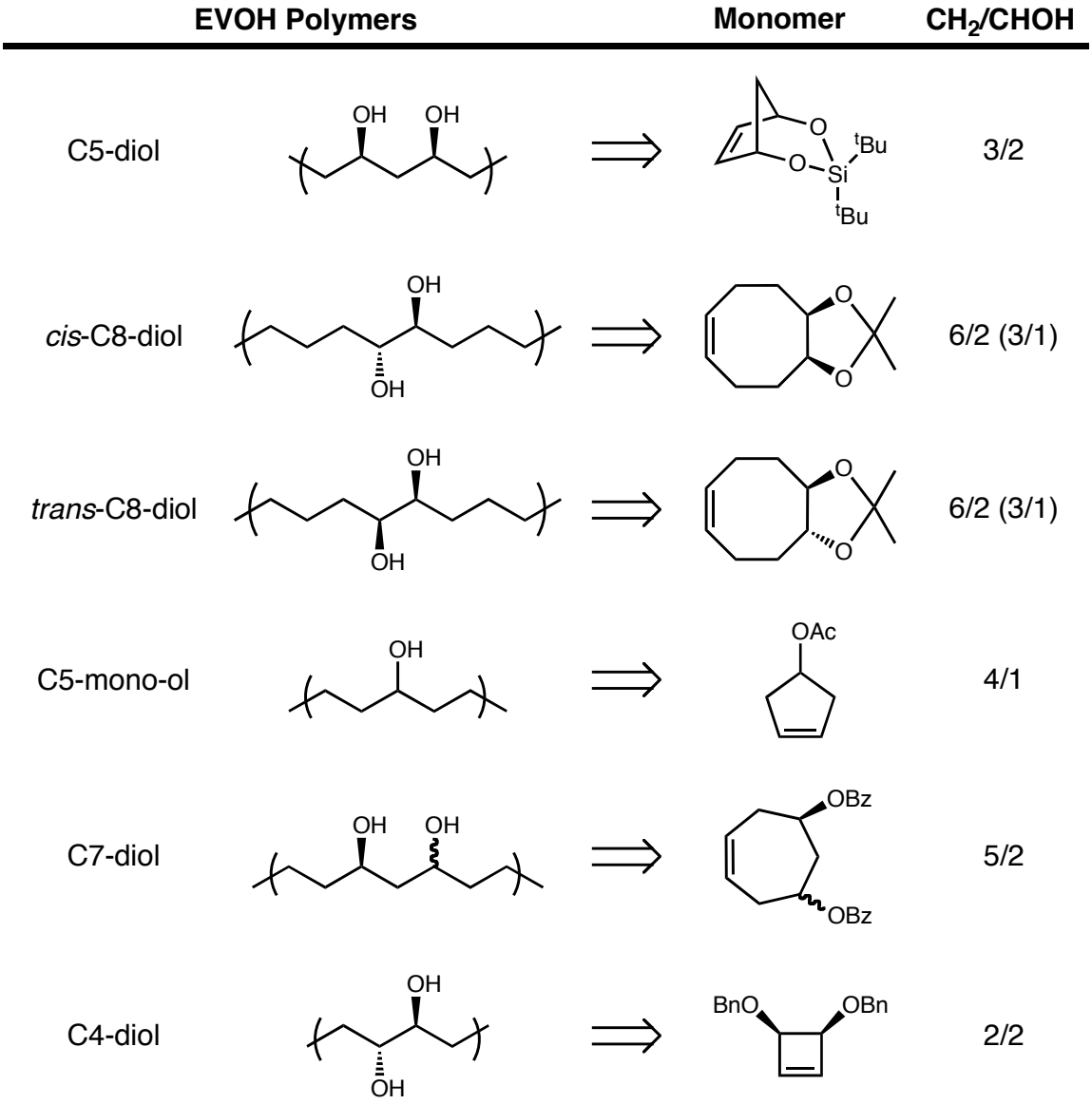



**Figure 2.2.** EVOH polymers developed using ROMP.

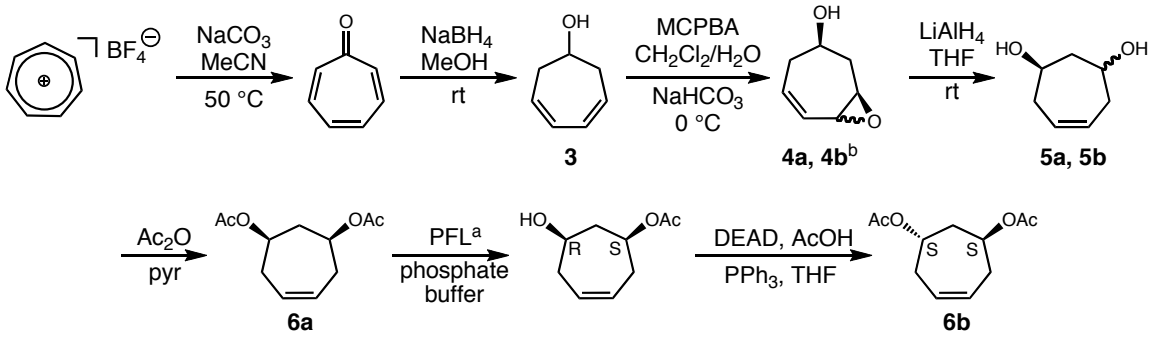
Previously we have developed vinyl alcohol containing polymers for use EVOH materials. This work was done in collaboration with Kuraray, Inc, a major manufacturer of EVOH materials. Initial interest in EVOH materials developed using ROMP began the synthesis and characterization of a methylene-vinyl alcohol copolymer, poly((vinyl alcohol)$_2$-*alt*-methylene) (MVOH) as seen in Figure 2.2(C5-diol).[12] The final MVOH material was determined by Kuraray, Inc to have improved barrier properties when compared to commercial Kuraray, Inc EVOH polymers of similar $CH_2$/CHOH ratios.

The work lead to the synthesis and characterization of *cis*- and *trans*-C8-diol polymers containing similar regioplacement of alcohol functionalities but different stereochemistries. It was determined that polymer bulk properties were greatly affected by the stereochemistry of the functional groups as well as their respective barrier properties.[13] The synthesis of EVOH copolymers *cis*- and *trans*-C8-diol was previously published (Appendix). Therefore the C7-diol polymer was next to be studied. The cycloheptene based C7-diol polymer contains a 1,3-diol configuration similar to C5-diol. However, it differs in that it has a higher $CH_2$/CHOH ratio.

## 2.2. Results and Discussion

### 2.2.1. Monomer Design and Synthesis

**Scheme 2.1.** Synthesis of Monomer **6a**/**6b**.

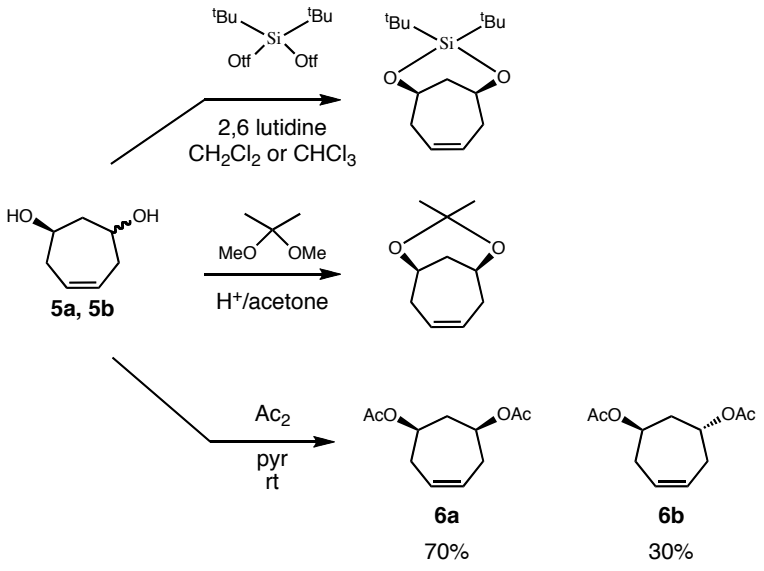



[a]PFL = Pseudomonas fluorescence lipase. [b]a = cis, b = trans

To arrive to the target monomer, a multi-step synthesis must be carried out as shown in Scheme 2.1.[14,15] Tropone can either be synthesized from tropylium tetrafluroborate or purchased commercially. Tropone is then reduced to 3,5-cycloheptadienol (**3)** with sodium borohydride. **3** is then distilled to afford 90% pure product. Selective epoxidation of **3** with MCPBA at 0 °C gave a yield in the range of 20%-30%. In the presence of 1.2 equiv of $NaHCO_3$, yields of 50%-60% were obtained. After purification on silica gel, the $^1$H NMR showed that the product was a mixture of the diastereomers **4a** and **4b**. By $^1$H NMR the cis:trans ratio was 40:50. This result was far from what was obtained the literature preparation. Several attempts were made at optimizing the epoxidation conditions in order to obtain **4a** as the major product. Temperature, addition of MCPBA, equivalents of $NaHCO_3$ and brands of MCPBA were all adjusted. Disappointingly the cis:trans ration never shifted significantly and the yields stayed constant. Therefore careful chromatography with silica gel was attempted in order to separate **4a** and **4b** similar to the literature prep. A number of solvent mixtures were

explored and none yielded any diastereomer separations. Since all attempts to obtain pure **4a** and **4b** failed, reduction of the epoxide with $LiAlH_4$ to afford the **5a** and **5b** was carried out on the mixture of diastereomers. A yellow viscous oil was obtained in 50% yield and $^1$H NMR of the also showed that both **5a** and **5b** were present when compared to the literature. In the literature prep it was noted that the **5a** is a white solid and **5b** is a clear oil. With this knowledge in hand attempts to crystallize the **5a** were attempted and all attempts failed. Therefore column chromatography on silica gel was attempted to purify and separate the diasteromers. Upon adding the eluent (90%EtOAc/10%Hexanes) to the diol mixture a white crystalline precipitate formed. $^1$H NMR and $^{13}$C NMR of the white crystalline precipitate proved this to be the **5a** in accordance with the literature. However all repeated attempts to reproduce this result failed.

**Scheme 2.2.** Protection of **5a**/**5b**.

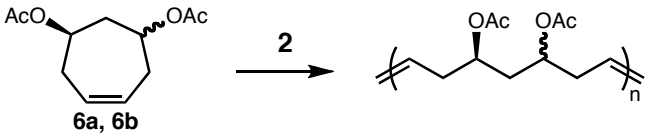



Several protection strategies were explored in order to selectively protect **5a**. Di-*tert*-butylsilanediyl bis(trifluoromethanesulfonate) was used as protecting agent but proved unable to protect the **5a** as shown in Scheme 2.2. By $^1$H NMR the product was a

mixture of starting material, mono protected diol and polymerized silane. Protection of the diol using 2,2'-dimethoxy propane to arrive to the acetonide cis protected alcohol also failed. Consequently, the mixture of diols were then protected as acetates and purified by column chromatography to obtain the final monomer in 90% yield. The diastereomers were also unable to be separated by column chromatograph.

### 2.2.2. ROMP of 6a and 6b with 2.

**Scheme 2.3.** ROMP of monomer **6a**/**6b**.



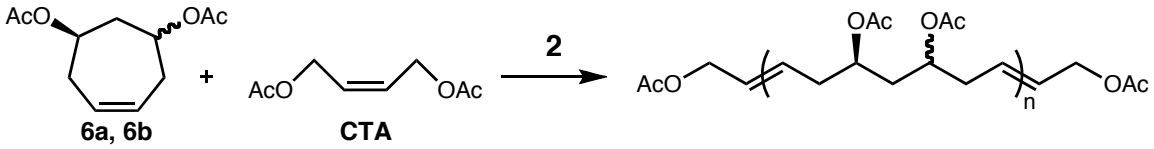

Polymerizations conducted at 55 °C in the absence of solvent.

As shown in Scheme 2.3, ROMP of the monomer was carried out neat at 50 °C with 0.1 mL solution of Grubbs second generation catalyst **2** in $CH_2Cl_2$. The reaction stopped proceeding after just a few hours indicated by the solution of monomer and catalyst becoming dark brown. The resulting solution did not precipitate into methanol and had to be precipitated into -78 °C hexanes where a brown, tacky polymer was obtained. Yield of this polymerization was on the order of 20%. Furthermore precipitation into hexanes did not rid the final polymer of unreacted monomer. Consequently, the yields of polymer obtained from the ROMP of **6a**/**6b** are not absolute. Our first thought as to the reason behind the low yield was because of some impurity in the monomer (8% by GC). Therefore further purification of the monomer was carried out. Careful distillation of the monomer gave 98.0% pure monomer by GC/MS with 2.0% unknown impurity. The polymerization was then repeated with $[M]_0$/**2** ratio of 600/1. The yield increased to 87% and the $M_n$ was 5.7 x $10^4$ g/mol with a PDI's of 1.87. A

second distillation was carried out to rid the monomer of the 2.0% unknown impurity, leading to monomer of 99.9% purity by GC. The polymerization was once again repeated under the same conditions. The yield increased to 90%, but interestingly the $M_n$ was now 1.5 x $10^5$ g/mol and the PDI's were 1.51. This result suggests that the impurity may have been another olefin, which hindered monomer consumption or deactivated the catalysts. The Hoveda catalyst was also used to polymerize the 98.0% pure monomer and surprisingly the yield was 87.8% with a $M_n$ of 1.2 x$10^5$ g/mol and a PDI of 1.45.

### 2.2.3. ROMP of 6a/6b with 2 and Chain Transfer Agent (CTA)

**Scheme 2.4.** ROMP of 6a/6b with CTA.




Polymerizations performed at 55 °C with $[M]_0$/**2** 1000:1.

**Table 2.1.** ROMP of **6a**/**6b** with **2** and CTA.

| $[M]_0$/CTA | $M_n$ (× $10^3$) | PDI | Yield (%)[a] |
|---|---|---|---|
| 25 | 11 | 1.21 | 90 |
| 50 | 22 | 1.22 | 90 |
| 50 | 24 | 1.23 | 90 |
| 100 | 25 | 1.25 | 91 |
| 100 | 29 | 1.25 | 97 |

Polymerization conducted neat at 55 ºC $[M]_0$/**2** 1000:1 [a]Isolated yields obtained from precipitation into hexanes containing some starting material.

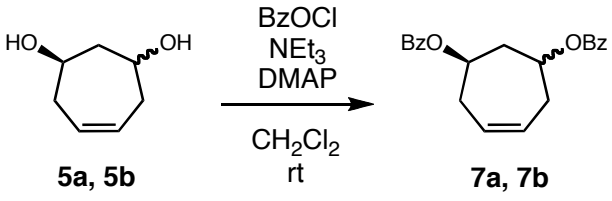
Molecular weight control was attempted by performing ROMP in the presence of symmetrical chain transfer agent 1,4-diacetoxybutane (CTA). The results depicted in Table 2.1 show the molecular weight does increase with increasing $[M]_0$/CTA and the PDI's remained consistent. However when polymers were purified by precipitated into MeOH, no precipitate was observed due to the polymers being soluble in MeOH. Upon

precipitation into hexanes, both monomer and polymer precipitate, which leads to unpure polymer containing some monomer.

The number of problems associated with the purification of the monomer and the precipitation of the final polymer lead us to design a more easily purified monomer and isolable polymer. From the previous monomer synthesis it seems that beginning with the epoxidation of MCPBA the monomer was very difficult to purify and all attempts to separate the diastereomers failed. A simpler epoxidation was then employed. The use of peracetic was attempted to selectively epoxidize **3**. Interestingly the final product yield was increased to 80% and the cis:trans ratio was similar to the epoxidation with MCPBA. Also the use of peracetic acid allowed ease of work up since acetic acid can be removed under a reduced atmosphere. Purification using silica gel provided a clear oil. The reduction of the epoxide with $LiAlH_4$ gave 70% yield of a white solid after drying under dynamic high vacuum unlike previously where a yellow viscous oil was obtained. Attempts to crystallize the diol failed along with attempts to separate the diasteremers using column chromatography.

### 2.2.4. Synthesis of monomer 7a/7b.

**Scheme 2.5.** Benzoate protection of **5a**/**5b** to form **7a**/**7b**.

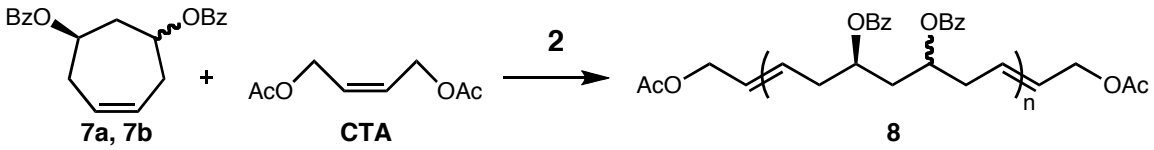



The use of a benzoate protection group was used to form **8a** and **8b** in order to simplify the purification of the finally monomer and allow precipitation of the final monomer into methanol. The protected monomer diastereomers still could not be

separated or crystallized. However the monomer could be purified by column chromatography.

### 2.2.5. ROMP of 7a/7b with 2 and CTA.

**Scheme 2.6.** ROMP of **7a**/**7b** with **2** and CTA.




Polymerizations performed at 55 °C with $[M]_0$/**2** 1000:1.

Polymerization of the benzoate-protected monomer as shown in Scheme 2.6 was carried out under the same neat conditions previously described. Precipitation of the polymer product into methanol afforded a white solid. The yields for these polymerizations are more absolute, unlike previously observed, since there is no monomer signal present by $^1$H NMR. As seen in Scheme 2.6 and Table 2.2 molecular weight was controlled using CTA. However, the PDI's increased to around 2.0. This is attributed to the increased viscosity of the monomer, as it is still a liquid with almost double the weight of the acetate-protected monomer. This increased viscosity along with the faster gel time may have slowed monomer consumption and increased the probability of chain transfer reactions to occur. Some reactions were carried out in toluene to counter act this problem. When the polymerizations were conducted toluene (4.0 M), the yields and molecular weights lower than expected. Also PDIs were increased, indicating inefficient chain transfer. The current conclusion to this phenomenon is that the benzoates are affecting either catalyst activity or the reactivity of the polymer olefins.

**Table 2.2.** ROMP of **7a**/**7b** with **2** and CTA.

| $[M]_0$/CTA | $M_n$ ($\times 10^3$) | PDI | Yield (%) |
|---|---|---|---|
| 102 | 21 | 2.09 | 46 |
| 230 | 47 | 2.15 | 68 |
| 384 | 82 | 2.21 | 70 |
| 98 | 10 | 2.40 | 42 |
| 199 | 21 | 2.61 | 45 |
| 393 | 24 | 3.16 | 42 |

Polymerizations performed at 55 °C with $[M]_0$/**2** 1000:1.

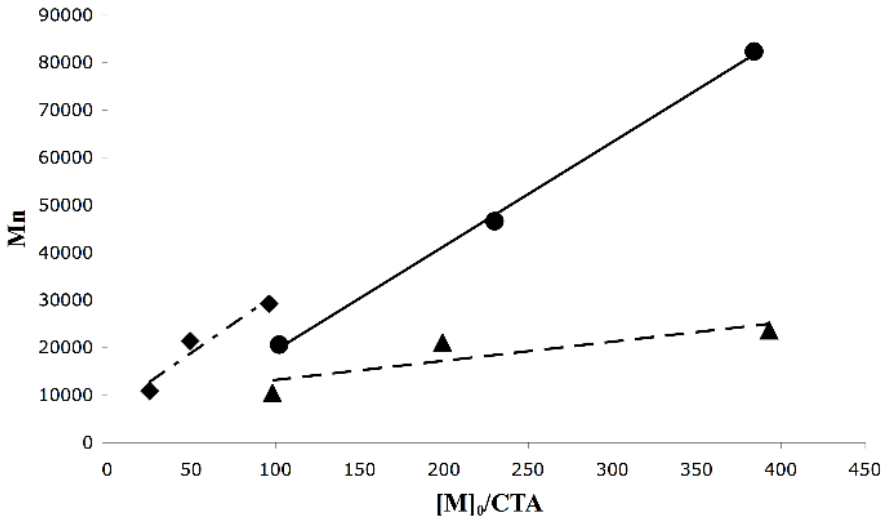
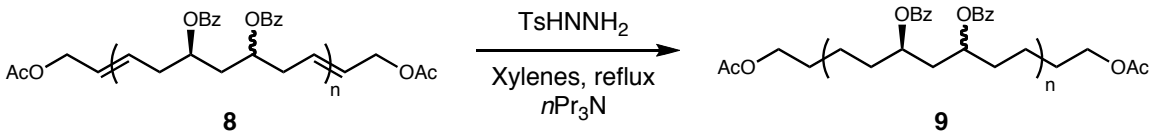



**Figure 2.3.** Molecular weight increases linearly with increasing $[M]_0$/CTA. **7a**/**7b** (circles, solid line), **7a**/**7b** in toluene (4.0 M) (triangle, dashed line), **6a**/**6b** (diamonds dash dot line).

### 2.2.6. Hydrogenation of 8.

**Scheme 2.7.** Hydrogenation of **8** to form **9**.

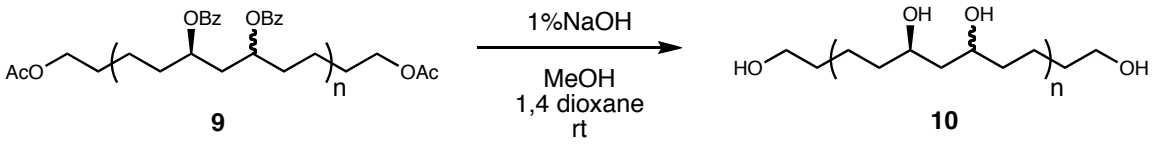



The direct formation of the diimide in situ afforded complete hydrogenation of the olefins without removing the benzoate protecting group as shown in Scheme 2.7. The hydrogenation reaction was carried out with 1 equiv of tri-propylamine (3 equivs per tosylhydrazide) with a trace amount of BHT to prevent radical cross-linking. . After 7 h

in refluxing xylenes, hydrogenation of the ROMP polymers was complete. Saturated polymer **9** remained soluble in organic solvents, which allowed characterization by $^1$H NMR and GPC, which confirmed by the absence of olefins.

