

Applications of Boron in Olefin Metathesis

By

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To my parents, family, and friends

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LIST OF ABBREVIATIONS

ADMET	Acyclic diene metathesis
DSC	Differential scanning calorimetry
GC	Gas chromatography
GPC	Gel permeation chromatography
HRMS	High resolution mass spectrometry
IR	Infrared spectroscopy
MS	Mass spectrometry
NMR	Nuclear magnetic resonance
SAXS	Small Angle X-ray scattering
TFAA	Trifluoroacetic anhydride

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APPLICATION OF BORON ON OLEFIN METATHESIS

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Controlling polymer morphology is key to controlling and predicting physical and electronic properties. However, in many cases polymer morphology is unknown because the primary structure of the polymer is unknown. This can be for a variety of reasons, but the most common is the use of imprecise polymerization techniques. Acyclic diene metathesis (ADMET) polymerization is unique in its ability to create polymers with precisely spaced pendant functionality. Many functional groups have been polymerized using ADMET, from alkyl pendant groups to ionic liquids. Precision ADMET polymers synthesized with pendant phosphonic and carboxylic acid moieties have shown never before seen morphologies. This dissertation will discuss the compatibility of boron-containing Lewis acids with olefin metathesis, the use of ionic liquids in ADMET polymerization, the synthesis of boronic acid containing ADMET monomers, and the morphology of precision polymers bearing pendant boronic acids and esters.

Boron-containing Lewis acids have shown a profound effect on the cross metathesis reaction of 1-hexene. Grubbs 1st generation catalyst shows over 100% improvement in conversion in some cases, while the yields of Grubbs 2nd generation

increase by up to 50%. With the inclusion of boron-containing Lewis acids, compounds prepared using Grubbs 2nd generation-type catalysts display significantly reduced levels of isomerization.

To manage the high viscosity of these polymers, ionic liquids were studied and can be an ideal medium for ADMET polymerization. Short reaction times of only 48 hours were observed even with low catalyst loading. Some common ionic liquid impurities were studied and only imidazole was shown to have a negative effect on molecular weight. Additives were also studied to neutralize the impurities and phosphoric acid has been shown to prevent catalyst poisoning with imidazole. When this system was applied to a triptycene monomer, high molecular weights were reached only at high temperatures.

Boronic acid ADMET monomers have been synthesized. Alkyl boronic acids and esters were first attempted but these proved difficult to synthesize due to the deboration of the monomer. To prevent this, aryl boronic acid and ester monomers were synthesized successfully. Deprotection of boronic acid was studied. Pinacol was found to be difficult to remove quantitatively, however protecting groups with benzylic alcohols proved to be readily cleavable under hydrogenation conditions.

Finally, precision boronic acid polymers were made. These precision polymers show unique thermal behaviors due to the interaction between pendant Lewis acids, further X-ray scattering studies to probe morphology are being pursued by collaborators.

CHAPTER 1

Introduction

1.1 Origins of Olefin Metathesis

Olefin metathesis was first reported in the early 1960s at Phillips Petroleum, Standard Oil, and Du Pont.¹⁻³ It was described as a “scrambling” of the substituents of the double bonds (Figure 1 - 1).

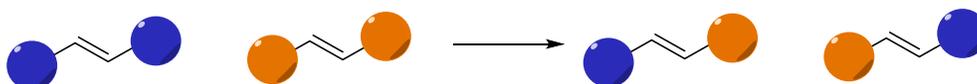


Figure 1 - 1. Olefin “scrambling” with cross metathesis

The mechanism of this reaction was largely unknown until 1971, when Chauvin and Hérisson proposed the formation of a metal alkylidene and metallacyclobutane as intermediates of olefin metathesis (Figure 1 - 2).⁴ The reaction proceeds in three steps that are all in equilibrium. The first step is the association of the metal alkylidene with the reactive olefin. These react to form the metallocyclic butane intermediate, which then falls apart into the product olefin and the new metal alkylidene.

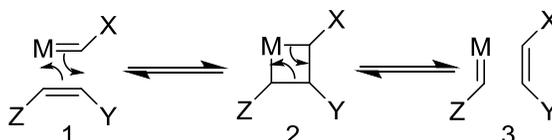


Figure 1 - 2. Proposed mechanism of olefin metathesis. 1) Metal alkylidene and starting olefin; 2) Metallacyclobutane; 3) Metal alkylidene and product.

The traditional catalysts used at the time were poorly defined, typically transition metal halides activated with an alkylation agent.^{5,6} These catalysts suffered from poor activity and a myriad of side reactions.⁷ Later, well-defined molybdenum and tungsten catalysts were designed by Richard Schrock and ruthenium centered catalysts were

synthesized by the Grubbs group.⁸⁻¹¹ Hoveyda further improved upon the Grubbs-type catalysts, creating Hoveyda-Grubbs catalysts (Figure 1 - 3).^{12,13}