### 2.2.7. Deprotection of 9.

**Scheme 2.8.** Deprotection of **9** to form **10**.




Removal of the benzoate groups lead to the final EVOH copolymer **10**. Removal of the benzoates was achieved by the addition of 1% NaOH in methanol to a solution of the polymer in 1,4-dioxane. When a ratio of 80%:20% 1,4 dioxane to MeOH was obtained full deprotection was observed by $^1$H NMR within minutes. The polymer was characterized by $^1$H NMR and GPC.

After obtaining the final polymer, one small scale attempt at a cis selective epoxidation of # was attempted using $V(AcAc)_2$ and t-Butyl hydroperoxide. This reaction yield 30% product 70% of which was cis product by $^1$H NMR. These diastereomers were also unable to be separated using column chromatograph.

### 2.2.8. Barrier Testing

The barrier properties of the final deprotected polymer along with the previous ROMP EVOH polymers were tested by Kuraray, Inc and are shown in Table 2.3. At 0% relative humidity all ROMP EVOH polymer exhibit improved barrier properties as compared to there commercial equivalents. However, when the relative humidity is increases their barrier performance decreases with the exception of *cis*-C8-diol . This difference in barrier properties at high relative humidity's was attributed to the polymer's

trans-1,2-diol configuration. The difference in barrier properties between the two polymers was studied by our group.[16] It was determined that *cis*-C8-diol was prone to intermolecular hydrogen bonding, whereas polymer *trans*-C8-diol was more prone to intramolecular hydrogen bonding. The intermolecular hydrogen bonding of the chains make it much more difficult for oxygen and water to diffuse through the bulk material.

**Table 2.3.** Kuraray, Inc EVOH $O_2$ Permeability testing results.

| EVOH | 0% Relative Humidity | > 90% Humidity |
|---|---|---|
| C5-diol | 0.2 | 3.2 |
| C7-Diol | 1.0 | 4.5 |
| *cis*-C8-diol | 1.5 | 1.5 |
| *trans*-C8-diol | 2.0 | 6.0 |

units: cc x 20um x $m^2$/day/atm

## 2.3. Conclusion

EVOH copolymer was obtained with a 1,3 diol configurations. Although the stereochemistry could not be controlled, the regio-regularity of the final EVOH copolymer was controlled. This was due to the difficulty in separating the diastereomers by a number of methods. Even though the monomer synthesis was synthetically challenging obtaining the final EVOH polymer was relatively simple with straightforward hydrogenation and quick deprotection.

## 2.4. Future Work

In order to obtain stereoregular EVOH copolymer a cis monomer must be synthesized. This will be done by epoxidation with purified MCPBA and more stringent $V(AcAc)_2$ conditions. If successful the selective deprotection with PFL followed by stereo inversion with DEAD will be attempted. Scaling up this reaction to obtain multigram amounts of polymers for full characterization including $^{13}C$ NMR, DSC and TGA analysis. Several grams will also be needed for oxygen barrier testing.

## 2.5. Experimental Section

**General Procedures.** NMR spectra were recorded on a Varian Mercury 300 (300 MHz for $^{1}H$ and 74.5 MHz for $^{13}C$). All NMR spectra were recorded in CDCl3, DMSO-$d_6$, or 1,4-dioxane-$d_8$ and referenced to residual proteo species. Gel permeation chromatography (GPC) was carried out on two PLgel 5 μm mixed-C columns (Polymer Labs) connected in series with a DAWN EOS multi angle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer (both from Wyatt Technology). No calibration standards were used, and d*n*/dc values were obtained for each injection assuming 100% mass elution from the columns.

**Materials.** Toluene and $CH_2Cl_2$ were dried by passage through solvent purification columns.[17] *cis*-1,4-Diacetoxy-2-butene (95+%) (13) was obtained from TCI America and degassed by an argon purge prior to use. Tropone and tropylium tetrafluroborate used as received from Lancaster. 1,1'-carbonyldiimidazole, p-toluene sulfonhydrazide, pyridinium p-toluene sulfonate, tripropylamine, benzoyl chloride, triethylamine, 1,4-dioxane, xylenes, acrylonitrile, sodium hydroxide, acetic anhydride, and 2,2'-dimethoxypropane were obtained from Aldrich and used as received. Imidazole (99%) was obtained from EM Science and used as received. Ruthenium catalysts $(PCy_2)(Cl)_2Ru{=}CHPh$ (**1**)[10] and $(H_2IMes)(PCy_2)(Cl)_2Ru{=}CHPh$ (**2**)[9] as well as organic compounds 3,5 cycloheptadien-1-ol (**3**), *cis*-3,4-epoxy-5-cyclohetpten-1-ol (**4a**), *trans*-3,4-epoxy-5-cyclohetpten-1-ol (**4b**), *cis*-5-cycloheptene-1,3-diol (**5a**), *trans*-5-cycloheptene-1,3-diol (**5b**), *cis*-1,3-diacetox-5-cycloheptene (**6a**) and *trans*-1,3-diacetox-5-cycloheptene (**6b**) were all synthesized according to literature procedures.[14,15]

**Synthesis of cis-1,3-benzoate-5-cycloheptene (7a) and trans-1,3-benzoate-5-cycloheptene (7b).** In a typical experiment 2.35 g (18.4 mmol) of **5a** and **5b**, stirbar, 5.5

mL (2.6 equive) of benzoyl chloride, 16.0 mL (6.2 equiv) of triethylamine and 0.097 g (4.3 mol%) of DMAP were combined in a round bottom flask at room temperature. After 24h reaction was quenched with brine and washed three times with $CH_2Cl_2$, one time with 1 N HCl, two times with $Na_2CO_3$(sat), and once more with brine. Solution was dried with $MgSO_4$, filtered and concentrated. Purified with silica gel (eluent 5% EtOAc/95% hexanes) obtained clear yellow oil; yield (80%). $^1$H NMR (300 MHz, $CDCl_3$): 8 (t, 4H), 7.48 (t, 2H), 7.4 (t, 6H), 5.89 (dd, 4H), 5.25 (m, 0.5H), 5.0 (m 1H), 3.80 (m, 1H), 2.6-2.25 (br m, 5H), 2.0 (m, 3H), 1.81 (br d, 1H).

**Polymerization procedure for acetate-protected monomers with catalyst 2.** In a typical experiment, a small vial was charged with 0..2002 g (0.1 mmol) of monomer **6a** and **6b** and a stirbar. Under an argon atmosphere 8 mg/mL catalyst **2** solution in $CH_2Cl_2$ was prepared. 0.1 mL of the catalyst solution was then added to the monomer solution via syringe under argon. The reaction vial was placed in a 50 °C aluminum heating block stirring under argon for 24 h. The reaction mixture was then quenched with 0.1 mL ethyl vinyl ether and then dissolved in 1 mL $CH_2Cl_2$ and precipitated

into 100 mL of stirring hexanes at -78 °C. A light brown precipitate was washed several times with hexanes and dried in vacuo overnight; yield (80%). $^1$H NMR (300 MHz, $CDCl_3$): 5.35 trans 5.4 cis (two br s, 2H), 4.9 (br s, 2H), 2.2–1.6 (br m, 12H).

**Polymerization procedure for acetate-protected monomers with catalyst 2 and CTA.** In a typical experiment, a small vial was charged with 0..2072 g (0.1 mmol) of monomer **6a** and **6b** and a stirbar. Under an argon atmosphere 8 mg/mL catalyst **2** solution in $CH_2Cl_2$ was prepared. 1.6 μL of CTA and 0.1 mL of the catalyst solution was then added to the monomer solution via syringe under argon. The reaction vial was

placed in a 50 °C aluminum heating block stirring under argon for 24 h. The reaction mixture was then quenched with 1.0 mL $CH_2Cl_2$ and then dissolved with an additional 1.0 mL $CH_2Cl_2$ and precipitated into 100 mL of stirring hexanes at -78 °C. A light brown precipitate was washed several times with hexanes and dried in vacuo overnight; yield (80%). $^1$H NMR (300 MHz, $CDCl_3$): 5.35 trans 5.4 cis (two br s, 2H), 4.9 (br s, 2H), 2.2–1.6 (br m, 12H).

**Polymerization procedure for benzoate-protected monomers with catalyst 2.** In a typical experiment, a small vial was charged with 0..2032 g (0.6 mmol) of monomer **7a** and **7b** and a stirbar. Under an argon atmosphere 8 mg/mL catalyst **2** solution in $CH_2Cl_2$ was prepared. 0.1 mL of the catalyst solution was then added to the monomer solution via syringe under argon. The reaction vial was placed in a 50 °C aluminum heating block stirring under argon for 24 h. The reaction mixture was then quenched with 0.1 mL ethyl vinyl ether and then dissolved in 1 mL $CH_2Cl_2$ and precipitated into 100 mL of stirring ice-cold stirring MeOH. A white precipitate was washed several times with MeOH and dried in vacuo overnight; yield (70%). $^1$H NMR (300 MHz, $CDCl_3$): 7.85 (br, 4H), 7.4 (br , 2H), 7.2 (s, 2H), 5.4 (br s, 2H), 5.15 (br s, 2H), 2.25-1.4 (br m, 6H).

**Polymerization procedure for benzoate-protected monomers with catalyst 2 and CTA.** In a typical experiment, a small vial was charged with 0..2072 g (0.6 mmol) of monomer **7a** and **7b** and a stirbar. Under an argon atmosphere 8 mg/mL catalyst **2** solution in $CH_2Cl_2$ was prepared. 1.6 μL of CTA and 0.1 mL of the catalyst solution was then added to the monomer solution via syringe under argon. The reaction vial was placed in a 50 °C aluminum heating block stirring under argon for 24 h. The reaction mixture was then quenched with 1.0 mL $CH_2Cl_2$ and then dissolved with an additional 1.0 mL $CH_2Cl_2$ and precipitated into 100 mL of ice-cold stirring MeOH. A light brown precipitate was washed several times with MeOh and dried in vacuo overnight; yield (70%). $^1$H NMR (300 MHz, $CDCl_3$): 7.85 (br, 4H), 7.4 (br , 2H), 7.2 (s, 2H), 5.4 (br s, 2H), 5.15 (br s, 2H), 2.25-1.4 (br m, 6H).

**Hydrogenation procedure for benzoate-protected polymers.** In a typical experiment, an oven-dried 25 mL round bottom flask was charged with a stirbar, 96.1 mg of polymer **8**, 352.0 mg of tosylhydrazide (6.5 equiv per double bond), 0.38 mL tri-propylamine (1 equiv per tosylhydrazide), 8.0 mL of xylenes, and a trace amount of BHT. The mixture was degassed by pulling high vacuum on the solution for about 45 s. Under an argon atmosphere, a flask was fitted with a reflux condenser. The reaction was heated to reflux for 7 h. It was then cooled to room temperature and then precipitated into 50 mL of stirring ice-cold stirring MeOH. The white precipitate was washed several times with MeOH and then dried in vacuo overnight; yield 90 mg (94%). $^1$H NMR (300 MHz, $CDCl_3$): 7.85 (br, 4H)7.4 (br , 2H), 7.2 (s, 2H), 5.15 (br s, 2H), 2.25-1.4 (br m, 8H).

**Deprotection of 9.** In a typical experiment, a NMR tube was charged with 5 mg polymer. The polymer was then dissolved in 0.8 mL of 1,4-dioxane. 0.2 mL of a solution

10% NaOH in MeOH was added via syringe to the NMR tube. After five minutes deprotection was complete. The reaction was precipitated into 50 mL of ice-cold stirring pentantes. A fluffy white solid was obtained and washed with pentanes and dried under vacuum overnight; yield 5 mg (99%). $^{1}$H NMR (300 MHz, $CDCl_3$): 5.15 (br s, 2H), 2.25-1.4 (br m, 10H).

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# Chapter 3

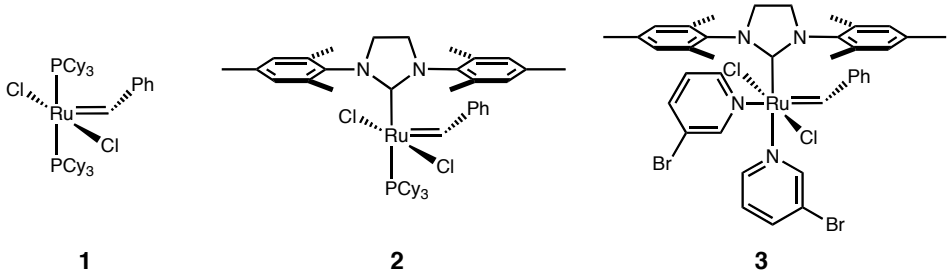
# The Synthesis of Regioregular Ethylene-Vinyl Alcohol Copolymers via Ring-Opening Metathesis Polymerization from 3,4-Difunctional Cyclobutenes

# Abstract

Ethylene-vinyl alcohol copolymers (EVOH) exhibit excellent barrier properties toward gases and hydrocarbons. They are typically synthesized through free radical polymerization of ethylene and vinyl acetate. The resultant polymer is then saponified to form the final polymer. This route does not allow for absolute control of the polymer architecture, which is key for understanding the structure-property relationships of these materials. The Ring-Opening Metathesis Polymerization of protected 3,4-substituted cyclobutenediol was carried out with Grubbs second-generation catalyst in an effort to control pendant group regioregularity and stereochemistry. Molecular weight of the polymers were controlled by varying the monomer to chain transfer agent ratio. Hydrogenation and subsequent deprotection of the ROMP polymer affords an EVOH polymer with maximum alcohol content.

## 3.1. Introduction

Studies at Kuraray have shown the 1,2-diol configuration of EVOH copolymers derived from cis-cylcooctene-1,2-diol[1] have excellent barrier properties when compared with commercially available EVOH polymers of similar methylene:alcohol ratios. This result prompted us to target cyclobutene-1,2-diol based monomers. The polymers resulting from the ROMP of these monomers should have an increased alcohol content and also retain their syn stereochemistry, similar to polycyclooctene-1,2-diol.

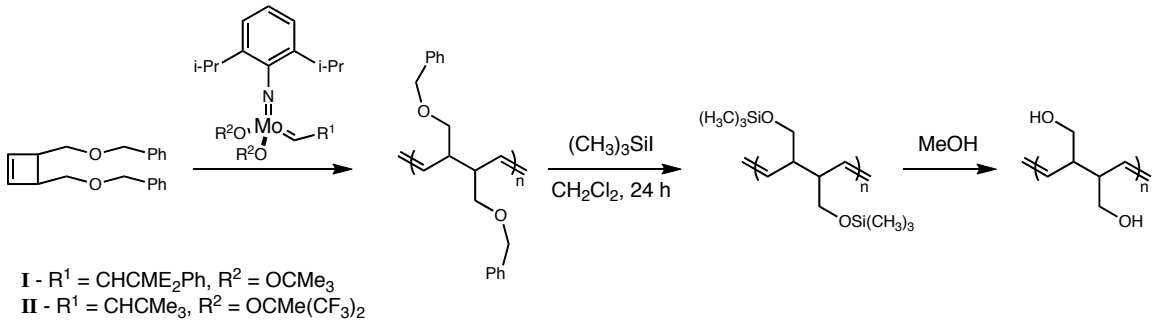



**1** **2** **3**

**Figure 3.1.** ROMP catalyst (Cy=cyclohexyl).

The ROMP of various substituted cyclobutenes has been well studied. Maughon reported the living ROMP of several 3-substituted cyclobutenes with a wide range of functionality using catalyst **1**.[6,7] Coordination of Lewis basic functional groups from the polymer side chains to the metal center was also observed. This coordination leads to lowered PDIs, but also catalyst decomposition. As the functionality was removed further from the ring system living polymerizations of more polar functionalities were observed. Novak et al. also showed the living polymerization of 3,4-substituted cyclobutenes (Scheme 3.1), which were subsequently deprotected to form hydroxyl-bearing polymers.[8,9] Novak also noted that polymerization was ineffective with Grubbs catalyst **1**, yet successful with molybdenum initiators **I** and **II**.

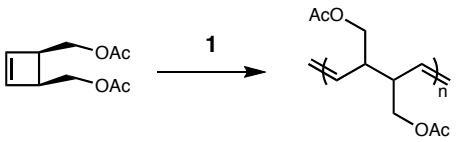
**Scheme 3.1.** Living ROMP of Substituted Cyclobutenes with a Mo Initiator.




**I** - $R^1$ = $CHCME_2Ph$, $R^2$ = $OCMe_3$
**II** - $R^1$ = $CHCMe_3$, $R^2$ = $OCMe(CF_3)_2$

Later Fontaine et al. showed the living polymerization of more polar substituted cyclobutene 3,4-diol (Scheme 3.2) using Grubbs catalyst **1**.[10] Although the PDIs were not as narrow (PDI=1.2), it proved the polymerization of a polar-functionalized cyclobutene diol could be conducted using well known Ru catalysts.

**Scheme 3.2.** ROMP of Bis(acetyloxymethyl)cyclobutene




The previously discussed reports provided good evidence that the ROMP of highly substituted cyclobutenes was feasible. However, there were no reports on the ROMP of monomer containing allylic polar functionalities such as alcohols or protected alcohols. Herein, we report the synthesis of highly functionalized polybutadiene from the ROMP of two allylic-functionalized cyclobutenes.

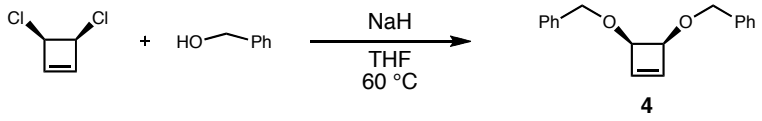
## 3.2. Results and Discussion

### 3.2.1. Monomer Design and Synthesis

There are few examples of cyclobutene diols reported in the literature, leaving only a limited number of synthetic routes available. Previously Choi synthesized the benzyl-protected cyclobutene **4** by performing a simple $S_n2$ reaction with commercially

availably 3,4-dichlorocyclobutene and benzyl alcohol in DMF. However, repeating this experiment gave, the observed yields that were less than 20%. Due to the exceptionally low yield of the reaction and prohibitive cost of the starting material ($400 per 5 g) these conditions were unattractive. Fortunately, a simply switching the solvent to THF afforded monomer **4** in high yield (95%).

**Scheme 3.3.** Synthesis of monomer **4**.




**4**

### 3.2.2. ROMP of 4

Because monomer **4** is highly strained, it was predicted be an excellent ROMP monomer. However, the allylic polar functionality has the potential to decrease ROMP activity enough to prevent full monomer conversion. Therefore, ROMP was carried out under neat conditions both at room temperature and at 55 °C, with symmetrical 1,4-diacetoxybutene as a chain transfer agent (CTA) and catalyst **2**. The polymerization afforded telechelic polymers with controllable molecular weights in high yields, as seen in Table 3.1.

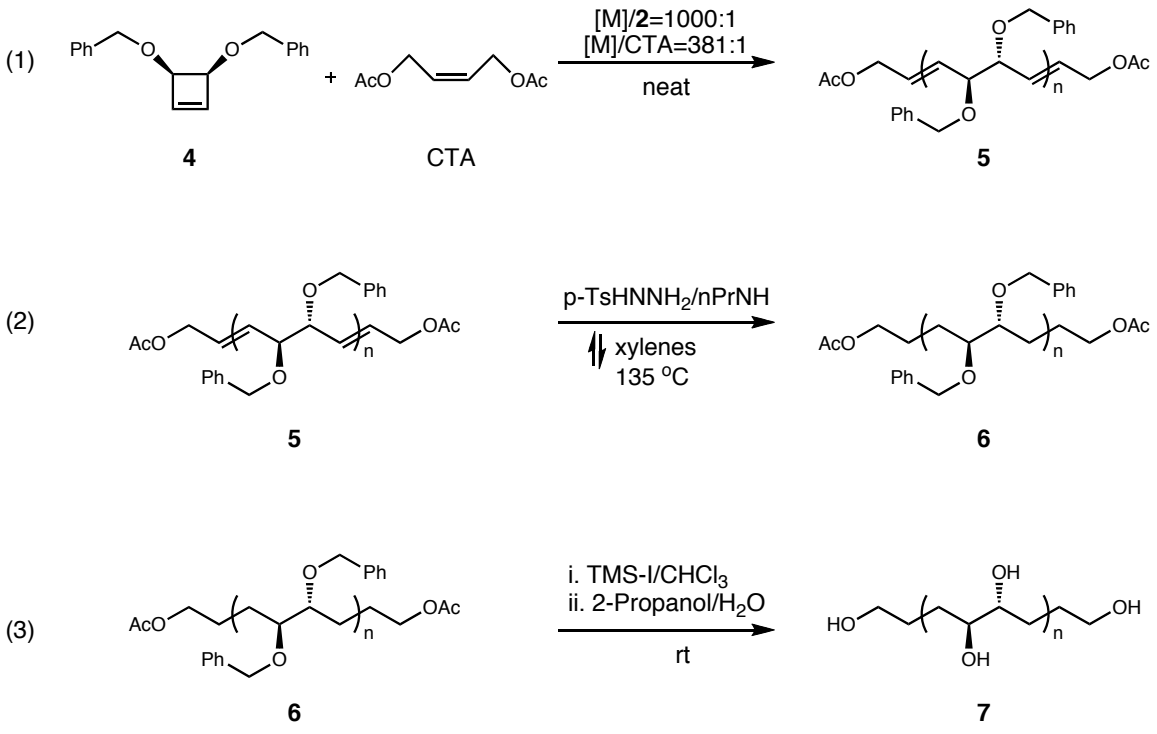
**Table 3.1.** ROMP of **4** with **2** and CTA.

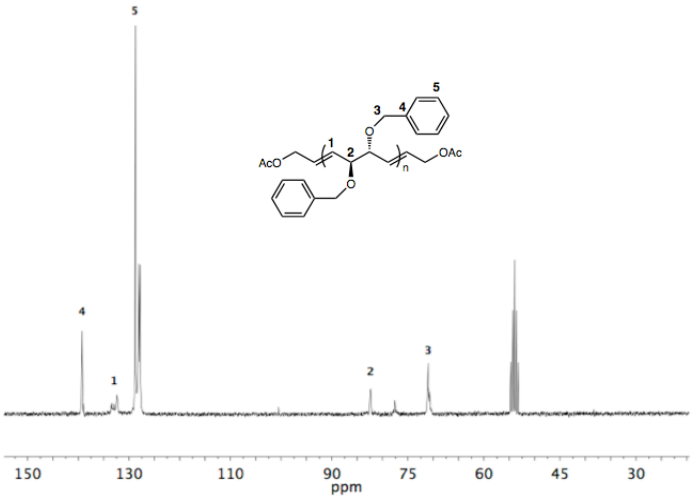
| Entry | $[M]_0$/CTA | $M_n$ ($\times 10^3$) | PDI | Yield (%) |
|---|---|---|---|---|
| **1** | 100 | 29 | 2.37 | 92 |
| **2** | 200 | 51 | 2.04 | 93 |
| **3** | 400 | 74 | 2.02 | 94 |
| **4** | 100 | 24 | 2.65 | 89 |
| **5** | 200 | 40 | 2.78 | 95 |
| **6** | 400 | 58 | 2.42 | 95 |

Polymerizations were conducted with a $[M]_0$/**2** = 1000:1. Entries 1-3 were conducted at room temperature, while Entries 4-6 were conducted at 55 °C.

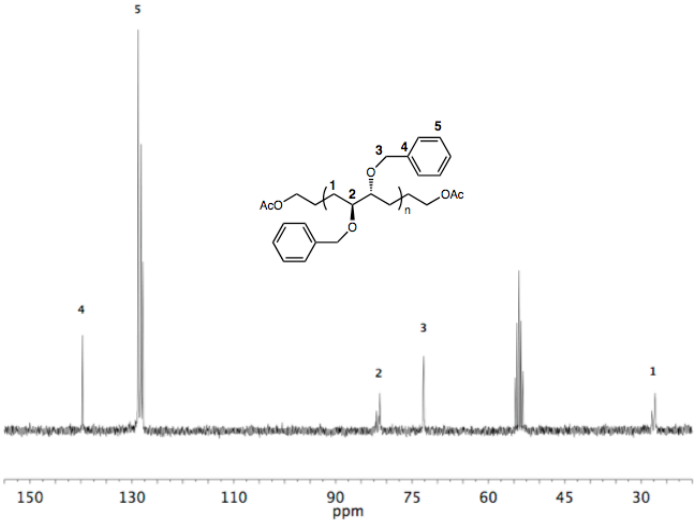
The resulting polymers were then hydrogenated through the direct formation of diimide in situ (Eq. 2, Scheme 3.4). After each hydrogenation the benzyl carbons were still present as evidenced by the $^{13}C$ peak at 128ppm (Figure 3.2b). Deprotection of the benzyl group using hydrogenation was avoided because of solubility issues. Therefore, a solution method involving treatment with trimethylsilyliodide followed by hydrolysis was employed.[8,11-13] However, upon hydrolysis, the polymer began to precipitate from solution preventing complete deprotection. Solid-state $^{13}C$ NMR (Figure 3.2c) displayed a peak at 128 ppm corresponding to benzyl carbons. This conclusively proved that the polymer precipitated from solution before full deprotection was achieved.

**Scheme 3.4.** ROMP, Hydrogenation, and Deprotection.

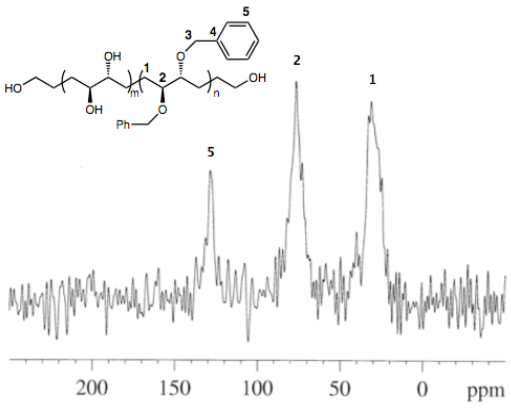





(a)




(b)

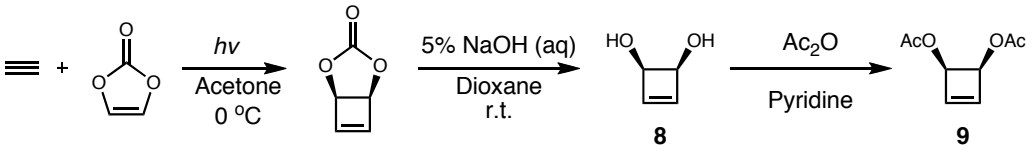



(c)

**Figure 3.2.** $^{13}C$ NMR

### 3.2.3. Synthesis of 9

**Scheme 3.5.** Synthesis of monomer **9**.




In order to avoid the difficulty of deprotecting the benzyl groups of polymer **6**, an alternative monomer synthesis was pursued (Scheme 3.5). The carbonate-protected monomer was synthesized by bubbling acetylene through a solution of vinlyene cabonate in dry acetone while irradiating with UV light. Next, the carbonate group was deprotected in an aqueous solution 5% NaOH and purified by recrystallization in ethyl acetate. Monomer **8** was then acetate-protected to form monomer **9**, which mimics the industrial monomer. Low yields and incomplete polymerization were observed when polymerizations were conducted in $CH_2Cl_2$, as seen in Table 3.2. When the reaction solvent was changed to THF, the yields increased. However, the reaction was slow to proceed. By switching solvents once again to toluene, efficient ROMP was achieved.

**Scheme 3.6.** ROMP of **9** with **2**.

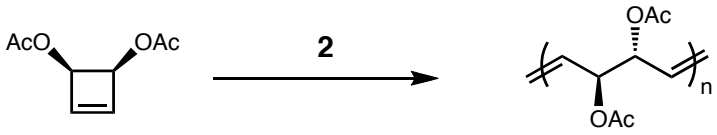



**Table 3.2.** ROMP of **9** with **2**. $[M]_0/\mathbf{2}$=600:1.

| Solvent | $M_n$ ($\times 10^3$) | Yield (%) | PDI | Time |
|---|---|---|---|---|
| $CH_2Cl_2$ | 383 | 44 | 1.41 | 4 d |
| THF | 200 | 80 | 1.61 | 3 d |
| Toluene | 169 | 80 | 1.23 | 24 h |

Polymerizations were conducted with CTA and **2** to determine if varying $[M]_0$/CTA could control the molecular weight. Table 3.3 depicts these results. As [M]/CTA was increase molecular weight increased linearly as shown in Figure 3.3. After obtaining these satisfactory results, the polymers were made on a multigram scale and sent to Kuraray, Inc for deprotection and characterization.

**Table 3.3** ROMP of **9** with CTA.

| $[M]_0$/CTA | $M_n$ ($\times 10^3$) | Yield (%) | PDI |
|---|---|---|---|
| 100 | 31 | 99 | 1.24 |
| 200 | 44 | 96 | 1.54 |
| 400 | 75 | 96 | 1.68 |

Polymerizations performed in toluene (1.0 M) at 55 °C

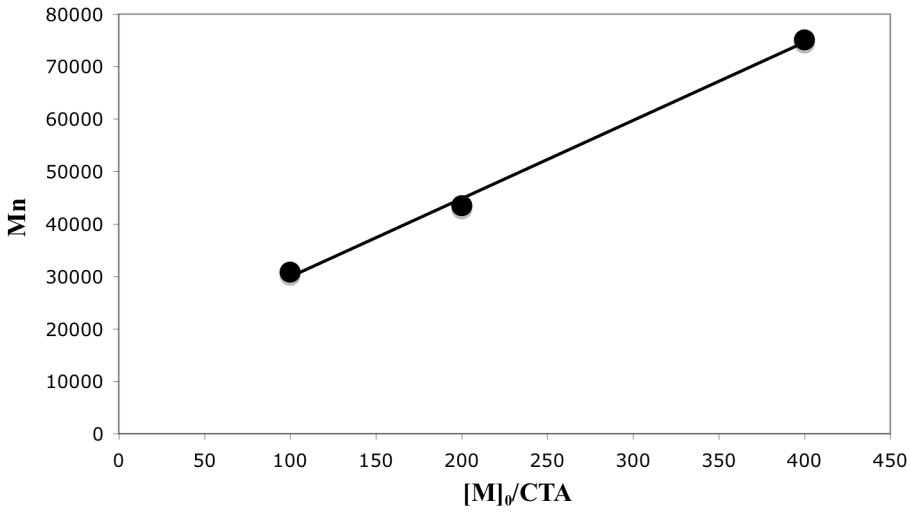
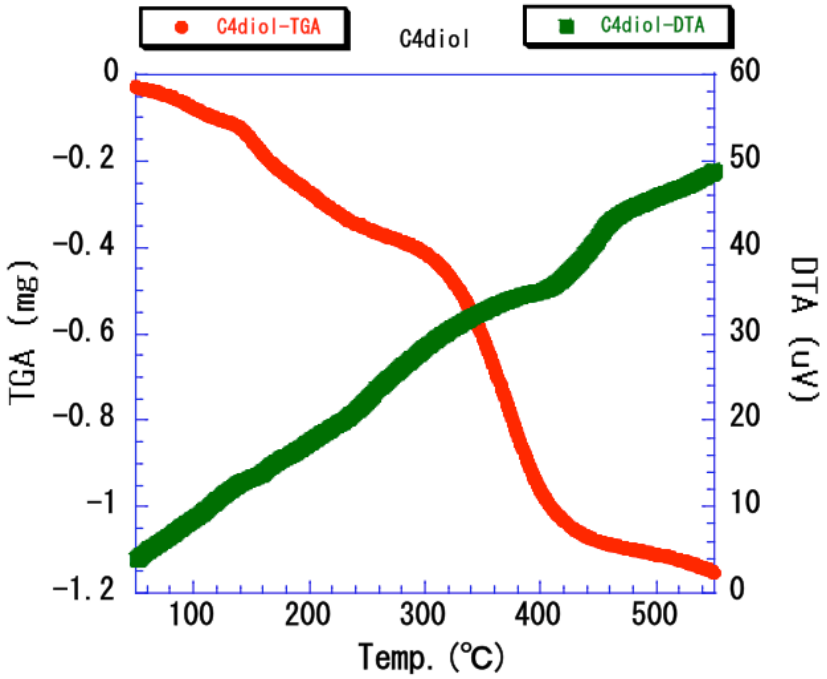
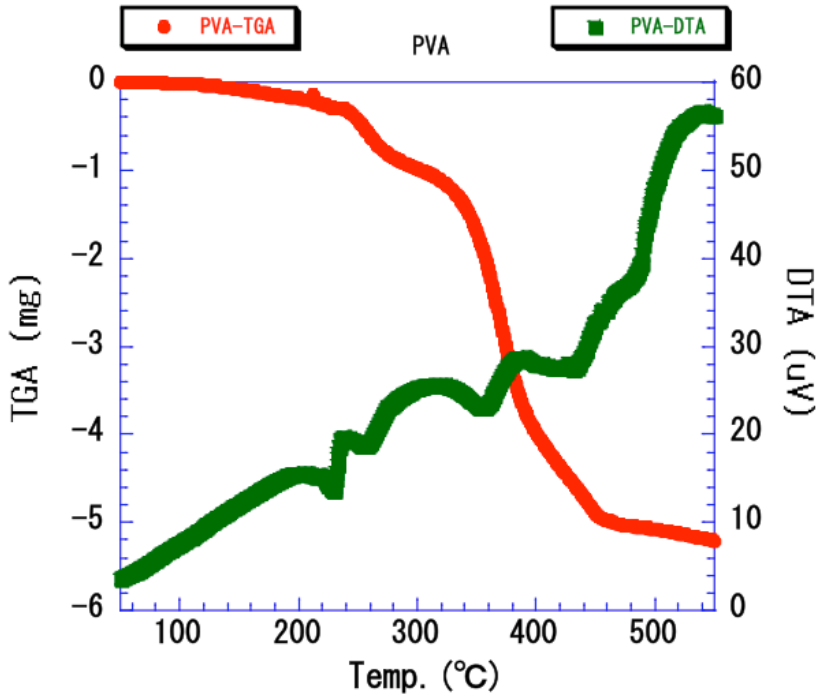



**Figure 3.3.** Linear increase in molecular with increasing $[M]_0$/CTA.

Thermal analysis of the polymers was conducted to determine the polymer melting and decomposition characteristics. Since polymer **7** is similar to polyvinylalcohol (PVA), it should exhibit a high melting temperature, which is observed just before decomposition.




(a)




(b)

**Figure 3.4.** (a)DSC/TGA data for polymer **7** obtained from Kuraray, Inc. (b)DSC/TGA data for PVA ($T_m$ = 253 °C, $T_d$ = 250 °C).

## 3.3. Conclusions

The ROMP of protected 3,4-substituted cyclobutenediol was carried out with Grubbs second generation catalyst **2** in an effort to control pendant group regioregularity and stereochemistry. Molecular weight of the polymers was controlled by varying the monomer to CTA ratio. Hydrogenation and subsequent deprotection of the ROMP polymer afforded an EVOH polymer with maximum alcohol content. Theoretically, these materials have the potential to possess excellent barrier properties. Furthermore, we have shown the efficient ROMP of cyclic olefins with allylic polar functionality. As of this report, Kuraray, Inc has not yet tested the barrier properties of these C4-diol EVOH polymers.

## 3.4. Living Polymerization of Cyclic-olefins

Living polymerizations are defined by their high conversions, lack irreversible of chain transfer and chain terminating events, and monomodal dispersities.[14,15] ROMP is primarily driven by ring-strain[2]; both monomers **4** and **9** are highly strained cyclobutenes making them good candidates for living ring-opening metathesis polymerization. Once again as previously discussed the allylic polar functionality could potentially lower the monomers' ROMP activity and may lead to inefficient ROMP.

Another factor to consider is that the potential chelation of monomer **9** to the metal center may or may not affect living ROMP. When initial polymerizations of monomer **4** were conducted using catalyst **1**, no polymer was observed. These results coincide well with those observed by Novak.[8,9] However, the results observed by Fontaine suggested a living polymerization should have occurred when **4** was polymerized using **1**.[10] Although Novak suggested and proved Mo catalyst are capable of polymerizing polar functionalized cyclobutenes, catalyst **3** was not available at that time.

Catalyst **3** has been shown to initiate much faster initiating than catalyst **1**, and is also more tolerant toward functional groups. Therefore, polymerizations of **4** and **9** were conducted using **3**. Interestingly, neither monomer polymerizes in living fashion in $CH_2Cl_2$. However, when a more coordinating solvent, such as THF, is used, the resultant polymers are narrowly dispersed. As seen in Figure 3.5 the ROMP of both monomers with catalyst **3** reach full conversion. Monomer **4** reaches full conversion after 3 hours, while monomer **9** reaches full conversion after 1 hour. We assume the difference in reaction times show sterics have a more pronounced effect on the rate of polymerization ($k_p$) than monomer chelation.

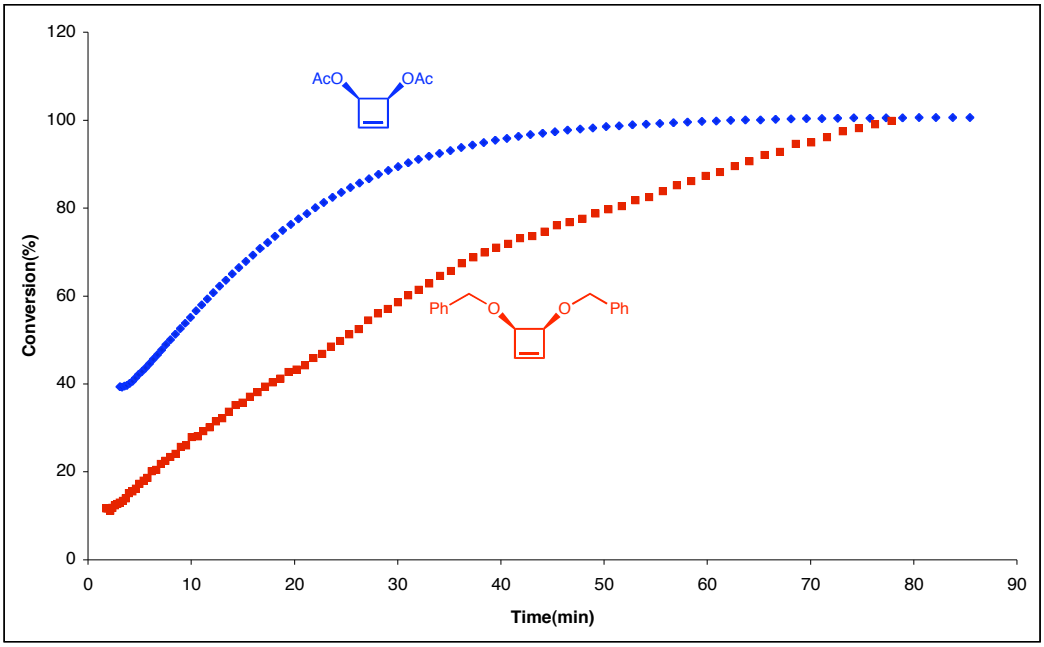



**Figure 3.5.** ROMP of monomers **8** and **10** with **3** carried out at 30 ºC.

## 3.5. Conclusions

We have demonstrated that highly strained cyclobutenes **4** and **10** can be polymerized in a living fashion by using catalyst **3** and varying solvent. Also we have demonstrated that functional groups can have a significant effect on the $k_p$. Also we have suggested that sterics have a larger effect on the $k_p$ than monomer chelation.

## 3.6. Experimental Section

**General Methods.** NMR spectra were recorded on a Varian Mercury 300 (300 MHz for $^{1}H$ and 74.5 MHz for $^{13}C$). All NMR spectra were recorded in $CDCl_3$, referenced to residual proteo species. Gel permeation chromatography (GPC) was carried out in THF on two PLgel 10 μm mixed-B LS columns (Polymer Laboratories) connected in series with a DAWN EOS multiangle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer (both from Wyatt Technology). No calibration standards were used, and dn/dc values were obtained for each injection by assuming 100% mass elution from the columns. Barrier testing, differential scanning calorimetry (DSC) and Thermogravimetric Analysis (TGA) were conducted by Kuraray, Inc.

**Materials.** Toluene, THF, and $CH_2Cl_2$ were dried by passage through solvent purification columns.[16] Dichlorocyclobutene was obtained from Alfa Aesar and used as recieved. All other chemicals were obtained from Aldrich and used as received. Ruthenium catalysts $(PCy_3)_2(Cl)_2RuCHPh$ (**1**)[5], $(PPh_3)_2(Cl)_2RuCHPh$ (**2**)[5], $(H_2IMes)(3\text{-}Br\text{-}pyr)_2(Cl)_2RuCHPh$ (**3**)[3] were all synthesized according to literature procedure.

**3,4-bis(benzyloxy)cyclobutene (4).** A 100ml round bottom was charged with NaH (117.5 mmol), a stirbar, and purged with argon. 40 mL of THF was slowly added to the round bottom while stirring in an ice/$H_2O$ bath. Next, benzyl alcohol (20 mmol) was added dropwise over a period of 10 min. The reaction mixture was allowed to warm to room temperature, and cis-3,4-dichlorobutene was added dropwise via syringe. The reaction mixture was then placed in a preheated oil bath at 60 °C and allowed to stir under argon for 20 h. The reaction was quenched with $NH_4^+Cl$ (aq) and extracted three times with ether. The organic layer was then washed with brine, dried with $MgSO_4$, and

concentrated by rotovap. Purification was done by column chromatography (1:15 EtOAc:Hexanes). A clear oil was obtained in 94.7% yield. $^1$H NMR (300 MHz, $CDCl_3$): 7.38–7.25 (m, 10H), 6.4 (t, 2H), 4.75 (d, 2H), 4.69 (d, 4H).

***cis*-cyclobutene-1,2-diol (9).** A UV reaction vessel was charged with vinylene carbonate (25g) and acetone (400 mL). Acetylene was then pre-bubled into acetone before being bubbled into the reaction mixture. Next, the reaction vessel was placed in an ice-bath and irradiated with UV light for 24 h. The reaction was then filtered to remove vinylene carbonate dimer and concentrated by rotavap. Yield = 20%. The product was then transferred to a 100 mL round bottom with dioxane (20 mL) and a stirbar. After all the product was dissolved, NaOH (5% in $H_2O$) (20 mL) was slowly added. The reaction was allowed to stir under argon for 3h, by which time the reaction had become clear orange. The reaction was quenched with $NH_4^+Cl$ (aq) and became clear light yellow. The reaction mixture was then concentrated to dryness by rotovap. The solid white mixture of $NH_4^+Cl$ and product was then sonicated in EtOAc and decanted three times. The organic layer was then dried over $Na_2SO_4$, filtered and concentrated by rotovap. A white solid was obtained, which was subsequently recrystallized in EtOAc/Hexanes. A crystalline white solid was obtained in 50% yield. $^1$H NMR (300 MHz, $CDCl_3$): 6.39 (d, 2H), 4.79 (d, 2H).

**3,4-bis(acetoxy)cyclobutene (10).** A 25 mL round bottom flask was charged with diol **9** and stirbar. The reaction flask was then purged with argon, and pyridine was added. After **9** had dissolved, the reaction flask was placed in a 0 °C ice/$H_2O$ bath and allowed to cool for a few minutes. Acetic anhydride was then added dropwise via syringe to the to cooled stirring reaction mixture while under argon. The reaction was then

allowed to warm to room temperature and stir under argon for 24 h. The reaction was stopped with $H_2O$ and extracted three times with EtOAc. The organic layer was washed five times with 10 mL of $CuSO_4$ (10% aq) to remove pyridine. The organic layer was then washed with brine and dried over $MgSO_4$. The dried organic layer was then filtered and concentrated by rotavap, upon which a white solid appeared. The product was then recrystallized in EtOAc/Hexanes. A crystalline white solid was obtained in 80% yield. $^1$H NMR (300 MHz, $CDCl_3$): 6.38 (d, 2H), 5.65 (d, 2H), 2.06 (s, 6H).