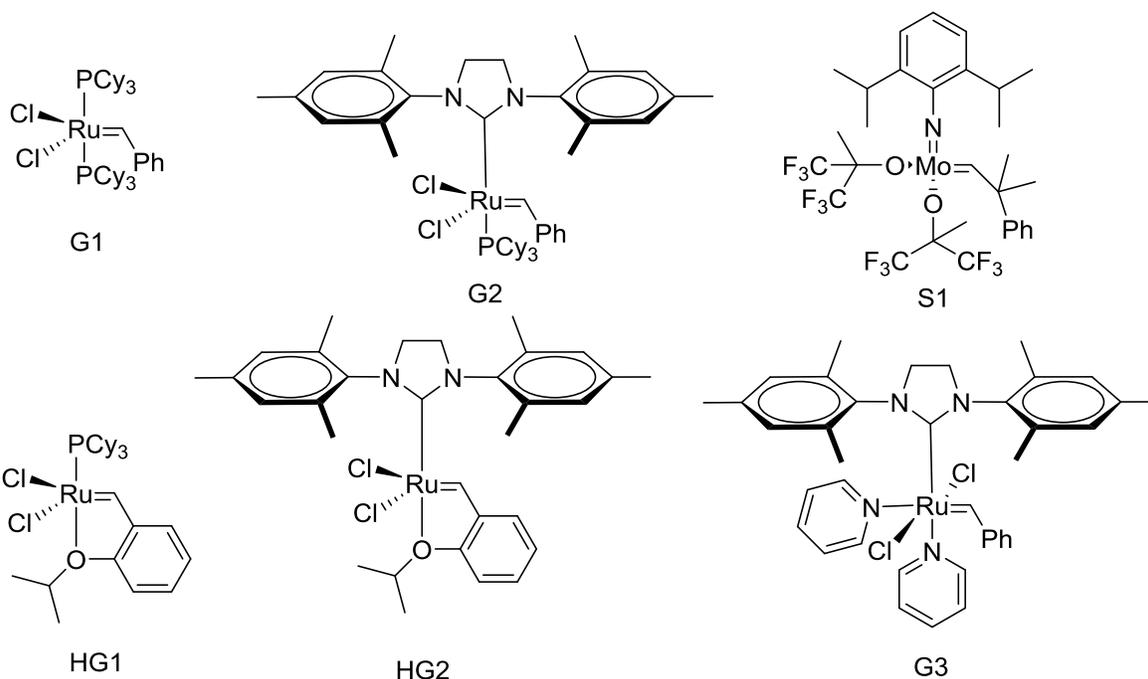


Figure 1 - 3. Variety of olefin metathesis catalysts: Grubbs 1st generation (G1), Grubbs 2nd Generation (G2), Schrock Molybdenum Catalyst (S1), Hoveyda-Grubbs 1st Generation (HG1), Hoveyda-Grubbs 2nd Generation (HG2), and Grubbs 3rd Generation (G3).

Each of these catalysts has their own strengths and weaknesses. Schrock's tungsten and molybdenum (S1) catalysts display excellent reactivity and has no unwanted side reactions, but the metal centers are extremely oxyphilic,¹⁴ reducing the functional group tolerance of the catalyst. Grubbs 1st generation catalyst (G1) is described as the first non-nucleophilic catalyst, which increases the functional group tolerance significantly. The price of this tolerance is reduced reactivity, making it the least active of the well-defined olefin metathesis catalysts.¹⁵ Hoveyda-Grubbs 1st generation catalyst (HG1) displays many similar traits as G1, with slightly higher reactivity and functional group tolerance¹². Both HG1 and G1 have minimal tendency to

cause double bond isomerization.¹⁶ Grubbs 2nd generation catalyst (G2) displays reactivity nearly as high as Schrock type catalysts and high levels of functional groups tolerance¹⁵. This activity comes at a price, as the G2 catalyst has been known to cause significant isomerization.¹⁶⁻¹⁸ Hoveyda-Grubbs 2nd generation catalyst (HG2) rivals Schrock type catalysts in terms of reactivity and also is the most functional group tolerant of all the catalysts.^{13,19} HG2, however, also displays the highest level of isomerization.²⁰ Grubbs 3rd generation catalyst (G3) displays high reactivity partially due the initiation step being much faster than any of the previous catalysts.²¹

The development of these well-defined catalysts has opened the door to a number of synthetically useful reactions (Figure 1 - 4) that have been used for synthesis of pharmaceuticals^{22,23}, total synthesis products²⁴, unique polymers²⁵, and materials²⁶. These reactions include: ring-opening metathesis (ROM),²⁷ ring-closing metathesis (RCM),^{14,28,29} ring-opening metathesis polymerization (ROMP),^{6,30} cross metathesis (CM),³¹ and acyclic diene metathesis polymerization (ADMET),³²

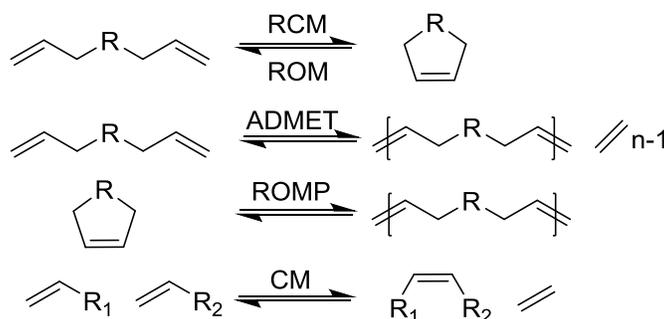


Figure 1 - 4. Types of olefin metathesis: ring-closing metathesis (RCM), ring-opening metathesis (ROM), acyclic diene metathesis polymerization (ADMET), ring-opening metathesis polymerization (ROMP), and cross metathesis (CM).

ROMP and ADMET are the two predominant forms of polymerization that utilize olefin metathesis. ROMP is a chain growth controlled polymerization method that utilizes cyclic olefins and can result in very high molecular weight polymers with very

narrow polydispersities.³³ The driving force of ring opening metathesis polymerization is the release of ring strain, so that only monomers with strained rings will undergo polymerization.³⁴ Since ROMP is a controlled polymerization technique, it has been used to create a variety of polymers with unique architectures, including di-block, tri-block, and alternating polymers.

ADMET, on the other hand, is the step-growth condensation polymerization of a symmetric α,ω diene which releases ethylene and has the ability to create precise polymers by building the precision into the monomer³⁵. After polymerization, the backbone is saturated to give to yield a material that is analogous to a polyethylene copolymer (Figure 1 - 5).

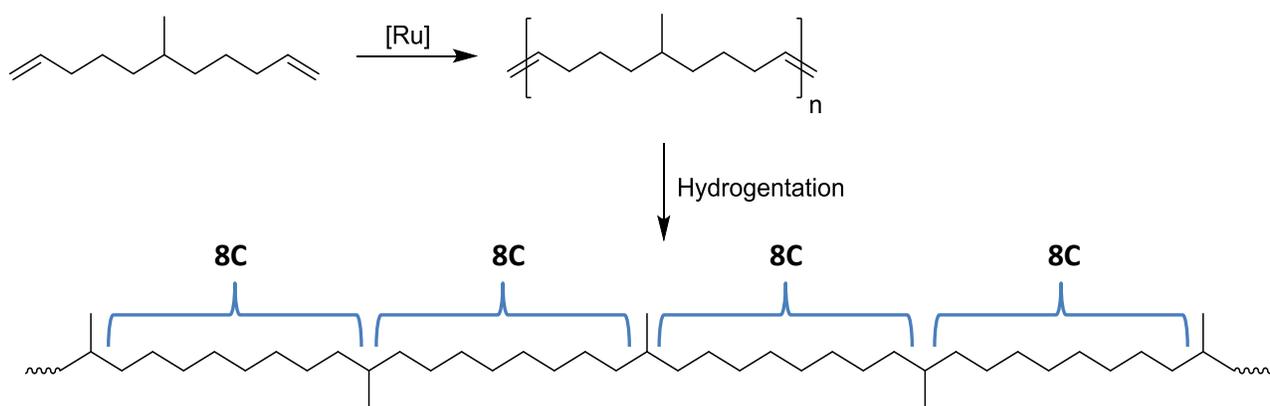


Figure 1 – 5. Precision polymer via ADMET polymerization: first the α,ω -diene is polymerized with an olefin metathesis catalyst, then the residual double bonds are saturated yielding a polymer with pendant groups at known and repeatable distances.

Traditional copolymerization techniques distribute the pendant groups in a statistical manner which leads to a non-uniform distribution (Figure 1 - 6).

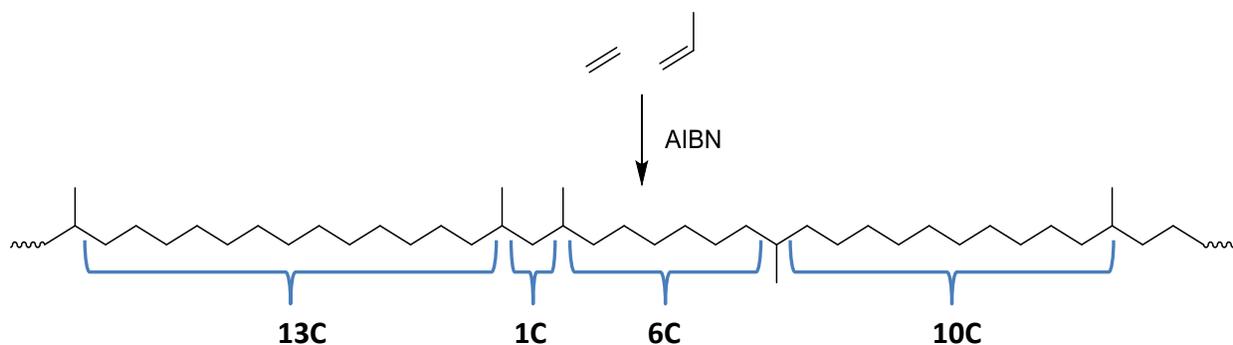


Figure 1 – 6. Statistical co-polymer via traditional radical polymerization: the pendant groups are at random and unknown distances.

To create precise polymers via ADMET, several requirements must be met during the polymerization process. The removal of ethylene is required to reach high degrees of polymerization. The equilibrium constant for ADMET is relatively low, ranging from 10^{-1} down to 10^{-6} .³² To drive the equilibrium forward, the ethylene must be removed either with the use of very low vacuum conditions or by purging the reaction with a neutral atmosphere such as argon.

The second criteria for precise polymer synthesis, is the need for a clean reaction pathway. Isomerization of the terminal olefin can ruin the precision of the polymer (Figure 1 - 7).¹⁶

1.2 Effects of Precision on Polymer Properties

Precision ADMET polymers display drastic differences in properties as compared to their random analogues. Early work done by *Rojas et al.* studied the effect of pendant alkyl group size on polymer morphology (Figure 1 - 8).^{54,60,61}