**General Procedure of Polymerization of 4 with 2.** A 4 mL vial with a septum cap was charged with the desired amount of monomer and a stirbar under a flow of argon. Solvent (THF, Toluene, or $CH_2Cl_2$) in the desired concentration was added to the vial. A stock solution of catalyst was quickly added to the vigorously stirring monomer solution via syringe while under argon. If the polymerization was to be heated, the reaction vial was placed in a 55 °C aluminum heating block stirring under argon for 24 h. Otherwise they were left stirring at room temperature. The reaction mixture was then dissolved in 1 mL $CH_2Cl_2$ and precipitated into 50 mL of stirring MeOH. The white precipitate was washed several times with MeOH and dried in vacuo overnight. See Tables for molecular weights and yields.

**General Procedure for Polymerization of 4/10 with 2.** A 4 mL vial with a septum cap was charged with the desired amount of monomer and a stirbar under a flow of argon. Solvent (THF, Toluene, or $CH_2Cl_2$) in the desired concentration was added to the vial. Then the desired amount of CTA (when needed) was added to the vial and the reaction was allowed to stir for a few minutes. A stock solution of catalyst was quickly added to the vigorously stirring monomer solution via syringe while under argon. If the

polymerization was to be heated, the reaction vial was placed in a 55 °C aluminum heating block stirring under argon for 24 h. Otherwise they were left stirring at room temperature. The reaction mixture was then dissolved in 1 mL $CH_2Cl_2$ and precipitated into 50 mL of stirring MeOH. The white precipitate was washed several times with MeOH and dried in vacuo overnight. See Tables for molecular weights and yields.

**poly(3,4-bis(benzyloxy)cyclobutene) (5).** $^1$H NMR (300 MHz, $CDCl_3$): 7.21 (br s, 10H, 5.75–5.61 (br m, 2H), 4.55–3.73 (br m, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): 139.24, 132.47, 128.74, 128.07, 127.84, 82.40, 71.03.

**poly(3,4-bis(acetoxy)cyclobutene) (10).** $^1$H NMR (300 MHz, $CDCl_3$): 5.79–5.31 (m, 4H), 2.03 (s, 6H).

**General Hydrogenation Procedure.** In a typical experiment, an oven-dried 100-mL round-bottom flask was charged with a stir bar and polymer (0.4g), tosylhydrazide (3.5 equiv per double bond), tripropylamine (1 equiv per tosylhydrazide), xylenes (0.2 M), and a trace amount of BHT (~10mg). The mixture was degassed by pulling high vacuum on the solution for about 45 s. Under an argon atmosphere, the flask was fitted with a reflux condenser, and the reaction was heated to reflux (150 °C) for 7 h. The reaction mixture was then cooled to room temperature and precipitated into stirring acetone. The white precipitate was washed several times with acetone and then dried in vacuo for several hours.

**Hydrogenated Poly(3,4-bis(benzyloxy)cyclobutene) (6).** $^1$H NMR (300 MHz, $CDCl_3$): 7.30–7.25 (br s, 10H), 4.64–4.5 (br d, 4H), 3.53 (br s, 2H), 1.86–1.63 (br d, 4H). $^{13}$C NMR (75 MHz, $CDCl_3$): 139.68, 129.02, 128.75, 128.27, 128.21, 81.96, 91.32, 72.87, 72.71, 27.88, 27.27.

**Deprotection of Hydrogenated Poly(3,4-bis(benzyloxy)cyclobutene) (7).** A 4 mL vial was charged with **6** (41.3 mg), DMSO (2.0 mL) and a stirbar. The polymer was sonicated to dissolve. Then, trimethylsilyliodide was added via syringe and the reaction was allowed to stir for 1 h. Next, MeOH was slowly added via syringe until the polymer precipitated from solution. A white powder was obtained in 98% yield. $^{13}$C NMR (solid state): 128, 77, 31.

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# Chapter 4

# The Controlled Living Ring-Opening Metathesis Polymerization of Trans-Cyclooctene

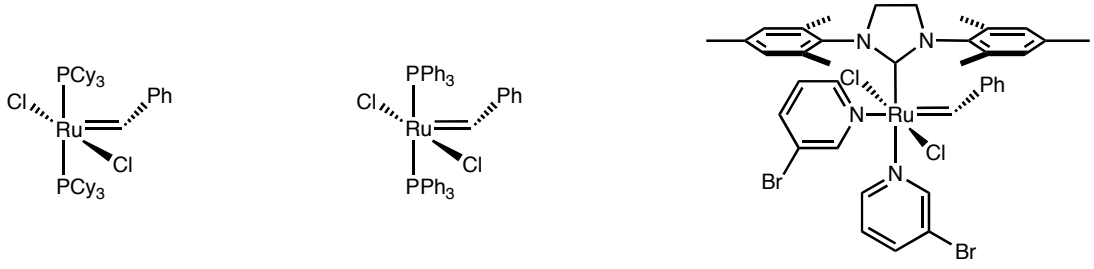
# Abstract

The living ring-opening metathesis polymerization (ROMP) of trans-cyclooctene (TCO) was investigated. ROMP of TCO in the presence of $PPh_3$ leads to the formation of narrow dispersed polycyclooctene PCO. However, a small amount of high molecular weight species is observed as a result of competing secondary metathesis when polymerizations are conducted in $CH_2Cl_2$. By switching the reaction solvent to THF, secondary metathesis is suppressed and the formation of narrowly dispersed PCO is achieved without any high molecular weight contaminates. The narrowly dispersed PCO was then hydrogenated to form linear narrow dispersed polyethylene with a melting temperature of 139 ºC. Block copolymers containing polynorbornene and PCO were also synthesized and hydrogenated to form block copolymers containing blocks of linear, narrowly dispersed polyethylene.

## 4.1. Introduction

Ring-opening metathesis polymerization (ROMP) has been employed in the synthesis of a wide range well-defined polymer architectures.[1,2] ROMP is a chain-growth polymerization in which a cyclic olefin is converted to polymer. This process is driven by the release of ring strain which provides the main driving force that is required to overcome the unfavorable entropy change in polymerization.[3] Typical cyclic olefins for ROMP include norbornene, cyclobutene, cyclooctene, and dicyclopentadiene. Also, many functionalized derivatives of these monomers can be polymerized using the functional-group tolerant late transition metal Grubbs catalysts 1-3 (Figure 4.1).[3]

In recent years, living ROMP has emerged as a valuable tool for polymer chemists.[4] A living and controlled ROMP polymerization is generally characterized by narrow PDIs <1.5 and a linear relationship between polymer molecular weight and monomer conversion.[3-5] This control is achieved when the rate of polymer chain initiation ($k_i$) occurs faster than chain propagation ($k_p$).[6] Additionally, the rate of termination and secondary metathesis reactions ($k_s$) must either be severely limited or non-existent. Therefore controlled living ROMP is achieved when $k_i/k_p$ is relatively high as compared to $k_s$.




**1** **2** **3**

**Figure 4.1.** Ruthenium Olefin Metathesis Catalysts (Cy = cyclohexyl).

Norbornene and its functionalized derivatives have become the monomers of choice for living ROMP due to widespread commercial availability, cost, and general ease of synthesis. Norbornene exhibits the characteristic high ring strain needed for ROMP (Figure 4.2) and consequently, polymers with low PDIs and controllable molecular weights are obtained when polymerized with fast-initiating catalysts **1** and **3**.[7] Competing secondary metathesis reactions during ROMP, which include intermolecular chain-transfer and intramolecular chain-transfer (back-biting), leading to broadened polymer PDIs and preventing living and controlled polymerization. This secondary metathesis is limited by the steric hindrance of the olefins in the polymer backbone of polynorbornene. In addition, the living ROMP of monocyclic alkenes has seen limited use due to significant secondary metathesis of the unhindered olefins in the polymer backbone. Cyclobutene and its functionalized derivatives have been used in controlled living ROMP but to a lesser extent than norbornene.[8-10] Polycyclobutene, with a PDI of 1.1, has been prepared from cyclobutene with well-defined tungsten catalysts in the presence of $PMe_3$, which was shown to limit secondary metathesis. Although highly-strained hindered monomers are typically used, Register et al has shown the living ROMP of low strain cyclopentene with well-defined molybdenum alkylidene initiators, also in the presence of $PMe_3$.[11] Despite the benefits of using a commercially available catalyst and monomer, the low strain of cyclopentene forces the polymerizations to be conducted at high concentration and terminated before full monomer conversion is achieved in order to prevent competing secondary metathesis.

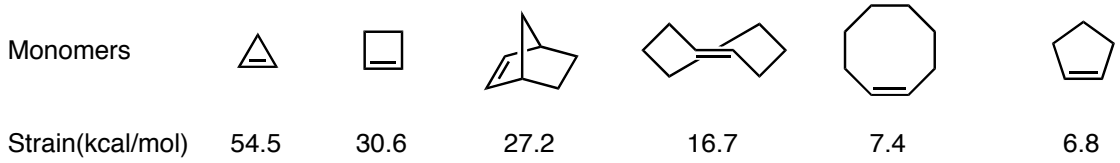



**Figure 4.2.** Typical cyclic olefins used in ROMP.

Cyclic trans-olefins have been noted as excellent candidates for ROMP because of their increased ring strain.[13-15] However, they are seldom used as compared with their cyclic cis counterparts. Nuckolls et al. recently reported the living polymerization of *trans,cis*-dibenzo[a,e]cyclooctatetrene.[13] Low polydispersity polymer having PDI's < 1.1 were formed by adding three equivalents of tricyclohexylphosphine,. It was also noted that *cis,cis*-dibenzo[a,e]cyclooctatetrene was unreactive under similar conditions. Currently, to the best of our knowledge, there are no reports of the controlled living polymerization of *cis*- or *trans*-cyclooctene (TCO). This is due to competing secondary metathesis of the unhindered polymer backbone making it difficult to polymerize in a controlled fashion. Additionally *cis*-cyclooctene has a low ring strain of 7.4 kcal/mol[12], which lowers its activity for controlled living ROMP. However, TCO has a ring strain of 16 kcal/mol[12] (Figure 4.2). If secondary metathesis can be prevented, the high ring strain of TCO makes it an excellent candidate for controlled living polymerization.

## 4.2. Results and Discussions

### 4.2.1. ROMP of Trans-Cyclooctene

The ROMP of *trans*-cyclooctene (TCO) was investigated with several well-known living ROMP initiators (Scheme 4.1). Table 4.1 depicts the results of an initial screen of conditions for ROMP of TCO. In runs 1 and 2, catalyst **1** was used to polymerize TCO at high and low concentration, respectively. Run 1 depicts the polymerization of TCO at an initial monomer concentration of 0.5 M in $CH_2Cl_2$. The observed molecular weight of 44,000 g/mol was slightly higher than the expected value of 33,000 g/mol, and the PDI was polydispersed (1.42). Initially, we attributed the broad PDI to competing secondary metathesis during ROMP. However, upon observation of the addition of catalyst **1** to the monomer solution, the solution did not exhibit the characteristic color change from purple to brown. This indicated that catalyst did not fully initiate even though all monomer had been consumed, leading us to assume that the $k_p$ of TCO is much faster than the $k_i$ of **1**. Since all the catalyst does not initiate, the observed molecular weight is higher than the calculated value. Also, this difference in $k_i/k_p$ along with competing secondary metathesis is the cause the broad PDI. When the polymerization was performed at a concentration of 0.05 M, no polymer was formed and only small molecular weight oligomers and cyclics were observed. Runs 4 and 5 show when faster initiating catalyst **3** was used, similar results were observed. Although catalysts **1** and **3** failed to polymerize TCO at low concentration, catalyst **2** was able to polymerize TCO at both high and low concentration. This is attributed to the much faster $k_i$ of catalyst **2** relative **1**[16] and slower $k_s$ relative to both **1** and **3**.[17,18] Although **2** initiates much faster than **1**, the observed molecular weights are higher and the PDIs are not narrow. Similar to the polymerization of TCO with **1**, the $k_i$ is still much slower than the

$k_p$ of TCO leading to uncontrolled polymerization. However the higher molecular weights and lower PDIs lead us to assume that $k_s$ is much slower than when polymerizations were conducted using catalyst **1**.

**Scheme 4.1.** ROMP of Trans-Cyclooctene.

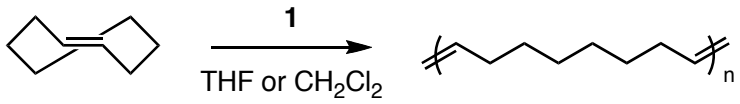
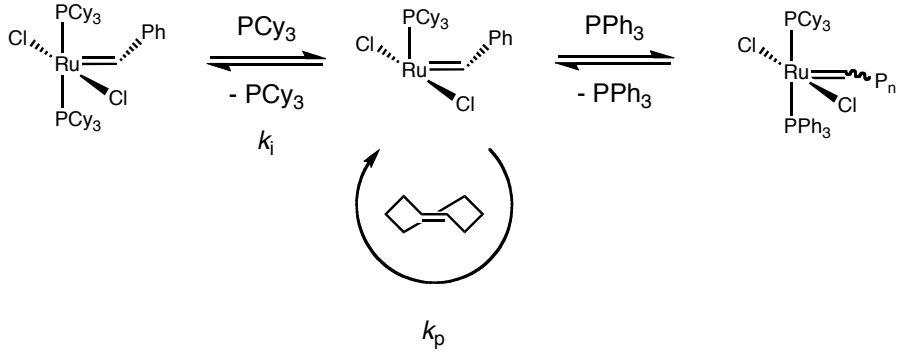



**Table 4.1.** Polymerization of TCO in $CH_2Cl_2$ $[M]_0$/Cat = 300:1.

| Run | Catalyst | $[M]_0$[a] | $M_n$ (× $10^3$) | Yield (%)[b] | PDI |
|---|---|---|---|---|---|
| 1 | **1** | 0.50 | 44 | 70 | 1.42 |
| 2 | **1** | 0.05 | - | - | - |
| 3 | **2** | 0.50 | 94 | 77 | 1.37 |
| 4 | **2** | 0.05 | 167 | 69 | 1.29 |
| 5 | **3** | 0.50 | 53 | 64 | 1.25 |
| 6 | **3** | 0.05 | - | - | - |

[a]Initial Monomer concentration, [b]Isolated yields.

**Scheme 4.2.** ROMP of TCO with excess $PPh_3$.




Bielawski showed the ROMP of a number of norbornene derivatives as well as cyclooctadiene (COD) using catalyst **1** and excess triphenylphosphine.[19] The resulting polymers had lower polydispersites and in addition the functional-group tolerance of the catalyst was maintained. The excess phosphine competes with monomer for the Ru center, which in turn decreases both the $k_p$ and $k_s$.[19] Based on this knowledge, we decided

to use catalyst **1** along with the addition of excess phosphine as shown in Scheme 4.2. By increasing the phosphine to catalyst ratio, the concentration of active catalyst is kept very low, similar to a controlled free radical polymerization. Entries 1-7 in

Table **4.2** depict our efforts to control the polymerization of TCO with varying equivalents of $PPh_3$ relative to catalyst. As the ratio of phosphine to initiator increases, the observed polymer molecular weights get closer to their theoretical values, and the PDI's decrease. However as the equivalents of $PPh_3$ are increased a high molecular weight peak is observed, as shown in the GPC of entry 7 traces in Figure 4.3. The refractive index detector (solid line) shows that only a small amount of high molecular weight polymer is present. This high molecular weight product can also be seen as a larger peak in the light scattering trace (dashed line), because light scattering is mostly affected by molecular weight. Both Wu and Register have also observed this high molecular weight species in the ROMP of cyclobutene and cyclopentene, respectively. Register later demonstrated that acyclic/secondary metathesis competes with ROMP in forming the observed high molecular weight polymers.[20]

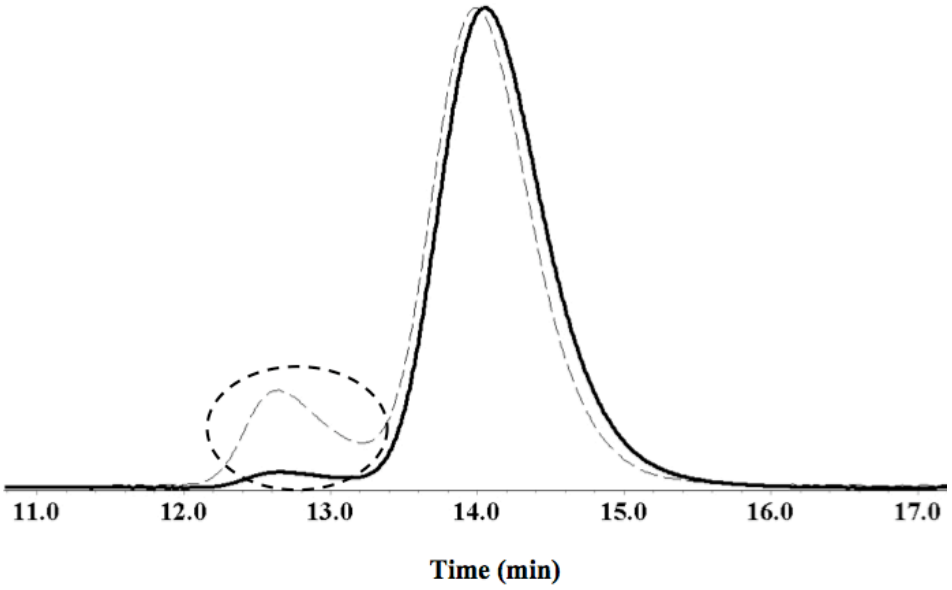



**Figure 4.3.** GPC trace of entry 7. RI trace (solid line) and Light scattering trace (dashed line). The minor peak is attributed to competing chain transfer.

**Table 4.2.** Polymerization of TCO with **1** and increasing $PPh_3$.

| Entry | $PPh_3$:**1** | $[M]_0$/**1** | $M_n$ ($\times 10^3$) | $M_n$ theo($\times 10^3$) | PDI | Yield (%) |
|---|---|---|---|---|---|---|
| **1** | 0 | 200 | 39 | 22 | 1.30 | 74 |
| **2** | 1 | 200 | 40 | 22 | 1.35 | 74 |
| **3** | 5 | 200 | 37 | 22 | 1.37 | 72 |
| **4** | 10 | 200 | 32 | 22 | 1.31 | 72 |
| **5** | 20 | 200 | 33 | 22 | 1.19 | 67 |
| **6** | 40 | 200 | 26 | 22 | 1.14 | 68 |
| **7** | 60 | 400 | 55 | 44 | 1.06 | 97 |
| **8** | 0 | 400 | 268 | 44 | 1.60 | 76 |
| **9** | 1 | 400 | 265 | 44 | 1.42 | 86 |
| **10** | 5 | 400 | 213 | 44 | 1.31 | 88 |
| **11** | 10 | 400 | 67 | 44 | 1.26 | 93 |
| **12** | 20 | 400 | 57 | 44 | 1.18 | 96 |
| **13** | 40 | 400 | 46 | 44 | 1.13 | 93 |
| **14** | 60 | 400 | 59 | 44 | 1.08 | 90 |

Entries 1-7 were conducted in $CH_2Cl_2$ (0.5 M) at room temperature; entries 8-14 conducted under similar conditions, except in THF.

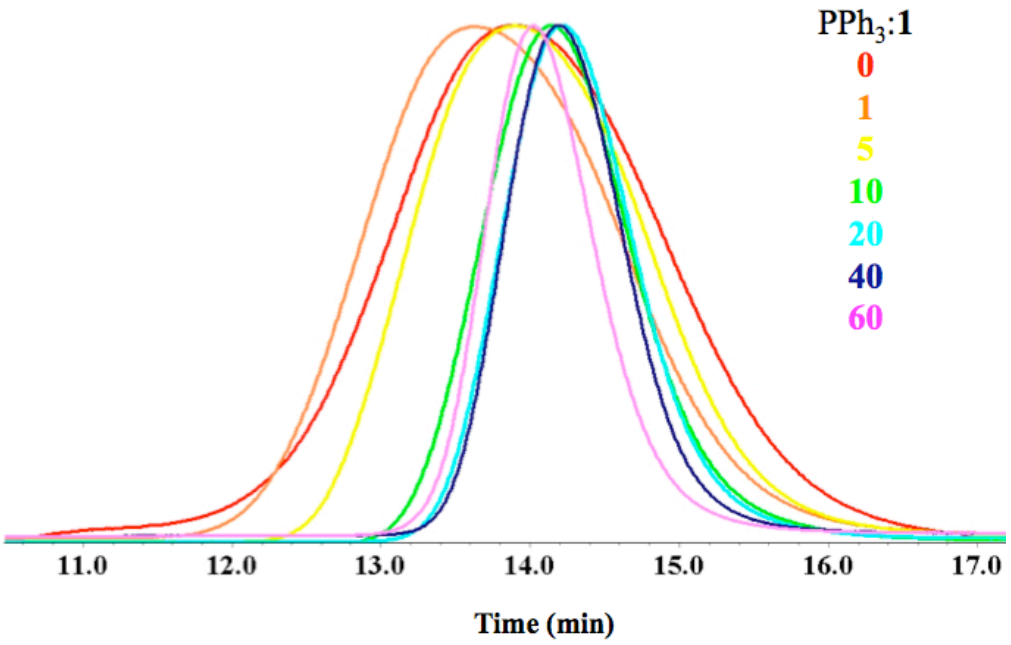



**Figure 4.4.** ROMP of TCO with **1** in THF (0.5 M) at room temperature with increasing equivalents of $PPh_3$. After the addition of 5 equivalents of $PPh_3$ no high molecular weight peak is observed.