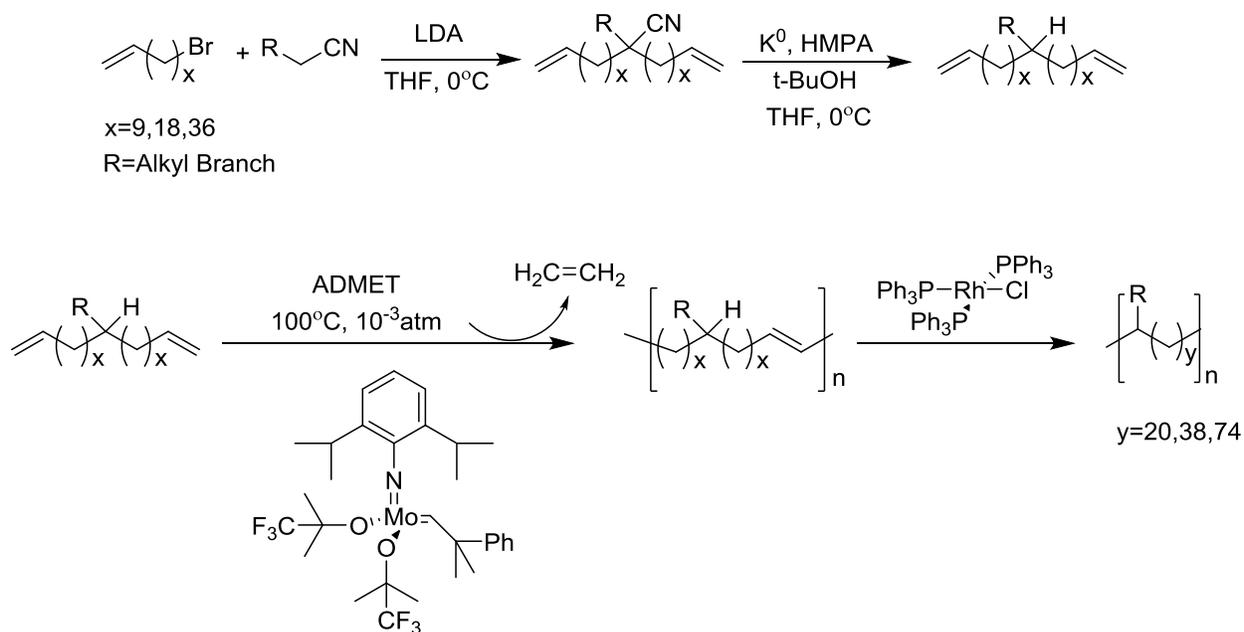


Figure 1 – 8. Synthesis of precision alkyl polymers

The size of the pendant group had an immediate effect on the melting temperature. ADMET polyethylene has a melting temperature of 134°C . A pendant methyl group on every 21st carbon reduces the melting point to 63°C and an ethyl group even more to 24°C . With propyl and larger pendant groups the melting point stabilizes at about 12°C . This is seen not only for linear alkyl chains such as butyl, pentyl, hexyl, and so on but also large bulky pendant groups like adamantyl, *tert*-butyl, and cyclohexyl (Figure 1 - 9).⁵⁴

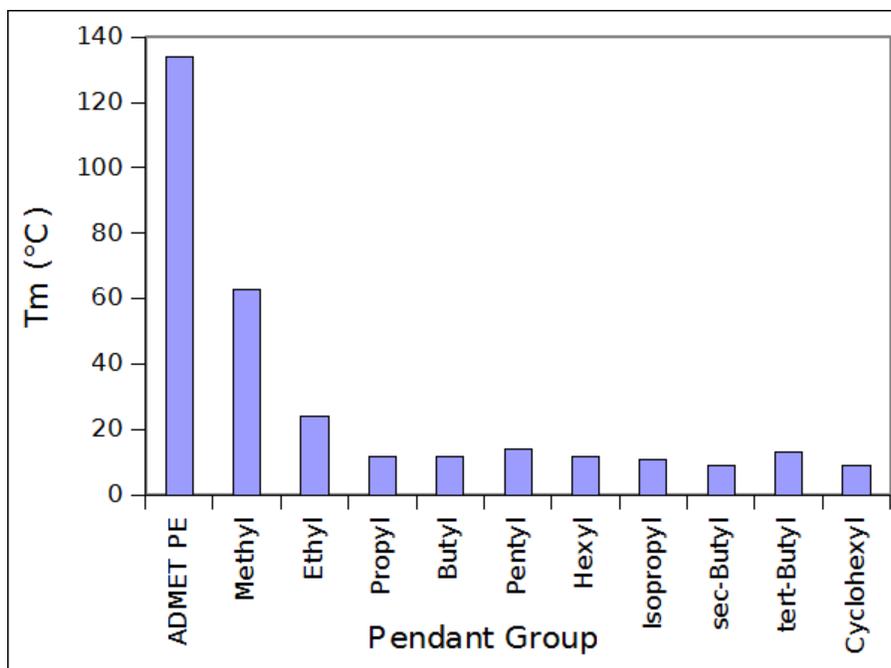


Figure 1 – 9. Effect of pendant group on polymer melting temperature. Larger pendant groups expelled from the polyethylene crystal structure, leading to a plateau in melting temperature. Data adapted from Rojas, G.; Inci, B.; Wei, Y.; Wagener, K. B. *Journal of the American Chemical Society* **2009**, *131*,17376–86.⁵⁴

What causes this leveling effect? In random polymers large pendant groups result in complete loss of T_m . However, with precision polymers the small pendant groups (methyl and ethyl) are incorporated into the polyethylene crystal structure. Large pendant groups are excluded, this allows the polyethylene spacer lengths between pendant groups to organize into crystalline lamellae^{54,62}. With carbon spacers of shorter than 20 carbons, crystallinity is not observed.⁵³

Bora et al. continued this research by synthesizing precision ADMET polymers with alkyl pendant groups on every 39th carbon.⁶¹ Again, small pendant groups (methyl) are shown to be incorporated into the polyethylene crystal. Larger pendant groups are excluded, leading to the leveling effect as seen in other studies. The T_m leveled off at

about 72°C due to the longer run length of polyethylene between each pendant group (Table 1 - 1).⁶¹

Table 1 - 1. Pendant Group Effect on Melting Point and Lamellar Thickness

Branch identity on every every 39th carbon	T_m (°C)	ΔH_m (J/g)	M_w(kg/mol) (PDI)	Thickness (nm)
No branch	134	211	70.2 (2.7)	9.75
Methyl	92	137	92.7 (2.0)	7.09
Ethyl	76	93	53.1 (2.4)	4.79
Propyl	78	71	225 (3.0)	N/A
Isopropyl	77	74	114 (3.5)	N/A
Butyl	75	66	66.5 (2.5)	4.25
Isobutyl	73	51	54.8 (2.4)	N/A
Pentyl	74	88	30.2 (2.0)	5.03
Hexyl	73	85	30.5 (1.9)	4.17
Heptyl	74	85	74.2 (2.9)	4.39
Octyl	74	73	181 (3.3)	4.06
Nonyl	73	84	34.3 (2.2)	4.67
Decyl	71	76	27.2 (1.8)	4.16
Pentydecyl	70	83	55.9 (2.4)	5.33

Data adapted from Inci, B.; Lieberwirth, I.; Steffen, W.; Mezger, M.; Graf, R.; Landfester, K.; Wagener, K. B. *Macromolecules* **2012**, *45*, 3367–3376.⁶¹

Exclusion of the pendant group is further supported by studying the lamellar thickness. The ADMET polyethylene displayed a thickness of 9.75nm and the methyl polymer was 7.09nm thick. Precision polymers with pendant groups larger than methyl, which were excluded from the crystal structure, all had thicknesses ranging from 4-5nm

regardless of the size of the pendant group.⁶¹ This corresponds to a thickness of 30-40 carbons in a chain, approximately the number of carbons between each pendant group.

Finally, to fully understand short chain branching in a polyethylene, a precision ADMET polymer with a butyl branch on every 75th carbon was studied.⁶⁰ This works out to only 13 butyl branches per 1000 carbon atoms, which allows, for the first time, for direct comparison with commercial polyethylene systems. Table 1 - 2 shows the melting temperature of precision polymers as a function of butyl branch concentration.

Table 1 - 2. Effect of Butyl Branch Concentration on Melting Point

Butyl branch on every nth carbon, n	Butyl branches per 1000 carbon atoms	T_m (°C)	ΔH_m (J/g)
5	200	amorphous	--
15	67	-33	13
21	48	14	47
39	26	75	66
75	13	104	152
ADMET PE	0	134	204

Data adapted from Inci, B.; Wagener, K. B. *Journal of the American Chemical Society* **2011**, *133*, 11872–5.⁶⁰

This final polymer allows for an experimental model to be determined that can project the branch concentration as a function of melting temperature (Figure 1 - 10).⁶⁰

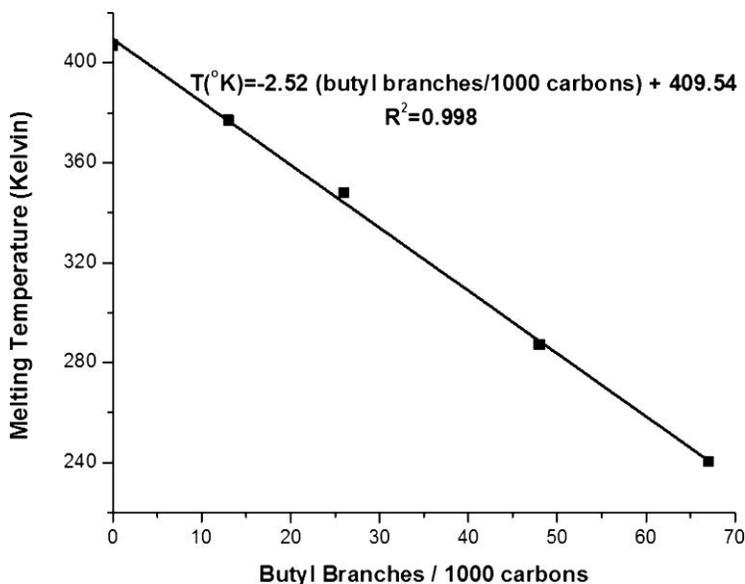


Figure 1 – 10. Melting temperature of precision butyl branch polymer as a function of branch concentration. Reprinted with permission from *Journal of the American Chemical Society* **2011**, 133, 11872–5. Copyright 2011 American Chemical Society.

Alkyl branch polymers are not unique among precision ADMET polymers.

Precise polymers with pendant halides^{37–39}, phenyl rings⁶³, esters⁶⁴, imidazolium hexafluorophosphate^{65,66}, chromophores^{67–69}, and many others have displayed unique properties.

1.3 Precision Acid and Ionic Polymers

Precision acid and ionic polymers also demonstrate unique morphologies and properties. In the past, the morphology of these materials has been poorly defined due to the random nature of the polymerization.⁷⁰ These polymers tend to be difficult to polymerize via ADMET due to nucleophilicity of the acid groups.²⁵ However, even with this difficulty, a number of precision analogues have been synthesized using ADMET, including carboxylic acids,⁴⁵ phosphonic acids,⁴⁶ and carboxylate ionomers⁷¹.

Baughman *et al.* prepared precision carboxylic acid polymers with varying acid concentrations via ADMET polymerization (Figure 1 - 11).⁴⁵