In order to limit the formation of the high molecular weight species, we decided to investigate a method of preventing secondary metathesis. The kinetics of ROMP demonstrates that as the monomer concentration in solution decreases, the $k_p$ decreases and $k_s$ increases. This results in the broadening of the PDIs or, in our case, the observed high molecular weight. There have been several suggestive reports that changing the reaction solvent to a more coordinating solvent such as THF can limit or even prevent secondary metathesis reactions. For example, THF has been used to slow the polymerization of cyclooctatetraene and also limit secondary metathesis.[21] It has also been shown that catalyst **1** initiates faster and is less prone to secondary metathesis in solvents such as THF.[19,22,23] Furthermore, when polymerizations are conducted with early transition metal metathesis catalysts and excess phosphine in THF, secondary metathesis is also suppressed..[8,23,24] Also, more recently, Register showed that addition of a small

amount THF limited the secondary metathesis in the ROMP of cylopentene.[25] After careful examination of these previous reports, polymerizations of TCO were carried out in THF with catalyst **1**. A similar trend of decreasing PDIs with increasing phosphine was observed. Interestingly, after the addition of 5 equivalents of $PPh_3$ relative to catalyst, no high MW species is observed, as shown in Figure 4.4, indicating that backbiting reactions are subdued. Also, the molecular weights are much higher at low loadings of $PPh_3$, which indicates that $k_s$ is much slower THF. As the ratio of $PPh_3$ to **1** increase, the observed molecular weight move closer to their theoretical values; demonstrating that $PPh_3$ has a greater effect on the $k_p$ than on the $k_s$ of the polymerization.

Controlled living ROMP was also attempted using catalyst **3** with increasing equivalent of $PPh_3$. Figure 4.5 and Table 4.3 depict these results. The same trend of decreasing PDIs as well as molecular weight was observed when polymerizations were conduction using **3** in the presence of $PPh_3$. Though no high molecular weight species is observed, the characteristic low molecular weight shoulder is observed, which indicates the formation of small molecular weight cyclics. Furthermore as the PDIs became more narrowly dispersed, the isolated yields decrease. This was attributed to the formation of small molecular weight oligomers.

**Table 4.3.** ROMP of TCO with **4**.

| $PPh_3$:**4** | $M_n$ ($\times 10^3$) | PDI | Yield (%) |
|---|---|---|---|
| 0 | 34420 | 1.45 | 74 |
| 1 | 33440 | 1.44 | 74 |
| 5 | 26300 | 1.54 | 72 |
| 10 | 19260 | 1.59 | 46 |
| 20 | 15430 | 1.33 | 47 |
| 40 | 8437 | 1.27 | 16 |

Polymerizations were conducted with $[M]_0$/**4** of 300:1.

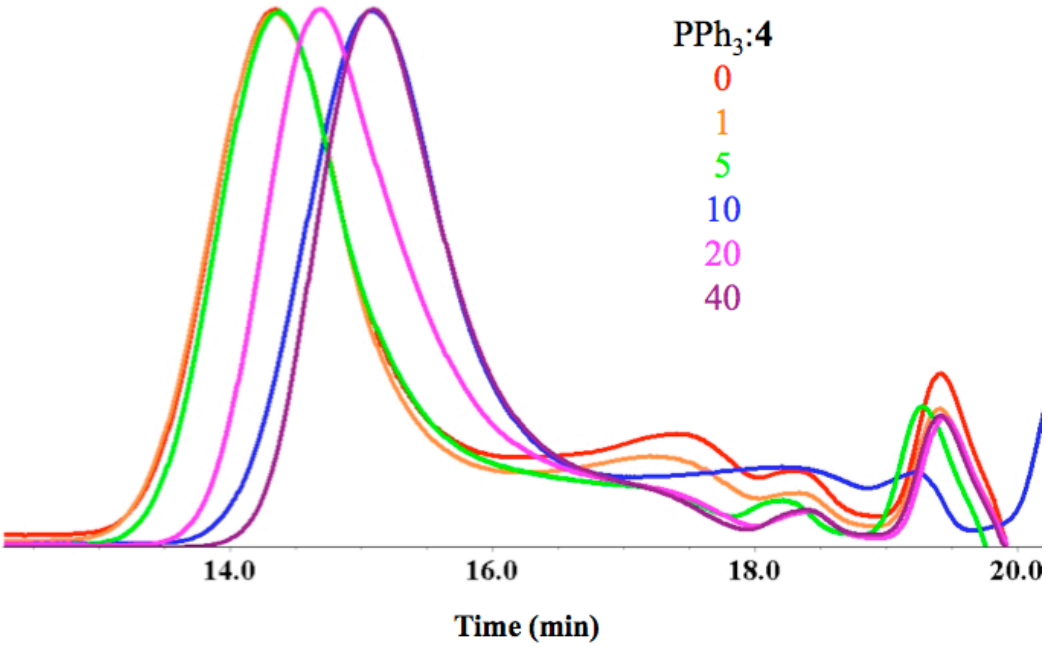



**Figure 4.5.** ROMP of TCO with increasing $PPh_3$:**4**.

As expected with controlled living polymerization, molecular weight should increase linearly with increasing monomer to catalyst ratio. The results depicted in Table 4.4 and Figure 4.6 clearly shows this relationship up to a molecular weight of 390,000 g/mol.

**Table 4.4.** Effect of Increasing $[M]_0$/**1**.

| Entry | $[M_0]$/**1**[a] | $M_n$ ($\times 10^3$) | PDI |
|---|---|---|---|
| **15** | 194 | 31 | 1.10 |
| **16** | 303 | 42 | 1.08 |
| **17** | 402 | 48 | 1.08 |
| **18** | 592 | 66 | 1.09 |
| **19**[b] | 3842 | 390 | 1.08 |

[a]Initial monomer concentration of 0.5 M. [b]Conducted at 0.05 M.

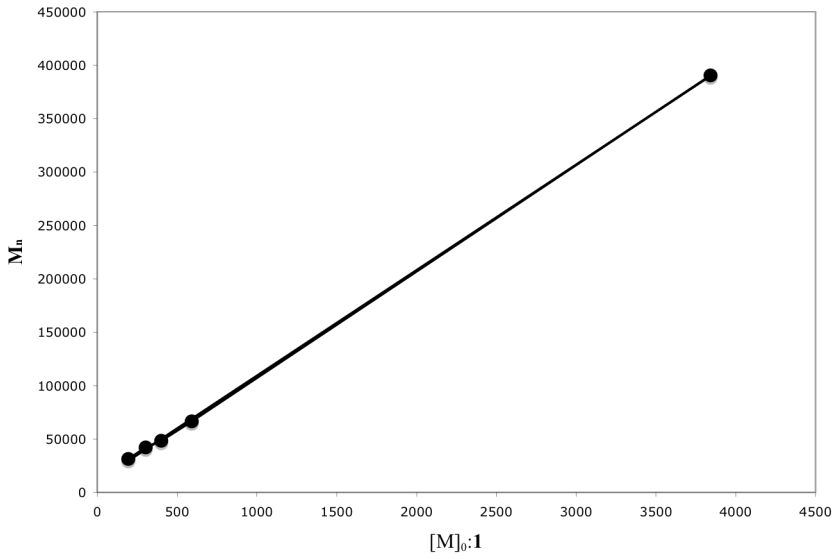
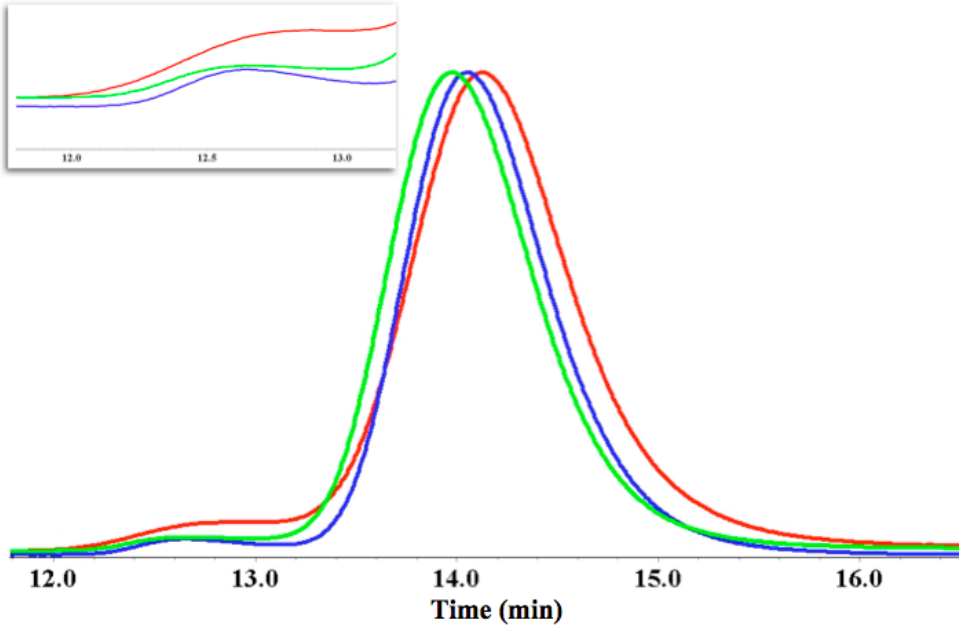


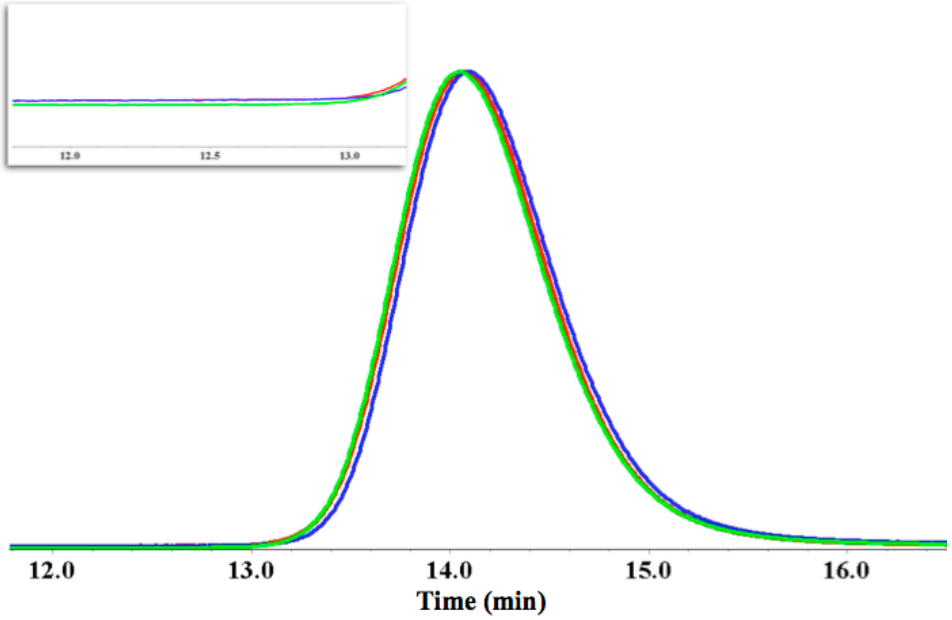

**Figure 4.6.** Molecular weight control by varying $[M]_0$/**1**. ROMP of TCO with **1** was carried out in THF (0.5 M) at room temperature for entries 15-18. The high MW point corresponding to entry 19 was conducted at 0.05 M.

### 4.2.2. Reaction Time Study

In order to determine when secondary metathesis was occurring during the reaction timeline, a timed study using catalyst **1** was performed, shown in Table 4.5 and Figure 4.7. Three samples in either THF or $CH_2Cl_2$ were polymerized and terminated at varying times. After a one-minute reaction time in $CH_2Cl_2$, the high MW peak was observed. Also after one minute the reaction was not yet complete, as was evident by the low molecular weight and the presence of unreacted monomer. After 5 and 10-minute reaction times, the high molecular weight peak was still observed. This result indicates that secondary metathesis is competing with chain propagation. However, in THF no such peak is observed, and the reaction is complete after one minute. Also after 10 minutes the polydispersity does not broaden and no high molecular weight species is observed, indicating a controlled living polymerization and no competing chain-transfer reactions. These results also demonstrate that while $k_p \approx k_s$ in $CH_2Cl_2$, $k_p >> k_s$ in THF.




(a)




(b)

**Figure 4.7.** GPC traces of polymerizations stopped at increasing times: 1 min in red, 5 min in blue and 10 min in green. (a) ROMP of TCO in $CH_2Cl_2$ (0.5 M) at room temperature. (b) Same as (a) except in THF. The reactions were stopped at varying time intervals with ethyl vinyl ether.

**Table 4.5.** Timed Study.

| Solvent | Time (min) | $M_n$ (x $10^3$) | PDI | Yield (%) |
|---|---|---|---|---|
| $CH_2Cl_2$ | 1 | 39 | 1.10 | 66 |
| | 5 | 52 | 1.05 | 98 |
| | 10 | 52 | 1.08 | 99 |
| THF | 1 | 55 | 1.08 | 90 |
| | 5 | 52 | 1.08 | 90 |
| | 10 | 54 | 1.08 | 87 |

Polymerization conducted with $[M]_0$/**1**= 400:1 with $PPh_3$:**1**=60.

## 4.3. Concentration Study

The limitation in forming monodispersed polycyclooctene using cis-cyclooctene is its low critical monomer concentration $[M]_c$, which is defined as the total amount of monomer per unit volume that forms cyclic products at ring-chain equilibrium.[26] Hocker et al. showed no polymers are formed until the monomer concentration of cis-cyclooctene exceeds 0.21 M.[27] If the initial monomer concentration is less than $[M]_c$, only low molecular weight cyclics and linear oligomers are formed. Upon exceeding $[M]_c$, the equilibrium cyclics concentration is almost constant, and linear polymers begin to appear. Therefore, $[M]_c$ characterizes the polymerizability of a given monomer.

Cyclooctene and cyclopentene both have to be polymerized at relatively high concentrations in order to increase conversion and limit the formation of cyclic oligomers. It has been shown that critical monomer concentration is directly related to monomer ring strain.[3,26] TCO has a ring strain of 16 kcal/mol, and, consequently, it can be polymerized at more dilute concentrations similarly to other highly strained ROMP monomers. Furthermore, it is difficult to polymerize ultra high molecular weight PCO (Mw >100,000 g/mol) from *cis*-cyclooctene because the polymerization gels or becomes too viscous when high molecular weight PCO is formed at high concentration. As is shown in Table 4.4 entry 19, the controlled living ROMP of TCO may be conducted at

concentrations well below the critical monomer concentration of cis-cyclooctene. Table 4.6 presents the result of decreasing concentration when polymerizations are performed in either THF or $CH_2Cl_2$. When initial monomer concentration is decreased in $CH_2Cl_2$ the molecular weight stays consistent, but isolated yields are low. This is attributed to an increase in $k_s$ at low concentration and high monomer conversion, which, in turn, forms low molecular polymers and cyclics. The low PDIs and isolated yields are obtained from the removal of these small molecular weight contaminates by fractionation in MeOH. When these same polymerizations are conducted in THF, backbiting is suppressed and high isolated yields are obtained, along with consistent molecular weights.

**Table 4.6.** Concentration Study.

| Solvent | $[M]_0$ | $M_n$ (x $10^3$ g/mol) | PDI | Yield (%) |
|---|---|---|---|---|
| | 0.25 | 54 | 1.08 | 95 |
| $CH_2Cl_2$ | 0.10 | 56 | 1.06 | 35 |
| | 0.05 | 54 | 1.08 | 42 |
| | 0.25 | 67 | 1.15 | 95 |
| THF | 0.10 | 64 | 1.10 | 80 |
| | 0.05 | 64 | 1.16 | 81 |

Polymerization conducted with m/cat 400:1 and allowed to run for 10 minutes.

## 4.4. Synthesis of Linear High Density Polyethylene

Linear monodispersed high-density polyethylene has previously been synthesized from the ROMP of monocyclic alkenes followed by hydrogenation. Commercially available cis-cyclooctene as well as COD are both well-known monomers for ROMP, and both have been polymerized to form polyethylene, via hydrogenation of polycyclooctene and polybutadiene.[1,2] Although HDPE synthesized from the ROMP of cis-cyclooctene or COD forms linear polymer, the PDIs are not narrow but because of secondary metathesis. Linear, narrowly dispersed HDPE has previously been synthesized from polycyclobutene and shown to have a $T_m$ of 129 °C. However, because cyclobutene

is gaseous at room temperature, technical challenges preclude its widespread usage. Register et al. have also shown the synthesis of HDPE from the hydrogenation of narrowly dispersed polycyclopentene. Using TCO overcomes many of these challenges since it is a liquid at room temperature. Also narrowly dispersed PCO may be synthesized from the living ROMP of TCO without the high molecular weight contaminates seen previously in the living ROMP of cyclopentene and cyclobutene. The polymer can then be hydrogenated to form linear narrow dispersed HDPE.

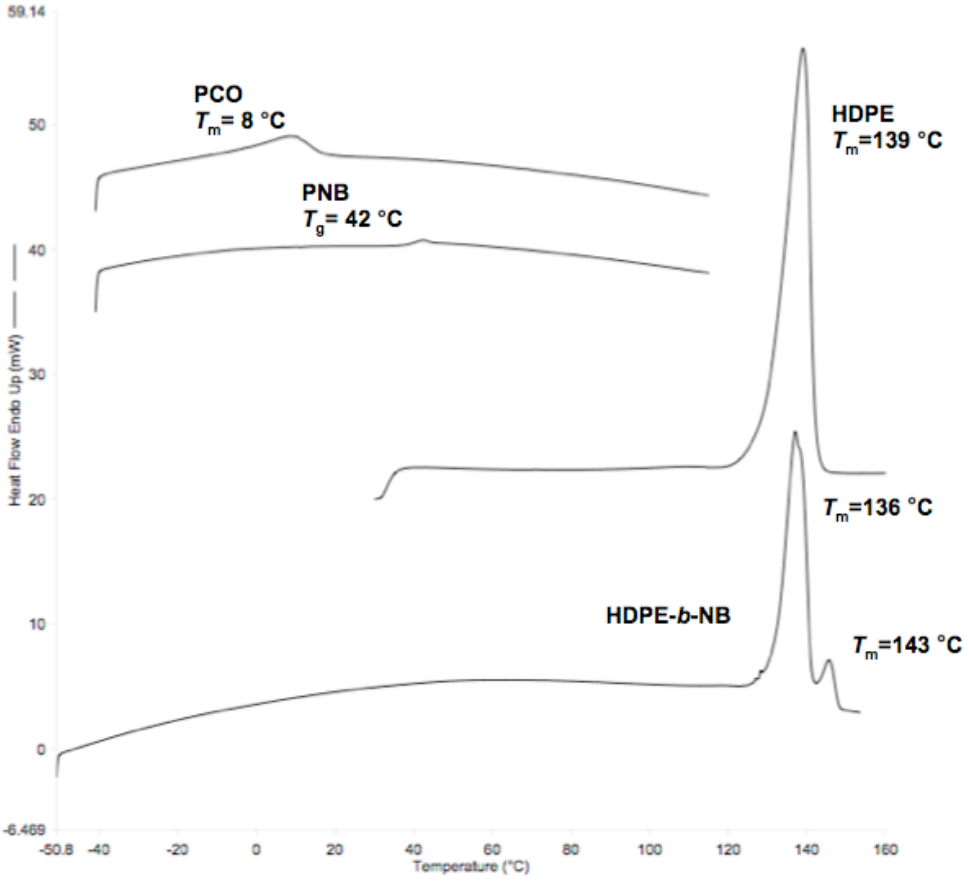


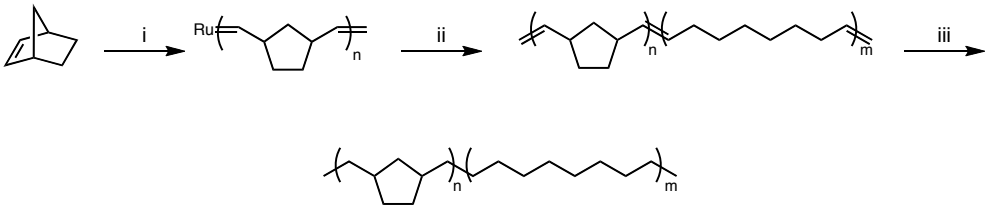

**Figure 4.8.** (a) PCO $M_n$=54,000 g/mol. (b) PNB $M_n$=10,000 g/mol. (c) HDPE from monodispersed PCO, (d) HPNB/HDPE diblock.

Linear polycyclooctene synthesized using catalyst **1** contains 56% cis olefin and exhibits a $T_m$ of 10 °C, which is in good agreement with published experimental values.[28]

The preference for predominant cis-olefin formation in THF is still unknown.[29] Hydrogenation of PCO (Entry 18) was conducted by direct formation of diimide in situ[9,30-34] and yielded linear, narrowly dispersed HDPE. The $T_m$ determined for HDPE was 139 °C, which is slightly higher than the published values for Wu and Register 129 °C and 133 °C respectively.[9,11]

### 4.4.1. Diblock Copolymer Syntehesis

**Scheme 4.3.** Block copolymers of Norbornene and Trans-cyclooctene.




(i) $[M]_0$:**1**=100 and 2 eq $PPh_3$, room temperature, 30 min. ii) Macroinitiator added to a solution of TCO in THF (0.1 **M**) with $PPh_3$:**1**=58, room temperature, 10 min. (iii) tosylhydrazide, triisopropyl amine, xylenes 150 °C.

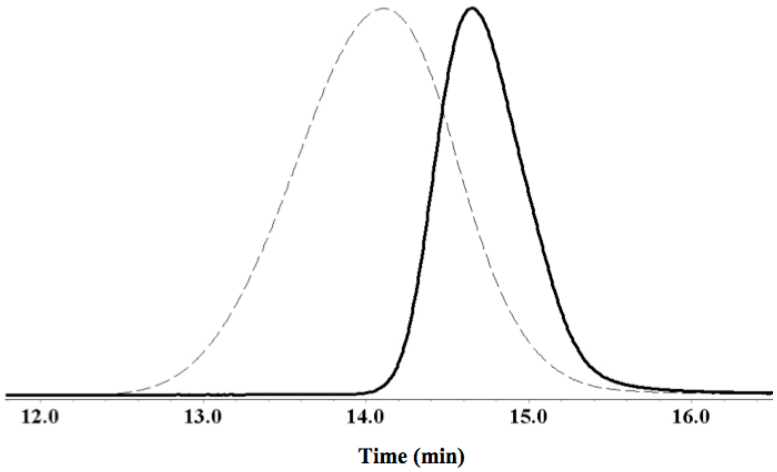



**Figure 4.9.** Polynorbornene (solid line), PNB-*b*-PCO (dashed line).

### 4.4.2. Synthesis of Hydrogenated Norbornene-*b*-Polyethylene

Diblock copolymers containing hydrogenated norbornene and polyethylene were synthesized by hydrogenation of block copolymers synthesized by the sequential addition

of monomers. First, the polynorbornene block was synthesized using catalyst **1** in the presence of two equivalents $PPh_3$ relative to **1**, and was subsequently added as a macroinitiator to a vigorously stirring solution of TCO (0.1 M in THF), as shown in Scheme 4.3. The reaction was allowed to proceed for 30 min before quenching with ethyl vinyl ether and then allowed to stir for 2 h. The final polymer was then precipitated into stirring acetone. The GPC trace in Figure 4.9 shows the traces for polynorbornene homopolymers (PNB, dashed line) and the PNB-*b*-PCO copolymer (solid line) made in THF. The monomodal trace of the polymer indicates the controlled formation of diblock copolymer.

The block copolymerization was also performed in $CH_2Cl_2$. The polymerization was performed similarly to the block copolymer synthesis in THF. The results compare well to the previous example, but the PDI is broader (PDI=1.22). This is attributed to formation of the high molecular weight species during polymerization.

The block copolymer synthesized in THF was then hydrogenated using the same procedure as above. The DSC trace in Figure 4.8 shows two clear melting points of 136 °C and 146 °C for the polyethylene and polynorbornene blocks respectively.

### 4.4.3. Triblock PNB-*b*-PCO-*b*-PNB

ABA triblock copolymers were also synthesized by sequential addition of monomer. First, the polynorbornene block was synthesized using catalyst **1** in the presence of two equivalents $PPh_3$ relative to **1**, and was subsequently added as a macroinitiator to a vigorously stirring solution of TCO (0.1 M in THF). The reaction was allowed to proceed for 30 min before quenching after which the desired amount of norbornene was added. The reaction was quenched with ethyl vinyl ether after 30 min.

The final polymer was then precipitated into stirring acetone. The ABA triblock copolymer was monomodal indicating the controlled formation of triblock copolymer.

## 4.5. Conclusions

The controlled living ROMP of TCO was successfully performed with catalyst **1** in the presence of $PPh_3$. The ratio of $PPh_3$ to **1** as well as the reaction solvent play a crucial role in the controlled living polymerization of this highly strained cyclic alkene. By varying reaction conditions, competing secondary metathesis reactions during ROMP were suppressed, leading to low PDI polymers and precise molecular weight control. Hydrogenation of polycyclooctene yielded low PDI HDPE, and block copolymers were also synthesized and hydrogenated, yielding polymers with linear polyethylene blocks. Future efforts in the group are aimed at exploiting the functional group tolerance of catalyst **1** to polymerize functionalized trans-cyclooctene derivatives. We anticipate that these results will lead to interesting block copolymer architectures that include blocks of polyethylene.

## 4.6. Acknowledgements

This work was supported by the National Science Foundation. The authors would like to thank John B. Matson, Rosemary Conrad, Paul C. Clark and Yan Xia for helpful discussions and critical reading of this manuscript.

## 4.7. Experimental Section

**General Methods.** NMR spectra were recorded on a Varian Mercury 300 (300 MHz for $^{1}H$ and 74.5 MHz for $^{13}C$). All NMR spectra were recorded in $CDCl_3$, referenced to residual proteo species. Gel permeation chromatography (GPC) was carried out in THF on two PLgel 10 μm mixed-B LS columns (Polymer Laboratories) connected in series with a DAWN EOS multiangle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer (both from Wyatt Technology). No calibration standards were used, and dn/dc values were obtained for each injection by assuming 100% mass elution from the columns. Differential scanning calorimetry (DSC) was carried out simultaneously on a Perkin-Elmer Pyris1 under a flow of helium at a heating rate of 10 °C/min.

**Materials.** THF and $CH_2Cl_2$ were dried by passage through solvent purification columns[35] and passed through basic alumina. Triphenylphosphine was obtained from Alfa Aesar and recrystallized from ethyl acetate prior to use. Norbornene was sublimed prior to use and acetone (technical grade) was dried over calcium sulfate and filtered prior to use as a solvent. All other chemicals were obtained from Aldrich and used as received. Ruthenium catalysts $(PCy_3)_2(Cl)_2RuCHPh$[16], $(PPh_3)_2(Cl)_2RuCHPh$[16], $(H_2IMes)(3\text{-Br-pyr})_2(Cl)_2RuCHPh$[17] and trans-cyclooctene[36] were all synthesized according to literature procedures.

**General Polymerization Procedure for Polycyclooctene.** A 4 mL vial with a septum cap was charged with the desired amount of trans-cyclooctene and a stirbar under a flow of argon. Solvent (THF or $CH_2Cl_2$) in the desired concentration was added to the vial. Then the desired amount of $PPh_3$ was added to the vial. A stock solution of catalyst

was quickly added to the vigorously stirring monomer solution via syringe while under argon. After stirring at room temperature for 10 min under a flow of argon, ethyl vinyl ether (0.2 mL) was added and the reaction was allowed to stir for one hour at room temperature. The reaction mixture was then precipitated into vigorously stirring acetone (100 mL) and a white precipitate was formed. The polymer was washed multiple times with acetone and dried in vacuo overnight. See Tables for molecular weights and yields.

**PNB-*b*-PCO Block Copolymer.** A 4 mL vial with a septum cap was charged with the desired amount of norbornene (1.83 mmol), a stirbar and THF (0.5 M) under a flow of argon. A second 20 mL vial was charged with a stirbar and the desired amount of TCO and THF (0.1 M). Then the desired amount of $PPh_3$ was added to the each vial. 2 equiv of $PPh_3$ relative to catalyst was added to the vial containing norbornene and 58 equiv of $PPh_3$ relative to catalyst was added to the vial containing TCO. A stock solution of catalyst was quickly added to the vigorously stirring norbornene solution via syringe while under argon. After stirring at room temperature for 10 min under a flow of argon, a desired amount of solution was taken up in syringe and added as a macroinitiator to the vigorously stirring solution of TCO (0.1 M in THF with 58 equiv $PPh_3$). The remaining norbornene solution and block copolymer reaction were quenched after 10 min with ethyl vinyl ether (0.2 mL) and allowed to stir for one hour at room temperature. Each reaction mixture was then precipitated into two separate flasks containing vigorously stirring acetone (100 mL). A white precipitate was observed for each. The polymers were then washed multiple times with acetone and dried in vacuo overnight. PNB: $M_n$ = 10, 000 g/mol, PDI = 1.04 yield = 90% (13% *cis* olefin), PNB-*b*-PCO: $M_n$ = 63, 000 g/mol, PDI = 1.10 yield = 90%.

**General Hydrogenation Procedure.** In a typical experiment, an oven-dried 100-mL round-bottom flask was charged with a stir bar and polymer (0.4g), tosylhydrazide (3.5 equiv per double bond), tripropylamine (1 equiv per tosylhydrazide), xylenes (0.2 M), and a trace amount of BHT (~10mg). The mixture was degassed by pulling high vacuum on the solution for about 45 s. Under an argon atmosphere, the flask was fitted with a reflux condenser, and the reaction was heated to reflux (150 °C) for 7 h. The reaction mixture was then cooled to room temperature and precipitated into stirring acetone. The white precipitate was washed several times with acetone and then dried in vacuo for several hours. HDPE yield = 95%, PNB-b-PCO yield = 94%

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# Chapter 5

# Synthesis of a Photodegradable Polybutadiene using Ring-Opening Metathesis Polymerization

# Abstract

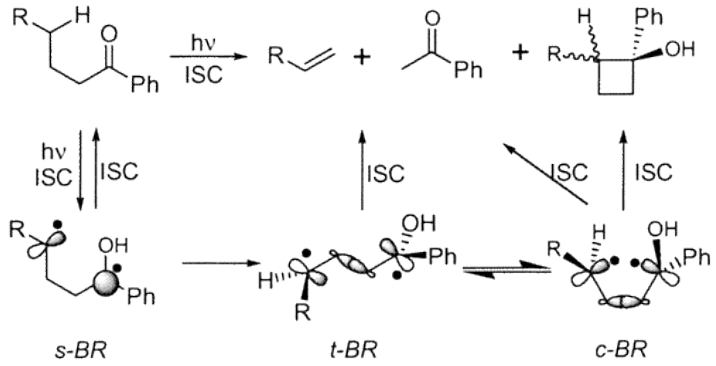
Photodegradable polymers have been well studied for their use as photoresists and environmentally friendly materials. Using ring-opening metathesis polymerization, we have successfully synthesized a photodegradable polybutadiene. This was accomplished by copolymerizing cyclooctadiene with an aryl-ketone fuctionalized cycloheptene. A two-stage polymerization method was used to overcome the limitations encountered by incorporating a low strain monomer into the ROMP of cyclooctadiene.

## 5.1. Introduction

Photodegrable polymers have been the subject of numerous investigations because of their potential applications as photoresists and environmentally friendly materials.[1] The incorporation of oxygen-containing moietys, such as hydroperoxide, peroxide, and various carbonyl groups into polymers to form photodegradable materials has been widely studied. One of the most useful methods of synthesizing photodegradable polymers is to incorporate carbonyl groups into copolymers, which may undergo Norrish type II reaction.[2,3]

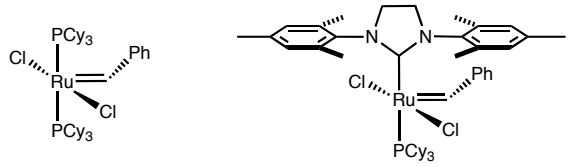
Norrish type II reactions of aryl ketones involves γ-hydrogen abstraction by the n,π* triplet excited state of the γ-carbonyl group. Products are derived from fragmentation and/or cyclization of the ensuing 1,4-biradical, namely, acetophenone enol/alkene and/or cyclobutanols (Scheme 5.1).[4,5]

**Scheme 5.1.** Mechanism of Norrish type II reaction.




In recent years, ring-opening metathesis polymerization (ROMP) has emerged as a powerful tool for polymer chemists.[6-8] The development of late transition-metal olefin metathesis catalysts **1**[9] and **2**[10], shown in Figure 5.1, has allowed the polymerization of a wide range of monomers with complex architectures and functionalities. Furthermore the

N-heterocyclic containing catalyst **2** displays a high level of activity in ROMP when compared to other ruthenium catalysts.[7,11] As a result of the high activity of **2**, secondary metathesis, such as intermolecular and intramolecular chain-transfer (back-biting), are much more facile. This characteristic trait of **2** has been exploited to polymerize a number of monomer in the presence of a symmetrical chain transfer agent to form telechelic polymers.[12-14] Also the functional group tolerance of **2**, which allows the polymerization of a wide range of functionalized monomers, may be exploited to copolymerize several monomers. Herein we report the synthesis of copolymers containing an a random distribution of polybutadiene and an aryl ketone, which may undergo Norrish type II reaction, yielding a photodegradable polybutadiene.




**1** **2**

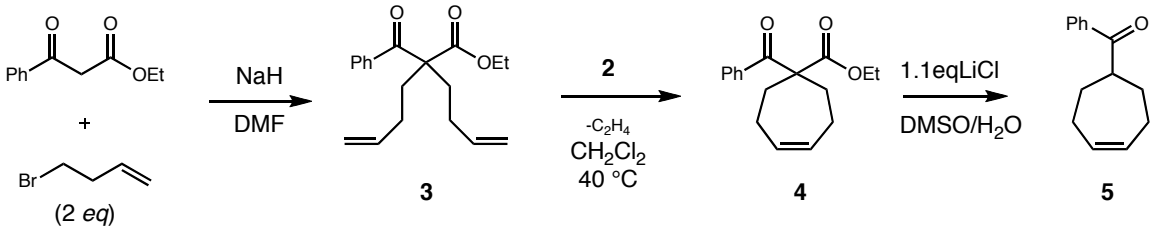
**Figure 5.1.** Ruthenium olefin metathesis catalysts.

## 5.2. Results and Discussion

### 5.2.1. Monomer Design and Synthesis

Synthesis of the Norrish monomer was conducted as outlined in Scheme 5.2. Substrate **3** was synthesized from the simple double alkylation of ethyl benzoate with 4-bromo-butene. After careful purification to remove any remaining terminal olefins, RCM was performed on **3** at 45 °C with catalyst **2** in $CH_2Cl_2$, followed by deethoxycarboxylation to form aryl-ketone containing monomer **5**.

**Scheme 5.2.** Synthesis of aryl ketone containing monomer **5**.




## 5.2.2. ROMP of 5 with 2

Since monomer **5** has a low strain, polymerizations were conducted in the absence of solvent and at a temperature of 55 °C Scheme 5.3). The initial results from the homopolymerization of **5** were unfavorable. Furthermore, the molecular weight and PDI of **6** were much higher than expected (Entry 1, Table 5.1).

**Scheme 5.3.** ROMP of **5** with **2**.

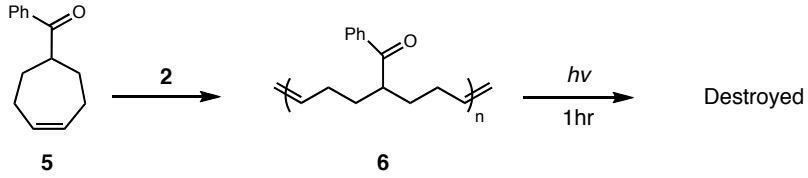



**Table 5.1.** Synthesis of photodegradable polymers containing an aryl ketone.

| Entry | $[\mathbf{5}]_0/\mathbf{2}$ | Polymer | $M_n$ ($\times 10^3$) | PDI | Yield (%) |
|---|---|---|---|---|---|
| **1** | 100 | **6** | 4.4 | 1.5 | 18 |
| **2** | 100 | **6** | 28 | 1.2 | 52 |
| **3**[a] | 5 | **7** | 35 | 1.3 | 95 |
| **4**[b] | 5 | **7** | 10 | 1.4 | 93 |
| **5**[c] | 5 | **7** | 4.3 | 1.9 | 98 |

Polymerization was conducted in the absence of solvent at 55 °C and a $[M]_0/\mathbf{2}$ = 100:1. [a]Conducted with a $[COD]_0/\mathbf{2}$ = 500:1. [b]Conducted similarly to 3 except $[COD]_0/\mathbf{2}$ = 100:1. [c]Characterized post UV irradiation.

Upon closer inspection of monomer purity, we observed trace amounts of terminal olefin that had been carried through the monomer synthesis. As a result, the synthesis of monomer **5** was repeated, and more attention was directed toward monomer purification. Once pure monomer **5,** free from terminal olefin, was obtained, ROMP was performed under similar conditions (Entry 2, Table 5.1). The yields were still not completely favorable, but were better than initially observed. We believe this to be a result of the low strain and inactivity of the monomer towards ROMP.

To test the photodegradablity of the homopolymer **6**, it was first dissolved as a 1.0 M solution in $CH_2Cl_2$. The solution was subsequently transferred to a quartz cuvette and irradiated with UV light. When the reaction was complete, the polymer solution was precipitated into MeOH. The absence of any precipitate indicated that the polymer had photodegraded. $^1$H NMR analysis of the products showed various small molecular weight products.

### 5.2.3. ROMP of 5 with COD

Incorporation of the photodegradable monomer into an existing polymer was attempted to determine if a larger chain could photodegrad into smaller chains. Initial studies began with the copolymerization of monomer **5** with cyclooctadiene (COD) to form polymer **7**. Both monomers were mixed together ($[COD]_0/\mathbf{2}$ = 100:1 and $[\mathbf{5}]_0/\mathbf{2}$ = 5:1) and dissolved in $CH_2Cl_2$ (2.0 M). Catalyst **2** was then added to the stirring mixture, resulting in immediate gellation of the reaction. After 12 h, the reaction was quenched with ethyl vinyl ether. The results are depicted in Entry 3 of Table 5.1. Unfortunately monomer incorporation was difficult to observed by $^1$H NMR. As a result, the polymer was subjected to UV irradiation to determine if **5** had incorporated. However after UV irradiation and subsequent precipitation, the polymer was still observed and the molecular

weight had not changed. The results of this experiment are not surprising considering the low ring strain of **5**. This low ring-strain makes **5** a poor candidate for ROMP.

Although the previous results were not favorable, incorporation of **5** was still possible. Recently, Macosko et al. was able to synthesize high molecular weight telechelic polybutadienes using ROMP via a two-stage polymerization process.[12] This two-stage polymerization process involved the formation of low molecular weight oligomers by adding the entire quantity of chain transfer agent and a small portion of the COD that was to be used to copolymerize in the presence of **2**. After all the reactant had been consumed, the remaining COD was added. This two-stage protocol was adapted for our purposed in order to incorporate monomer **5** into the polybutadiene chain. First, **5** was added to a vial and placed in 55 °C oil bath. Next, catalyst **2** was quickly added ($[\mathbf{5}]_0/\mathbf{2}$ = 100:1) and the reaction gelled within a few minutes. A small portion of COD (COD/**5** = 5:1) was then added and allowed to stir until all reactants had been consumed. Finally the remaining **2** and COD were added and allowed to react for 7 h, after which the reaction was quenched with ethyl vinyl ether. These results are depicted in Entry 4 of Table 5.1.

The polymer was then subjected to UV irradiation and then subsequently precipitated into methanol. Upon precipitation, no precipitate was observed; however the solution did become cloudy, indicating that photoscission had occurred. GPC analysis shown in Figure 5.2 depicts polymer **7** before (solid line) and after UV irradiation (dashed line). An obvious shift toward lower molecular weight polymer is observed, as well as a broadening of the peaks.

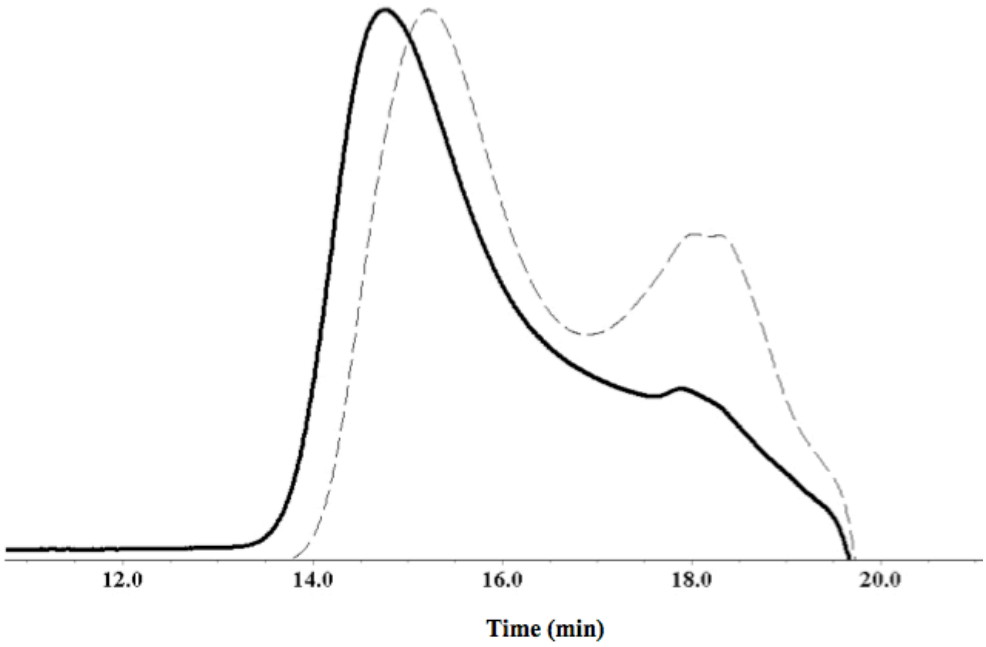



**Figure 5.2.** GPC traces of polymer 7 (solid line) before and after photoirradiation (dashed line).

Although there is decrease in molecular weight and increase in PDI, complete photoscission may not have occurred. This may be due to the short irradiation time or incomplete monomer incorporation. Further studies with different monomer and longer irradiation times should be conducted.

## 5.3. Conclusions

We have successfully synthesized a photodegradable polybutadiene using ROMP. By copolymerizing an aryl ketone into the backbone of a polybutadiene chain, photoscission was able to occur under UV irradiation. Furthermore, the difficulties in incorporating low strain monomer **5** using ROMP were overcome by using a two-stage polymerization method.

## 5.4. Experimental Section

**General Methods.** NMR spectra were recorded on a Varian Mercury 300 (300 MHz for $^{1}H$ and 74.5 MHz for $^{13}C$). All NMR spectra were recorded in $CDCl_3$, referenced to residual proteo species. Gel permeation chromatography (GPC) was carried out in THF on two PLgel 10 μm mixed-B LS columns (Polymer Laboratories) connected in series with a DAWN EOS multiangle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer (both from Wyatt Technology). No calibration standards were used, and dn/dc values were obtained for each injection by assuming 100% mass elution from the columns. UV irradiation was performed with a water-cooled Hanovia type L, 450-watt lamp.

**Materials.** $CH_2Cl_2$ were dried by passage through solvent purification columns. All other chemicals and solvents were obtained from Aldrich and used as received. Ruthenium catalyst $(IMesH_2)$-$(PCy_3)(Cl)_2RuCHPh$ (**2**)[10] was synthesized according to a literature procedure.