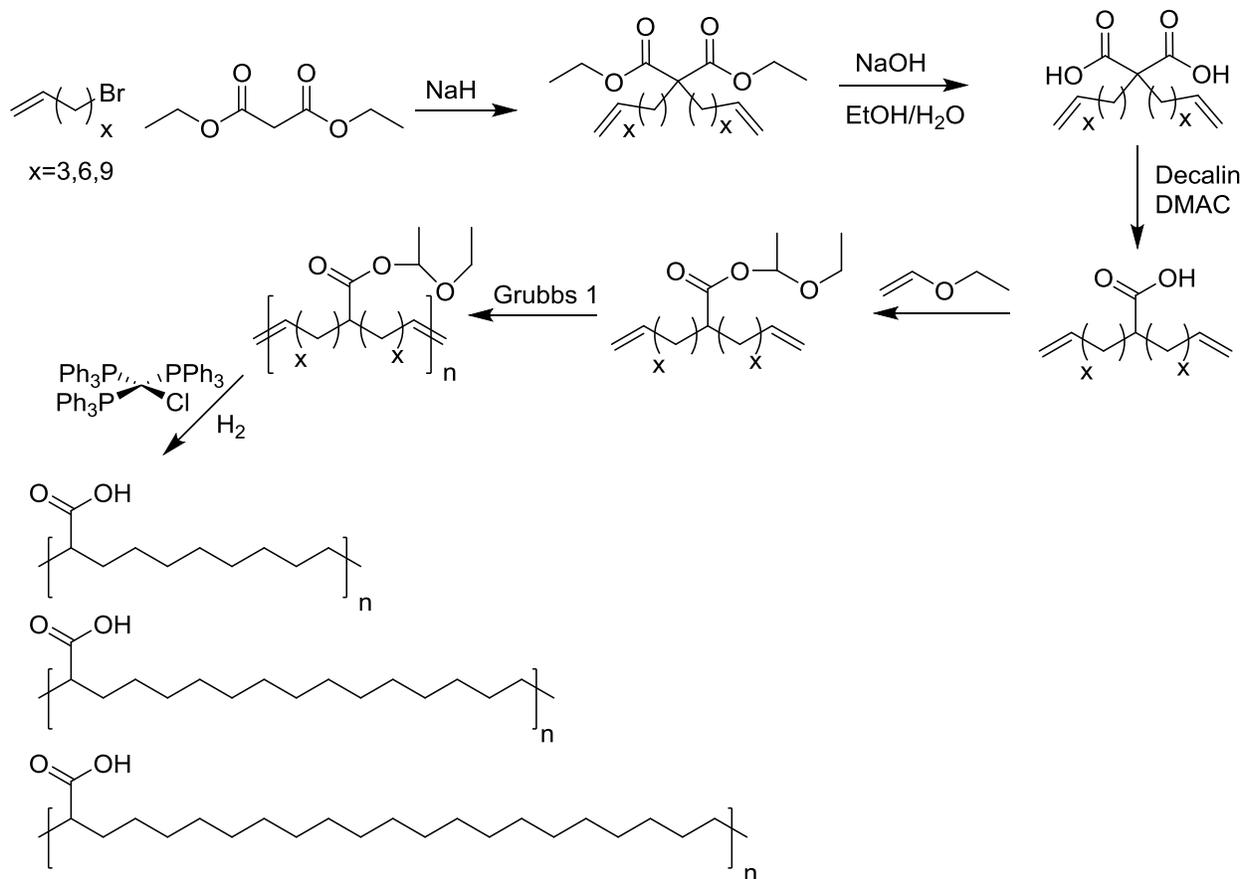


Figure 1 – 11. Synthesis of precision carboxylic acid polymers⁴⁵

The polymers with the lowest concentration of acid groups, $x=9$, form dimers around the PE lamellar and create a layered stacking morphology (Figure 1 - 12). This morphology is not seen in the analogous random polymers.

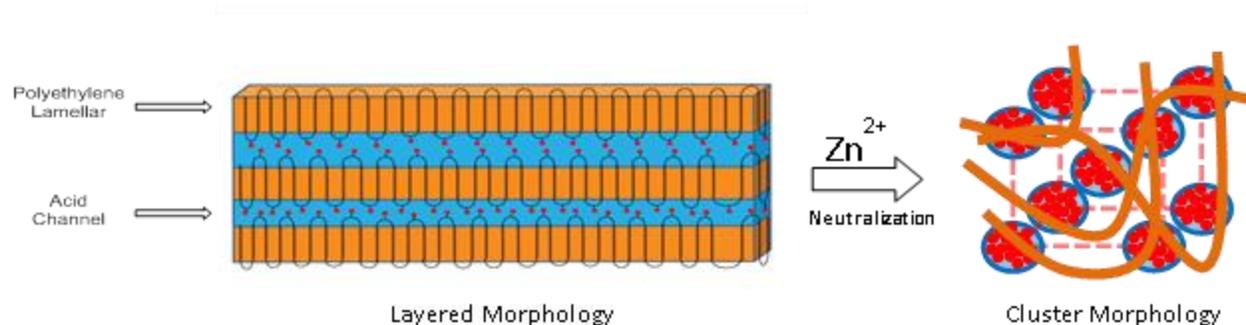


Figure 1 - 12. Layered morphology of carboxylic acid polymer (left) converts to an organized cluster morphology (right) on neutralization.

Both the precision and random polymers were then neutralized with either Li^+ or Zn^{2+} counter ions and the morphologies of unneutralized and neutralized polymers were compared via DSC, SAXS, ^1H , ^{13}C , and ^7Li NMR.⁷¹⁻⁷³

Work done by Seitz *et al.* demonstrates that upon neutralization the polymer converts from the layered acid morphology to a cluster morphology.⁷¹ The extent of neutralization ranged from 0% (parent polymer) up to 116% (only for the polymer with acid groups on every 21st carbon atom). As the percent neutralization increased, the crystallinity decreased as demonstrated by DSC and SAXS. In the case of the zinc ionomer, spherical aggregates formed and disrupted the layered morphology described above for the pure acid polymer. At the highest neutralized acid content, the packing of the aggregates (Figure 1 - 12) transforms from random packing shown by polymers with ionic groups on every 21st and 15th carbon atom, to a body-centered cubic lattice shown in the polymer with a carboxylate substituent on every 9th carbon. High concentration of carboxylate ions promotes self-assembly of the polymer into a cubic lattice.⁷¹ This is the first time this type of behavior has been observed and is presumably a result of the precise nature of the polymers.

NMR studies have been conducted on both the zinc and lithium neutralized acid polymers. Solid state ^{13}C NMR experiments have been utilized by Jenkins *et al.* at Sandia National Laboratory to study the crystallization of the zinc neutralized ionomer.⁷² They demonstrated that higher concentrations of protonated acid groups increase the tendency for “conformational defects,” which reduce the overall crystallinity. Increased neutralization was also found to decrease the crystallinity due to aggregation of the pendant groups around the zinc ions. These studies also found an increase in motion along the chain axis in the crystalline phase of the precision polymers, but a restriction of movement in the amorphous phase. Proton and ^7Li NMR were carried out to examine the proton environment in lithium-neutralized polymers.⁷³ The results indicated the presence of several different carboxylate structures, but only one environment for the lithium-neutralized portion of the polymer. These results are consistent across acid concentrations and neutralization percentages, with the major structural differences among the acid groups depending on their coordination to a lithium ion. These NMR studies demonstrate how structure and morphology can be controlled with precise carboxylate spacing, percent neutralization, and counter ion identity.