**ethyl 2-benzoyl-2-(but-3-enyl)hex-5-enoate (3).** A 2-neck 250 mL round bottom flask fitted with a reflux condensor was charged with ethyl benzoylacetate (52 mmol), DMF (52 mL) and a stirbar while under argon. The reaction vessel was placed in an ice/$H_2O$ bath and allowed to cool for 20 min. NaH (60 mmol) was then added to the stirring solution. The reaction was allowed to warm to room temperature and 4-bromo-butene (60 mmol) was added. The reaction vessel was then placed in an 80 °C oil bath and allowed to react until complete by TLC (12 h). The reaction was then removed from the oil bath and allowed to cool to room temperature. Once cooled, a second equivalent of NaH (60 mmol) was added over the course of 20 min and allowed to stir for 1 h, which

was then followed by another slow addition of 4-bromobutene (60 mmol). The reaction vessel was again place into the 80 °C oil bath and allowed to react for 36 h, after which the reaction was allowed to cool to room temperature. The reaction mixture was then quenched with $NH_4^+Cl^-$ (aq) and extracted three times with diethyl ether. The organic layer was given a final wash with brine and dried over $MgSO_4$. The organic layer was then concentrated by rotovap. Purification was performed by column chromatography with silica gel and $CH_2Cl_2$/hexanes (60/40) as the eluent. A clear oil was obtained in 70% yield. $^1$H NMR (300 MHz, $CDCl_3$): 7.83 (Ar d, 2H), 7.50 (Ar m, 1H), 7.42 (Ar m, 2H), 5.74 (dt, 2H), 4.98 (m, 4H), 4.12 (q, 2H), 2.17 (t, 3H).

**ethyl 1-benzoylcyclohept-4-enecarboxylate (4).** A 1 L round bottom flask was charged with **3** (16.7 mmol) and a stirbar while under argon. $CH_2Cl_2$ (300 mL) was added to the reaction flask via syringe and allowed stir for 5 min at room temperature. Catalyst **2** (5 mol%) was added to the flask as powder and capped with a septa. The reaction vessel was then fitted with an exit bubbler and placed in a 45 °C oil bath. The reaction was complete after 2 h and was subsequently concentrated by rotovap. Purification was performed by column chromatography with silica gel and $CH_2Cl_2$/hexanes (50/50) as the eluent. A clear oil was obtained in 90% yield. . $^1$H NMR (300 MHz, $CDCl_3$): 7.81 (Ar d, 2H), 7.49 (Ar m, 1H), 7.41 (Ar m, 2H), 5.65 (t, 2H), 4.11 (q, 2H), 2.42 (m, 4H), 2.29 (m, 4H), 1.05 (t, 3H). HRMS: calculated 272.1412; found 272.1418.

**cyclohept-4-enyl(phenyl)methanone (5).** A 2-neck 10 mL round bottom flask fitted with a reflux condensor was charged with **4** (1.83 mmol), DMSO (3.68 mL), and a stirbar. The reaction mixture was allowed to dissolve, $H_2O$ (4.0 mmol) and LiCl (2.02 mmol) were subsequently added to the reaction mixture. The reaction vessel was then

heated to 180 °C. After 24 h, the reaction was cooled to room temperture and extracted five times with hexanes. The organic layer was then washed once with water, once with brine and dried over $MgSO_4$. The dried organic layer was then filtered and concentrated by rotovap. Purification was performed by column chromatography with silica gel and EtOAc/hexanes (5/95) as the eluent. A clear oil was obtained in 20% yield. $^1$H NMR (300 MHz, $CDCl_3$): 7.96 (Ar d, 2H), 7.56 (Ar m, 1H), 7.47 (Ar m, 2H), 5.82 (q, 2H), 3.53 (quin, 1H), 2.36 (m, 2H), 2.20 (m, 2H), 1.97 (m, 2H), 1.69 (m, 2H).HRMS: calculated 200.1201; found 200.1199.

**Homopolymerization of 5 (6)**. A 4 mL vial with a septum cap was charged with **5** (0.34 mmol) and a stirbar under a flow of argon. 100 μL of a solution of catalyst **2** (58.0 mg/ml in $CH_2Cl_2$) was quickly added to the vigorously stirring monomer solution via syringe while under argon. The reaction vial was then placed in a 55 °C aluminum heating block stirring under argon for 6 h. The reaction mixture was then dissolved in 1 mL $CH_2Cl_2$ and precipitated into 50 mL of ice-cold vigorously stirring MeOH. The brown precipitate was washed several times with MeOH and dried in vacuo overnight. A tacky brown solid was obtained in 52% yield. $^1$H NMR (300 MHz, $CDCl_3$): 7.88 (Ar br d, 2H), 7.49 (Ar br t, 1H), 7.40 (Ar br m, 2H), 5.22 (br s, 2H), 3.68 (br m, 1H), 1.84-1.22 (br m, 8H)

**Copolymerization of 5 with COD and 2 (7).** A 4 mL vial with a septum cap was charged with **5** (0.34 mmol), COD (1.85 mmol) and a stirbar under a flow of argon. A 100 μL aliquot of a solution of catalyst **2** (30.0 mg/ml in $CH_2Cl_2$) was quickly added to the vigorously stirring monomer solution via syringe while under argon. The reaction vial was then placed in a 55 °C aluminum heating block stirring under argon for 6 h. The

reaction mixture was then quenched with ethyl vinyl ether (0.2 mL) and dissolved in 1 mL $CH_2Cl_2$. The viscous solution was precipitated into 50 mL of ice-cold vigorously stirring MeOH. The precipitate was washed several times with MeOH and dried in vacuo overnight. A tacky light brown solid was obtained in 95% yield. $^1$H NMR (300 MHz, $CDCl_3$): 5.42 (br s, 2H), 2.04 (br s, 4H).

**"Two-stage method"Copolymerization of 5 with COD and 2 (7).** A 4 mL vial with a septum cap was charged with **5** (0.1 mmol) was added to a vial and placed in 55 °C oil bath. Next catalyst **5** (0.001 mmol) was quickly added and the reaction gelled within a few minutes. A small portion of COD (0.5 mmol) was then added and allowed to stir until all reactants had been consumed. Finally the remaining **2** (0.018 mmol) and COD (1.3 mmol) were added and allowed to react for 7 h, after which the reaction was quenched with ethyl vinyl ether (0.2 mL). A tacky light brown solid was obtained in 93% yield. $^1$H NMR (300 MHz, $CDCl_3$): 5.42 (br s, 2H), 2.04 (br s, 4H).

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# Appendix A

## Synthesis and Characterization of Stereoregular Ethylene-Vinyl Alcohol Copolymers made by Ring-Opening Metathesis Polymerization

Portions of this chapter have previously appeared as: Scherman, O. A.; Walker, R.: Grubbs R. H. *Macromolecules* **2005**, *38*, 9009–9014.

# Abstract

The syntheses of regioregular as well as stereoregular ethylene vinyl alcohol (EVOH) copolymers by ring-opening metathesis polymerization (ROMP) with ruthenium catalysts are reported. Symmetric cyclooctene-diol monomers were protected as acetates, carbonates, or acetonides to temporarily increase ring strain as well as impart solubility to the monomer. Polymer molecular weights could be easily controlled by either varying the monomer-to-catalyst ratio or by the addition of a chain transfer agent. Hydrogenation and subsequent deprotection of the ROMP polymers afforded the EVOH materials in high yields and the structures were confirmed by $^{1}$H NMR and $^{13}$C NMR spectroscopies. Thermal properties of the corresponding EVOH copolymers are reported and suggest that differences in diol stereochemistry significantly affect the polymer morphology.

## A.1 Introduction

Ethylene vinyl alcohol (EVOH) copolymers have found commercial utility in food packaging as well as in the biomedical and pharmaceutical industries as a result of their excellent barrier properties toward gases and hydrocarbons.[1-6] The structures of EVOH copolymers affect the materials' ability to limit gas or hydrocarbon diffusion through a membrane.[7,8] The current commercial route to these materials involves the free-radical polymerization of vinyl acetate and ethylene monomers followed by saponification.[9] As a result of the free-radical polymerization, the overall architecture is impossible to control, and EVOH produced in this fashion contains a degree of branching similar to low-density polyethylene (LDPE).[6,10] Furthermore, while the relative amount of vinyl alcohol can be controlled in the feed ratio of the two monomers, exact placement of alcohol functionality along the polymer backbone cannot be controlled.[8] This has resulted in a poor understanding of structure—property relationships in EVOH.

It has been demonstrated that the incorporation of polar functional groups pendent from a linear polymer backbone can be readily accomplished through ring-opening metathesis polymerization (ROMP) with functional group-tolerant late transition metal catalysts.[8,9,11-15] Polar, substituted cyclic olefins such as alcohol-, ketone-, or even halogen-substituted cyclooctenes undergo ROMP to form absolutely linear polymer bearing pendent functional groups.[11,16] The asymmetric monomer, however, prevents absolute control over the placement of the polar group along the polymer backbone. Head-to-head (HH), head-to-tail (HT), and tail-to-tail (TT) couplings are all possible, leading to a regiorandom distribution of functionality.[11] This problem has been addressed

by two different olefin metathesis polymerization techniques, displayed in Figure A.1.[8,10,17]

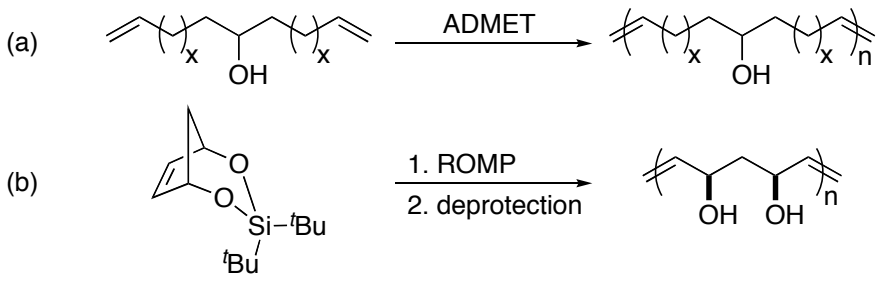



**Figure A.1.** (a) ADMET of a symmetric alcohol-containing monomer to produce a regioregular EVOH copolymer. (b) ROMP of a temporarily strained, symmetric monomer to produce a regioregular EVOH material with a higher vinyl alcohol content.

Valenti et al. reported the acyclic diene metathesis polymerization (ADMET) of a symmetric alcohol-containing monomer (Figure A.1a).[10] The molecular weights, however, are restricted to < 3 x $10^4$ g/mol when employing ADMET. Moreover, the relatively high hydrocarbon to alcohol ratio limits the overall barrier properties of these EVOH materials.[5,10] More recently, we illustrated that ROMP of a symmetric monomer could be carried out in high yield to afford a linear EVOH type material (Figure A.1b) with controlled placement of the alcohol functionality, molecular weight control over a wide range, and a much higher incorporation of alcohol groups.[8] Functional group-tolerant ruthenium catalysts **1**[18] and **2**[19] (Figure A.2) were necessary to carry out the ROMP of the polar monomer.

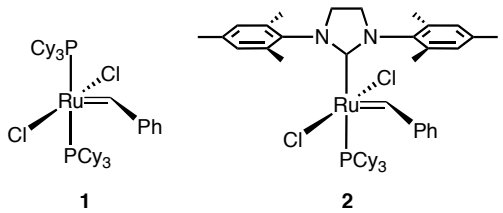
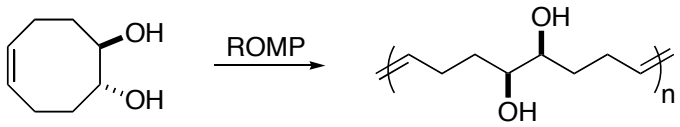



**Figure A.2.** Ruthenium olefin metathesis catalysts (Cy=cyclohexyl).

While ROMP is capable of producing linear high molecular weight polymer, the amount of ring strain inherent in the cyclic olefin monomer plays a critical role in the polymerizability of each monomer.[20,21] The addition of substituents to cyclic olefins often serves to lower the ring strain and can render a monomer non-polymerizable via ROMP.[20] Therefore, we introduced a method to temporarily increase ring strain through carefully chosen protecting groups while keeping the monomers symmetric to avoid issues of regiorandom monomer addition.[8] While ROMP of symmetric monomers resolves the problems of branching and regiocontrol of functional groups, the effect of stereochemistry between neighboring alcohols has yet to be addressed. We would like to report our attempts to separately gauge the effect of relative stereocontrol on material properties. This will allow for more detailed structure—property studies with respect to barrier properties of architecture-controlled EVOH materials.

**Scheme A.1.** ROMP of trans-diol **3**.




**3**

The direct ROMP of cyclooctene-*trans*-diol (**3**) was achieved by the addition of ruthenium catalyst **1** to monomer **3** as depicted in Scheme A.1.[1] Unfortunately, this polymerization could only be carried out in neat monomer, as solubility of the unprotected diol b in common organic solvents suitable for ROMP was minimal.[1] Moreover, the molecular weight of the resulting ROMP polymer was limited to *ca.* 2 x $10^4$ g/mol due to diffusion in the highly viscous polymerization mixture.[1-3] All attempts to ROMP cyclooctene-*cis*-diol (**4**) failed as **4** is a crystalline solid with a melting point

well above the temperature range useful for catalysts **1** and **2**. Again, the lack of solubility of **4** in organic solvents suitable for ROMP prevented solution polymerization of the unprotected diol monomer. In order to produce perfectly linear EVOH materials that differed only in the relative stereochemistry between the neighboring 1,2-diols along the polymer backbone, protection of the diols was used to enhance the solubility of monomers **3** and **4**.

## A.2 Results and Discussion

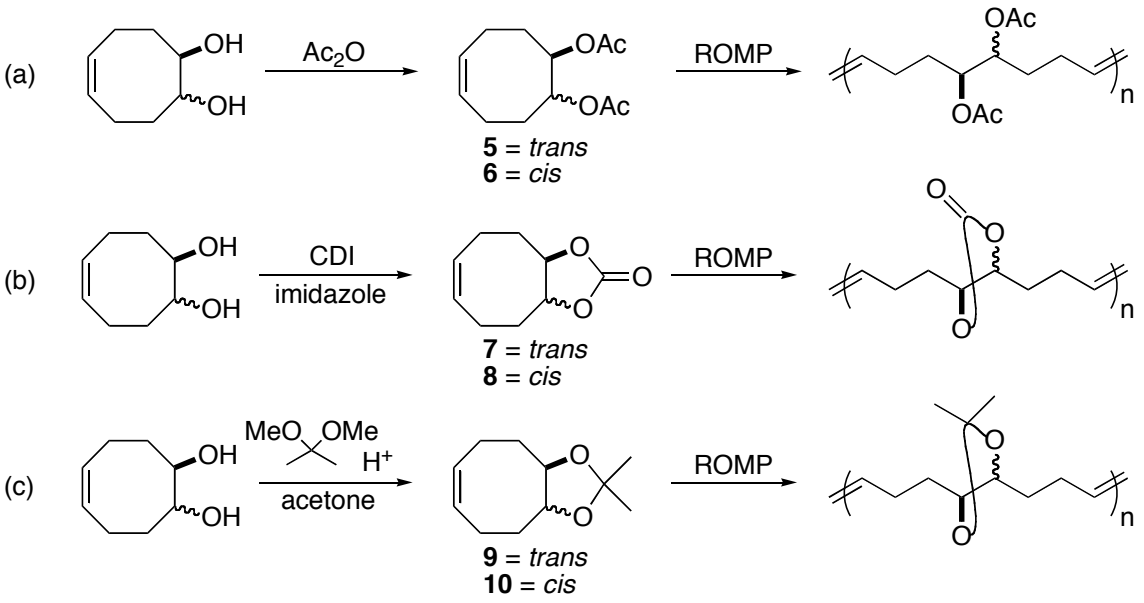
### A-2.1. Monomer design and synthesis

In order to compare the effect that relative stereochemistry has on EVOH material properties, two monomers differing only in diol stereochemistry were selected: cyclooctene-*trans*-diol **3** and cyclooctene-*cis*-diol **4**. Due to the limited solubility of the diols in organic solvents suitable for ROMP, the free alcohols were protected prior to polymerization. Considerations of monomer symmetry as well as ring stain were taken into account so that the resulting ROMP polymers would retain regioregular placement of alcohol groups along the polymer backbone and that high yields could be achieved.

Acetate protection of **3** and **4** afforded both the *trans* and *cis* monomers **5** and **6**, respectively (Scheme A.2a). Both of these monomers underwent ROMP to yield the acetate-protected polymers, although higher monomer concentrations were necessary to achieve reasonable yields of polymer due to a decrease in ring strain relative to unsubstituted cyclooctene. Both ROMP polymers, however, formed gels and did not dissolve in common organic solvents. Therefore, another protection strategy was employed. In an attempt to increase polymer yields at low monomer concentrations,

carbonate protection was chosen to make bicyclic (8,5-fused) monomers with higher ring strain that would retain symmetry as illustrated in Scheme A.2. While both the *trans*-carbonate **7** and *cis*-carbonate **8** did undergo ROMP, the resulting ROMP polymers were intractable in $CH_2Cl_2$, toluene, and THF and were only mildly soluble in DMF. A different bicyclic protection was carried out to form the *trans*-acetonide **9** and *cis*-acetonide **10** as shown in Scheme A.2c. The ROMP of these monomers produced polymers that remained soluble in common organic solvents and allowed for subsequent hydrogenation and deprotection steps to arrive at EVOH copolymers differing only in relative stereochemistry between neighboring alcohol functionalities.

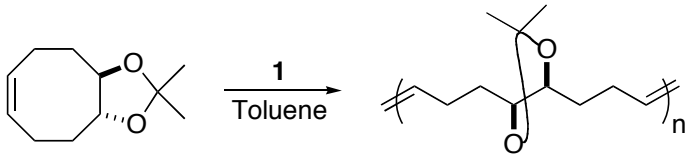
**Scheme A.2.** Protection strategies for *trans*- and *cis*-cyclooctene diol monomers.



## A-2.2. ROMP of acetonide monomers with catalyst 1

It has been previously demonstrated that ROMP of highly strained cyclic olefins with catalyst **1** occurs in a controlled and living fashion.[22,23] Therefore, ROMP of monomers **9** and **10** was expected to yield polymers in which the molecular weight could be controlled by setting the monomer to catalyst ratio, $[M]_0/[\mathbf{1}]$.

**Scheme A.3.** ROMP of **9** with catalyst **1** yields acetonide-protected polymer **11**.




**9** **11**

ROMP polymer **11** forms upon introduction of catalyst **1** to a solution of *trans* monomer **9**, as shown in Scheme A.3. Product yield, however, greatly depends on the monomer concentration, as shown in Figure A.3a. Polymer yields are poor when $[M]_0 <$ **2** M, although yields are reasonable and MW control is dictated by M/**1** ratio when the polymerization is carried out at 3 or 4 M (Figure A.3b). The low yields of polymer produced from polymerizations below $[M]_0 = 2$ M are likely due to low ring strain as a result of the *trans*-8,5-ring fusion in **9**.[20]

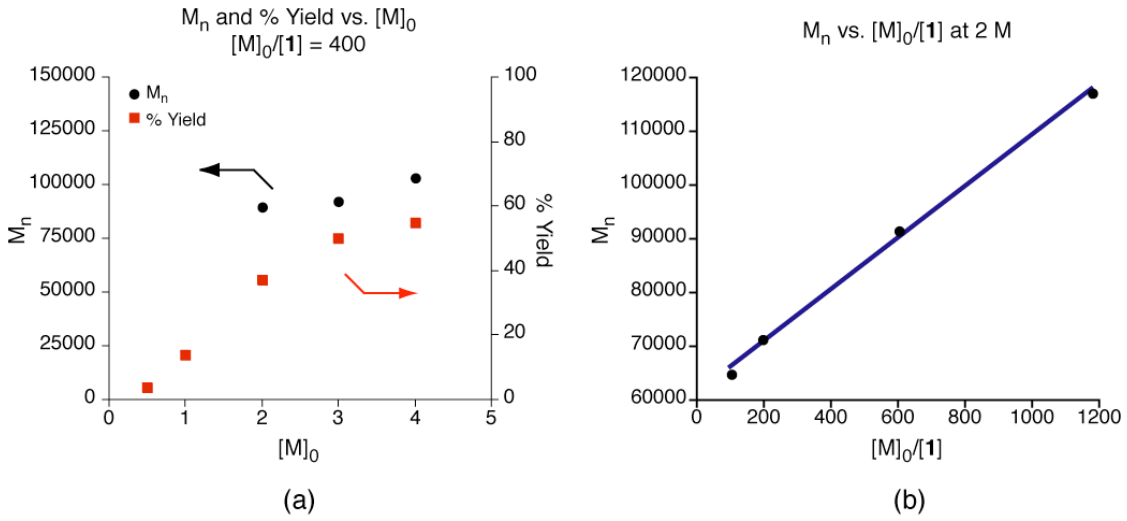
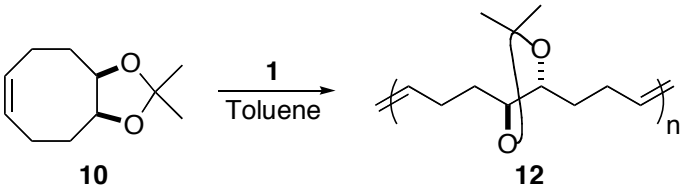



**Figure A.3.** (a) ROMP of **9** with catalyst **1** at 55 °C, $[M]_0/[1]=400$ at varying $[M]_0$. (b) Molecular weight control is achieved by varying $[M]_0/[1]$ ratio.

This has been observed previously with *trans*-8,6-ring fusions by Miller, et al.[24] Miller noted that the ring-closing metathesis (RCM) of acyclic dienes to produce *trans*-8,6-fused bicyclic compounds afforded higher yields than for the corresponding RCM of *cis*-8,6-fused compounds.[24] This suggests that *trans*-8,5 fused materials like **9** might also prefer the ring-closed form while the opposite might be true for *cis*-8,5 fused materials such as **10**. In fact, this trend holds for the ROMP of monomers **9** and **10**, as the ability for these two monomers to undergo ROMP is markedly different.

As illustrated in Scheme A.4, when catalyst **1** is introduced to a solution of monomer **10** ROMP polymer **12** is formed in high yield at much lower initial monomer concentrations. Reasonable yields (50-60%) can be achieved at $[M]_0$ = 0.25 M and yields exceed 75% at $[M]_0$ = 1 M. Figure A.4 shows excellent molecular weight control over a wide range for the ROMP of **10** with catalyst **1** at 1 M. As indicated by the data in Table A.1, $M_n$ is directly related to the [monomer]/[catalyst] ratio in a linear manner, and the polymerizations reach high yields within 24 h with relatively narrow PDIs.

**Scheme A.4.** ROMP of **10** with catalyst **1** yields acetonide-protected polymer **12**.



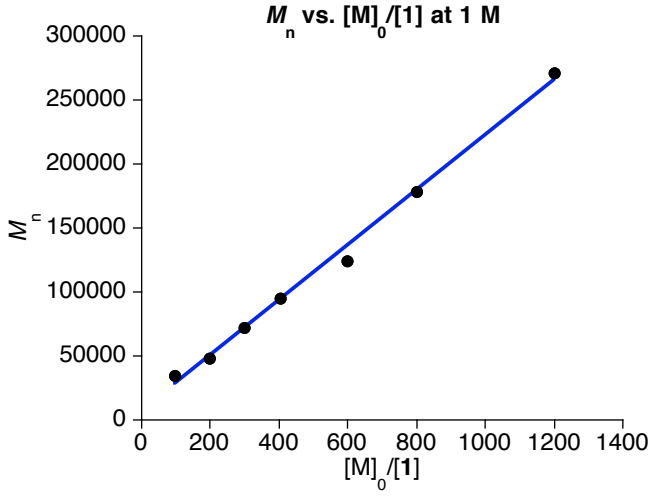




**Figure A.4.** ROMP of **10** carried out at 1 M and 55 °C with catalyst **1** to produce polymer **12**; molecular weight control is achieved by varying $[M]_0/[\mathbf{1}]$ ratio.

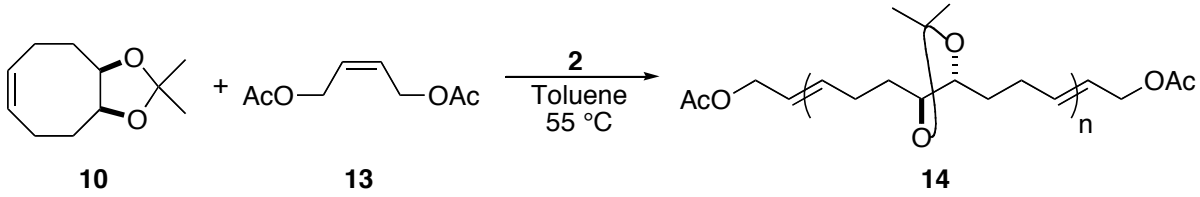
**Table A.1.** ROMP of **10** at $[M]_0$ = 1 M with **1** at 55 °C for 24 h.

| [**10**]/[**1**] | $M_n$ | PDI | % Yield |
|---|---|---|---|
| 100 | 34400 | 1.3 | 79 |
| 200 | 47700 | 1.7 | 81 |
| 300 | 72400 | 1.6 | 78 |
| 400 | 94700 | 1.6 | 80 |
| 600 | 124000 | 1.5 | 76 |
| 800 | 178000 | 1.5 | 72 |
| 1200 | 271000 | 1.3 | 73 |

### A-2.3. ROMP of acetonide monomers with catalyst 2.

While controlling the polymer molecular weight by adjusting the monomer to catalyst ratio is straightforward, the amount of catalyst employed directly affects the polymer produced. In an effort to reduce the amount of catalyst necessary to carry out the ROMP of monomers **9** and **10**, the use of highly active catalyst **2** was investigated.[12] It has been shown previously that the use of catalyst **2** with an acyclic chain transfer agent (CTA) affords telechelic polymers of controlled molecular weight.[8,25-28] The addition of a CTA such as **13** to the ROMP of **10** yielded telechelic polymer **14** as depicted in Scheme A.5.

**Scheme A.5.** ROMP of **10** with catalyst **2** in the presence of chain transfer agent **13** to yield telechelic acetonide-protected polymer **14**.




**10** **13** **14**

Polymers **12** and **14** differ only by the functional groups at the termini of the latter. Moreover, the molecular weight of **14** can be easily controlled by the ratio of monomer to CTA, [**10**]/[**13**],[8,25,26,28] thereby reducing the amount of catalyst needed for polymerization and simultaneously removing effect of catalyst in determining polymer molecular weight.[27]

Through the use of catalyst **2** and a CTA, much higher monomer-to-catalyst ratios can be employed allowing access to a large range of polymer molecular weights. The plot in Figure A.5 and the data in **Table A.2** show excellent molecular weight control for the ROMP of **10** with CTA **13** at 1 M with $[M]_0/[\mathbf{2}]$ ratio of 5000.

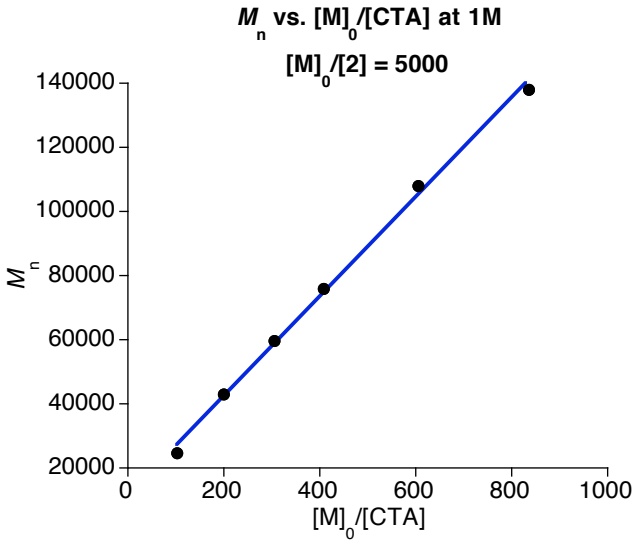



**Figure A.5.** ROMP of **10** carried out at 1 M and 55 °C with catalyst **1** to produce polymer **12**; molecular weight control is achieved by varying $[M]_0/[\mathbf{1}]$.

**Table A.2.** ROMP of **10** at $[M]_0$=1 M with **2** and CTA **13** at 55 °C for 24h,[**10**]/[**2**]=5000

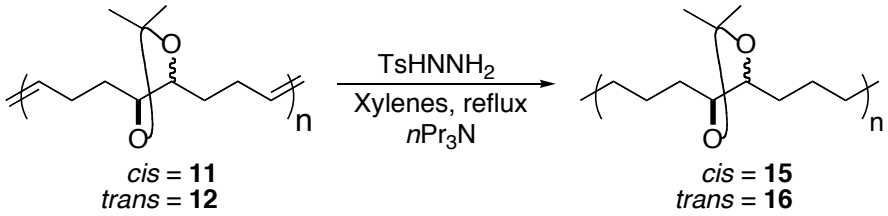
| [**10**]/[**13**] | $M_n$ | PDI | % Yield |
|---|---|---|---|
| 100 | 24500 | 1.9 | 70 |
| 200 | 4300 | 1.6 | 74 |
| 300 | 59800 | 1.6 | 74 |
| 400 | 75700 | 1.6 | 75 |
| 600 | 108000 | 1.6 | 76 |
| 800 | 138000 | 1.5 | 76 |

### A-2.4. Hydrogenation of acetonide-protected ROMP polymers.

While polymers resulting from the ROMP of monomers **5**—**8** led to gelled or intractable materials, polymers **11** and **12** were soluble in common organic solvents, allowing for mild hydrogenations to be carried out. Direct formation of diimide in situ[8,29-33] afforded complete hydrogenation of the olefins without removing the acetonide protecting group as depicted in Scheme A.6. After 5-6 h in refluxing xylenes, hydrogenation of the ROMP polymers was complete as evidenced by the lack of olefin signals in both the $^1$H and $^{13}$C NMR spectra. The hydrogenation reaction was carried out

with 1 equiv of tri-propylamine (per tosylhydrazide) in order to keep the acetonides from catalytically deprotecting with the formation of tosic acid.[8] Saturated polymers **15** and **16** remained soluble in organic solvents, allowing characterization by $^{1}H$ and $^{13}C$ NMR, GPC, as well as thermal analysis by DSC.

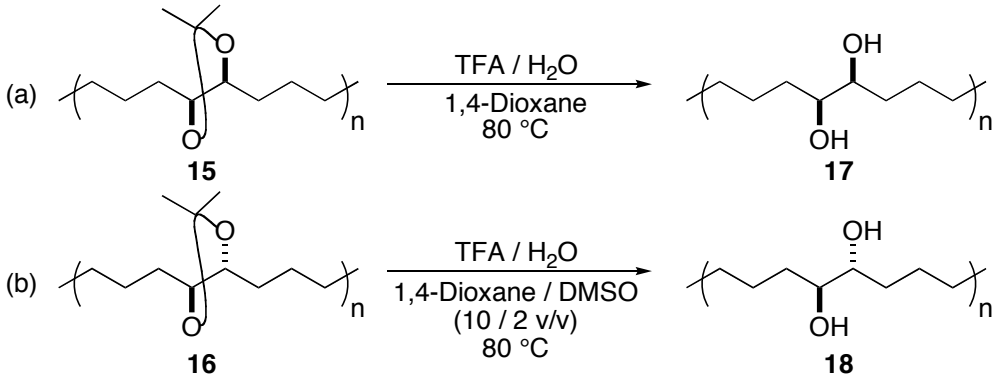
**Scheme A.6.** Hydrogenation of ROMP polymers by in situ diimide formation.




## A-2.5. Deprotection of acetonide groups.

In order to arrive at the final EVOH structure, deprotection of the acetonide groups was necessary. As shown in Scheme A.7, removal of the acetonides was accomplished by extended heating at 80 °C in 1,4-dioxane with a catalytic amount of trifluoroacetic acid (TFA) and water. This reaction proved quite challenging as polymers **15** and **16** are quite hydrophobic and displayed a very different solubilities than the hydrophilic EVOH copolymers **17** and **18**.[8] While the formation of EVOH **17** occurred readily, the transformation of **16** to **18** required 10-20% DMSO as a co-solvent in order to keep the polymer soluble throughout the entire reaction. In the absence of DMSO, the reaction resulted in incomplete deprotection due to polymer precipitation from solution.

**Scheme A.7.** Deprotection of acetonides.




## A-2.6. Thermal analysis of ROMP-, hydrogenated-, and deprotected-polymers.

Thermal analysis was carried out on polymers **11** and **12** and **15—18** by differential scanning calorimetry (DSC). Glass transition temperatures, $T_g$, as well as the relevant melting transition temperatures, $T_m$, are listed in Table A.3.

**Table A.3.** Thermal analysis data.

| Polymer | $T_g$ (°C) (onset) | $T_m$ (°C) (onset) |
|---|---|---|
| 11 | -12.4 | -- |
| 12 | -6.6 | -- |
| 15 | -14.1 | -- |
| 16 | -2.7 | -- |
| 17 | 34.4 | 111 (119, peak) |
| 18 | 50 | 157 |

Only glass transitions are observed for the amorphous acetonide-protected ROMP polymers **11** and **12**. While both $T_g$ values are sub-ambient, they differ by nearly 6 °C, suggesting that the *syn* and *anti* diols impose a slightly different packing in the solid state. This difference is even more pronounced (11.4 °C) in the hydrogenated forms, **15** and **16**.

Finally, the fully deprotected EVOH copolymers **17** and **18** show a clear difference in both the $T_g$ and $T_m$ values with a nearly 40 °C increase in the melting transition temperature between the *syn* and *anti* 1,2-diols. Moreover, the ΔH for the

melting transition observed for the *syn* 1,2-diol EVOH **17** was 21.17 J/g, while the ΔH for the *anti* 1,2-diol EVOH **18** nearly doubled, with a value of 42.12 J/g. This indicates that the *anti* stereochemical relationship between the diols along the polymer backbone allowed for more crystalline regions in the EVOH material relative to the *syn* stereochemical relationship. Previously, it has been observed that higher melting transitions in EVOH copolymers arise from higher alcohol content.[8,34] The dramatic increase in $T_m$ between **17** and **18**, however, suggests that the relative stereochemistry between the pendent alcohol groups can also have a remarkable effect on material morphology and crystalline packing of the polymer chains.

## A.3 Conclusions

The successful ROMP of symmetric cyclooctene diol monomers that differ only in the relative stereochemistry between the alcohols has been demonstrated with the functional group-tolerant ruthenium catalysts **1** and **2**. In order to obtain molecular weight control over the polymers, a protection strategy was required due to the poor solubility of cyclooctene diol in common organic solvents. Acetonide protection for the diols provided the necessary solubility as well as enhanced ring strain for the *cis* diol (**4**) in the form of a bicyclic 8,5-fused system while keeping the symmetry of the monomer. Hydrogenation and subsequent deprotection afforded regioregular EVOH copolymers with 1,2-diols along the polymer backbone differing only in a *syn* and *anti* relationship. This allowed for direct examination of the effect of relative stereochemistry on EVOH copolymer properties. Thermal analysis indicated that a mere change in the relative stereochemistry greatly affects both the glass and melting transitions of the EVOH materials without requiring an increase in overall alcohol content. The ability to modify the properties of a

material by simply imposing regularity on the structure of a polymer chain is evident. Finally, the use of ROMP with late transition metal ruthenium catalysts combined with rational monomer design has allowed us to elucidate the effects of polymer architecture on the material properties of EVOH copolymers.

## A.4 Acknowledgements

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## A.5 Experimental Section

**General Procedures.** NMR spectra were recorded on a Varian Mercury 300 (300 MHz for $^{1}H$ and 74.5 MHz for $^{13}C$). All NMR spectra were recorded in CDCl3, DMSO-$d_6$, or 1,4-dioxane-$d_8$ and referenced to residual proteo species. Gel permeation chromatography (GPC) was carried out on two PLgel 5 μm mixed-C columns (Polymer Labs) connected in series with a DAWN EOS multi angle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer (both from Wyatt Technology). No calibration standards were used, and d*n*/dc values were obtained for each injection assuming 100% mass elution from the columns. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) was carried out simultaneously on a Netzsch STA 449C under a flow of $N_2$ at a heating rate of 10 °C/min or on a Perkin Elmer Pyris1 under a flow of Helium at a heating rate of 10 °C/min.

**Materials.** Toluene and CH2Cl2 were dried by passage through solvent purification columns.[35] *cis*-1,4-Diacetoxy-2-butene (95+%) (**13**) was obtained from TCI America and degassed by an argon purge prior to use. 1,5-Cyclooctadiene (redistilled, 99+%), 9-oxabicyclo[6.1.0]non-4-ene (95%), N,N-dimethylformamide (anhydrous, 99.8%) (DMF), 1,1'-carbonyldiimidazole, p-toluene sulfonhydrazide (97%), pyridinium p-toluene sulfonate (98%), tripropylamine (99+%), 1,4-dioxane (99+%), xylenes (98.5+%), trifluoroacetic acid (99+%), acetic anhydride (99+%), and 2,2'-dimethoxypropane (98%) were obtained from Aldrich and used as received. Potassium osmate (VI) dihydrate (99%) was obtained from Strem and used as received. Dimethylsulfoxide was obtained from ACROS Organics and used as received. Imidazole (99%) was obtained from EM Science and used as received. Acetone (technical grade)

was dried over calcium sulfate and filtered prior to use as a solvent. Ruthenium catalysts $(PCy_2)(Cl)_2Ru{=}CHPh$ (**1**)[18] and $(H_2IMes)(PCy_2)(Cl)_2Ru{=}CHPh$ (**2**)[19] as well as organic compounds cyclooctene-*trans*-diol (**3**),[36] cyclooctene-*cis*-diol (**4**),[37] cyclooctene-*trans*-diacetate (**5**),[38,39] cyclooctene-*cis*-diacetate (**6**),[38,39] cyclooctene-*trans*-carbonate (**7**),[38] cyclooctene-*cis*-carbonate (**8**),[38] cyclooctene-*trans*-acetonide (**9**),[40] and cyclooctene-*cis*-acetonide (**10**)[41] were all synthesized according to literature procedures.

**Polymerization procedure for acetonide-protected monomers with catalyst 1.** In a typical experiment, a small vial was charged with 0.185 g (1.0 mmol) of monomer **10** and a stirbar. Under an argon atmosphere, 0.6 mL of degassed toluene was added via syringe. In a separate vial, a 21.2 mg/mL catalyst **1** solution in toluene was prepared. 0.4 mL of the catalyst solution was then added to the monomer solution via syringe under argon. The reaction vial was placed in a 55 °C aluminum heating block stirring under argon for 24 h. The reaction mixture was then quenched with 0.1 mL ethyl vinyl ether and then dissolved in 1 mL $CH_2Cl_2$ and precipitated into 50 mL of stirring MeOH. A light brown ppt. was washed several times with MeOH and dried in vacuo overnight; yield (79%). See Tables for molecular weight data. $^1$H NMR (300 MHz, $CDCl_3$): 5.5 trans 5.4 cis (two br s, 2H), 4.05 (br s, 2H), 1.95–2.35 (m, 4H), 1.3–1.65 (m, 10H). $^{13}$C NMR (75 MHz, $CDCl_3$): 130.2, 129.8, 107.6, 77.5, 30.1, 29.9, 29.4, 29.0, 26.4, 24.2.

**Polymerization procedure for acetonide-protected monomers with catalyst 2 and CTA 13.** In a typical experiment, a small vial was charged with 0.185 g (1.0 mmol) of monomer **10** and a stirbar. Under an argon atmosphere, 0.8 mL of a 2.2 mg/mL solution of **13** in toluene was added. Next 0.2 mL of a 0.9 mg/mL solution of catalyst **2** in toluene was added via syringe. The reaction vial was placed in a 55 °C aluminum heating

block stirring under argon for 24 h. The reaction mixture was then dissolved in 1 mL $CH_2Cl_2$ and precipitated into 50 mL of stirring MeOH. The white precipitate was washed several times with MeOH and dried in vacuo overnight; yield (75%). See Tables for molecular weight data. $^1$H NMR (300 MHz, $CDCl_3$): 5.5 *trans* 5.4 *cis* (two br s, 2H), 4.05 (br s, 2H), 1.95–2.35 (m, 4H), 1.3–1.65 (m, 10H). $^{13}$C NMR (75 MHz, CDCl3): 130.1, 129.7, 107.5, 77.6, 30.1, 29.9, 29.4, 28.9, 26.3, 24.2.

**Hydrogenation procedure for acetonide-protected polymers.** In a typical experiment, an oven-dried 500 mL round bottom flask was charged with a stirbar, 1.0 g of polymer **11**, 6.83 g of tosylhydrazide (35.6 mmol, 6.5 equiv per double bond), 7.3 mL tri-propylamine (37.6 mmol, 1 equiv per tosylhydrazide), 125 mL of xylenes, and a trace of BHT. The mixture was degassed by pulling high vacuum on the solution for about 45 s. Under an argon atmosphere, a flask was fitted with a reflux condenser. The reaction was heated to reflux for 7 h. It was then cooled to room temperature and then precipitated into 700 mL of stirring ice-cold stirring MeOH. The white precipitate was washed several times with MeOH and then dried in vacuo overnight; yield 1.01 g (99%). $^1$H NMR (300 MHz, $CDCl_3$): 3.58 (br s, 2H), 1.25–1.6 (m, 18 H). $^{13}$C NMR (75 MHz, $CDCl_3$): 107.9, 81.2, 33.3, 30.0, 27.7, 26.5.

**Deprotection of 15.** In a typical experiment, a 25 mL round bottom flask was charged with a stirbar and 0.25 g polymer. The polymer was then dissolved in 10 mL of 1,4-dioxane. A reflux condenser was attached to the flask and the reaction was stirred at 80 °C for 10 min under argon. 1 mL of $H_2O$ and 1 mL of TFA were added via syringe and the reaction was allowed to stir at 80 °C under argon. An additional 2.5 mL of $H_2O$ was added to the reaction over the course of 72 h, after which the reaction was allowed to

cool to room temperature and precipitated into 200 mL of acetone stirring at room temperature. A fluffy white solid was obtained through several centrifugation, decant, rinse cycles and dried under vacuum overnight; yield 0.19 g (99%). $^{1}$H NMR (300 MHz, DMSO-$d_6$, 85 °C): 3.55 (br s, 2H), 1.22–1.62 (br m, 12H). $^{13}$C NMR (75 MHz, DMSO-$d_6$, 85 °C): 76.0, 32.9, 29.2, 25.4.

**Deprotection of 16.** In a typical experiment, a 25 mL round bottom was charged with a stirbar and 255.9 mg of polymer. It was first dissolved in 8 mL of 1,4-dioxane and then under an argon atmosphere 1 mL of DMSO was slowly added to the solution over the course of 30 min. A reflux condenser was attached and the reaction was heated to 80 °C for 2 h. Next 0.2 mL of TFA was added and the reaction was stirred overnight under argon at 80 °C. After 24 h, an additional 0.2 mL of TFA and 1 mL of DMSO were added and the reaction was kept at 80 °C. After 72 h, an additional 1 mL of DMSO and 0.1 mL TFA and 0.2 mL $H_2O$ were added to the reaction. 1 mL of DMSO was also added after 96 h as well as 0.2 mL TFA. Finally, after 144 h, the reaction was stopped and precipitated into 100 mL of acetone stirring at room temperature. A whitish precipitate was obtained through several centrifugation, decant, rinse cycles and dried under vacuum overnight; yield 200.0 mg (99%). $^{1}$H NMR (300 MHz, DMSO-$d_6$, 85 °C): 3.18 (br s, 2H), 1.05–1.58 (br m, 12H).

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