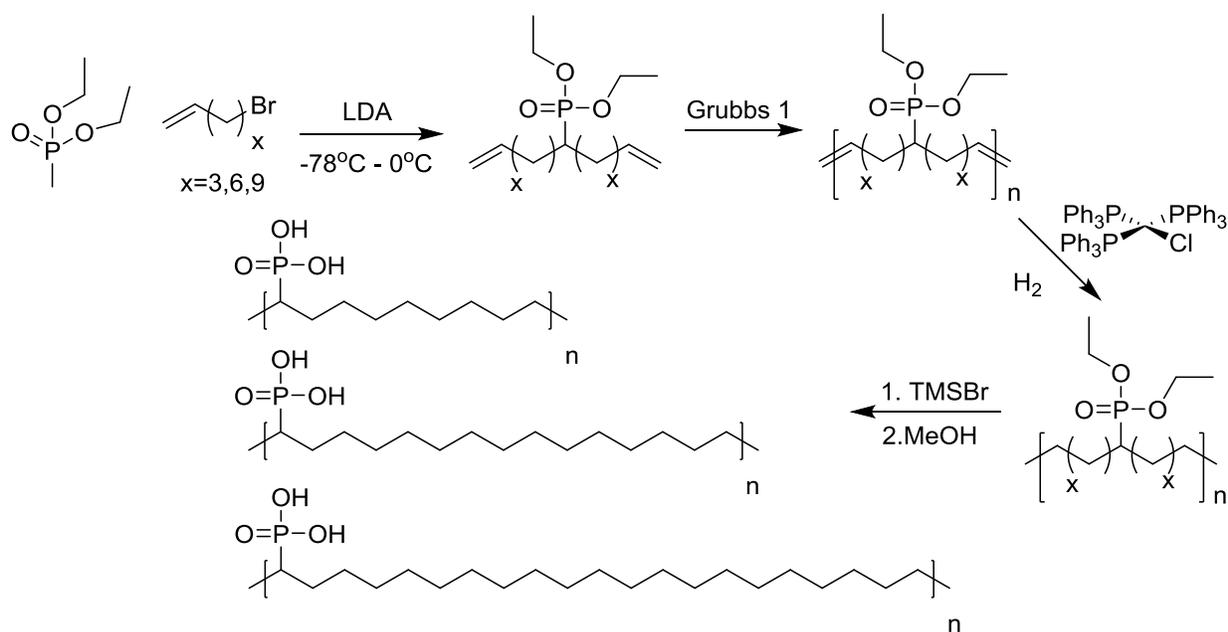


Figure 1 – 13. Synthesis of precision mono phosphonic acid polymers⁴⁶

Opper *et al.* have prepared a variety of precision phosphonic acid polymers.^{46,47}

The first polymers synthesized were the phosphonic acid analogues to the carboxylic acid polymers described above. The distance between the phosphonic acid groups of these polymers were the same as those for the carboxylic acid polymers, and each repeat unit contained only a single phosphonic acid group (Figure 1 - 13). The behavior of these polymers is similar to that of the corresponding carboxylic acids; as the acid concentration increases the crystallinity decreases.⁴⁶ Geminal phosphonic acid polymers have also been synthesized, as shown in Figure 1 - 14, effectively doubling the acid content of the polymer with the same branch frequency.⁴⁷

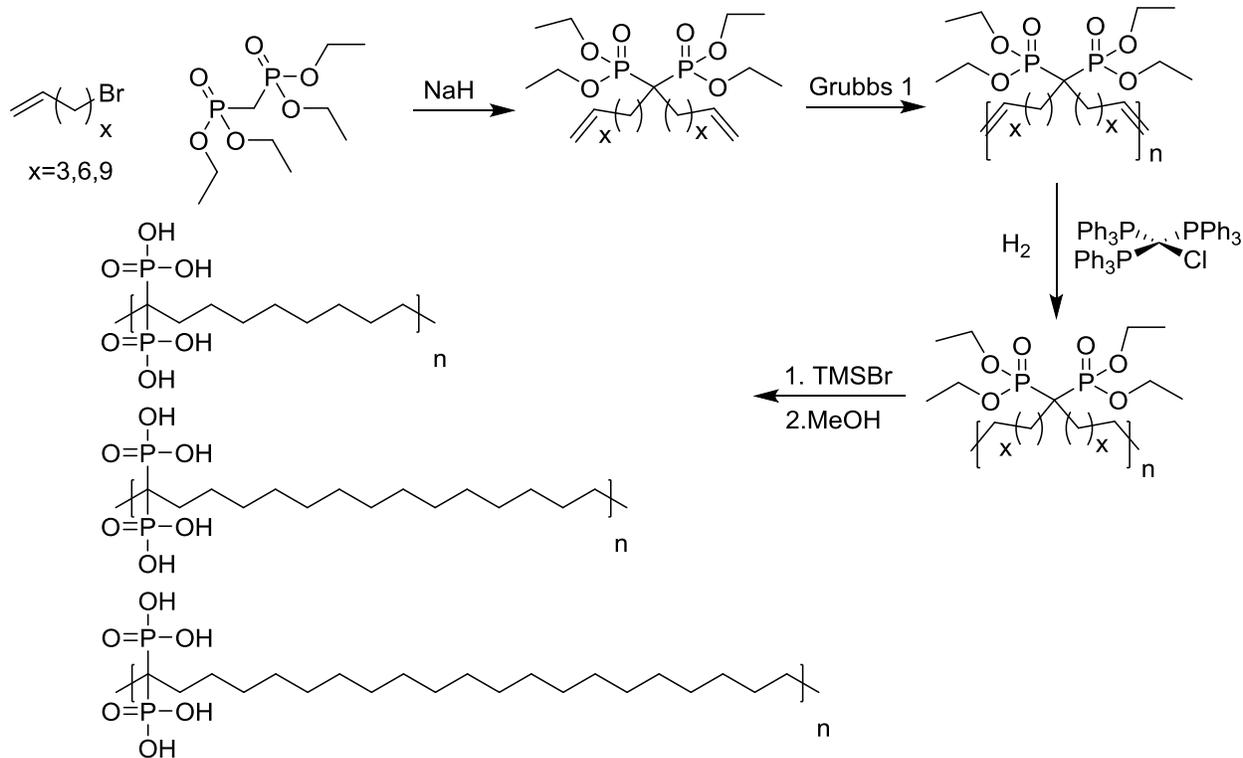


Figure 1 – 14. Synthesis of precision geminal phosphonic acid polymers⁴⁷

The crystalline behavior of the geminal diphosphonic acid polymer is similar to that of the monoacid polymer, with the exception that increased concentration of acid groups causes an increase in melting temperature with a broader DSC endotherm. This could indicate a less perfect crystal formation due to the higher order of hydrogen bonding available with phosphonic acids. The SAXS data collected by Buitrago *et al.* indicates that microphase separation of the polyethylene backbone and the phosphonic acid is occurring.⁷⁴ The geminal phosphonic acids phase aggregate in a face-centered cubic lattice, which is persistent well above the melting point of the polyethylene backbone (Figure 1 - 15). Work is currently ongoing to study the morphology of the mono-phosphonic acid polymer.

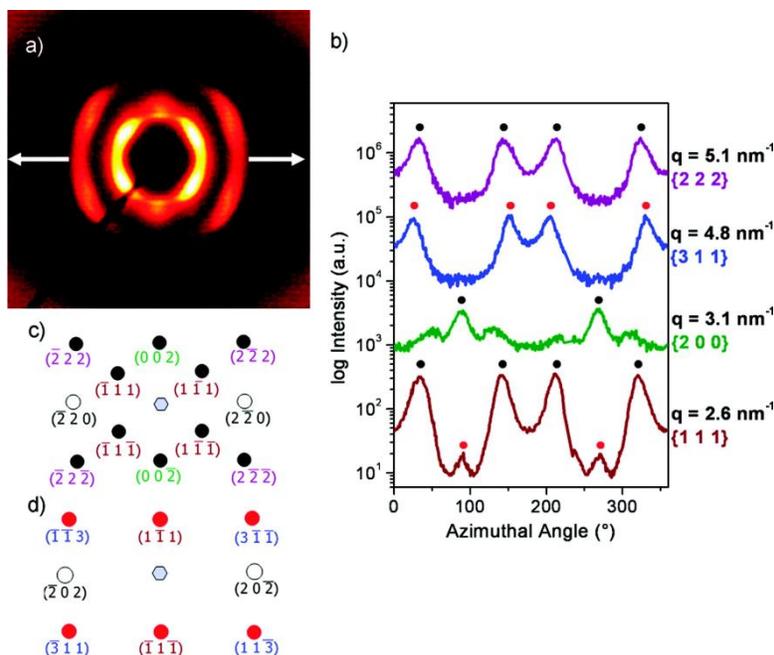


Figure 1 – 15. Unique morphologies observed with geminal phosphonic acid polymers. a) SAXS of the drawn polymer. b) SAXS as a function of angle at different q values. c) Simulated diffraction pattern in the $[1\ 1\ 0]$ direction. d) Simulated diffraction pattern along the $[1\ 2\ 1]$ direction. Reprinted with permission from *Buitrago, C. F.; Oppen, K. L.; Wagener, K. B.; Winey, K.I. ACS Macro Letters* **2012**, *1*, 71–74.. Copyright 2012 American Chemical Society.

Both the precise carboxylic acid and phosphonic acid polymers have demonstrated unique and different morphologies, presumably controlled by their pK_a . The purpose of this study is to determine the effect on acid pK_a on morphology (Figure 1 - 16). Research on precision sulfonic acid polymers ($pK_a \approx -1$) is currently underway.

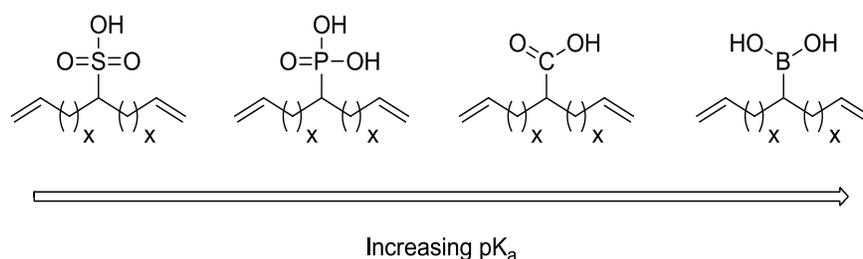


Figure 1 – 16. Acid monomers ranked by pK_a

This dissertation will describe the use of boron-containing compounds in ADMET polymerization. Chapter 2 will explore the effects of boron-containing Lewis acids on olefin metathesis. Isomerization and conversions are discussed.

Chapter 3 examines the use of ionic liquids as an ADMET polymerization reaction medium. Catalyst concentration, reaction time, and temperatures are explored. Common impurities are evaluated for their effect on ADMET polymerization as well additives that can be used to neutralize the impurities. Finally, a variety of triptycene monomers were polymerized to fully evaluate the new reaction medium.

Chapter 4 discusses the synthesis of boronic acid and ester monomers. First, the synthesis of alky boronic esters is investigated. Next, the synthesis of aryl boronic acids and esters are explored, and finally deprotection of boronic acids is discussed.

Chapter 5 examines the polymerization of boronic acid and ester monomers. Polymerization conditions are discussed and thermal stability is investigated. Both precision and random boronic acid polymers are investigated.

CHAPTER 2 Effects of Boron-Containing Lewis Acids on Olefin Metathesis

2.1 Background

Increasing the yields and decreasing the isomerization of olefin metathesis reactions is important in the fields of organic synthesis, polymer chemistry, and pharmaceuticals. Herein, we use a model system to prove that boron-containing Lewis acids increase the yields of olefin metathesis reactions containing Grubbs 1st and 2nd generation catalysts. By use of GC-MS we demonstrate that olefin isomerization is nearly eliminated in the presence of boron-containing Lewis acids.

Olefin metathesis has opened many new avenues for the synthesis of carbon-carbon double bonds and has proven invaluable for many fields of chemistry.²⁷ Ring-closing metathesis (RCM) and cross metathesis (CM) have revolutionized the synthesis of pharmaceuticals and large total synthesis targets.^{28,29,31} Ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) polymerization have provided ways to synthesize new materials, often with unique morphologies.^{25,26,32,33} As knowledge of these techniques increases, researchers are continuing to expand the range of olefin metathesis applications.

Numerous Grubbs-type olefin metathesis catalysts have been developed over the past 15 years.⁷⁵ Each catalyst has specific strengths and weaknesses, generally in reference to stability, activity, and tendency for isomerization of the olefin.¹⁶ Grubbs 1st generation catalyst (G1) is less active and less stable than 2nd generation Grubbs catalysts, but G1 does not display a propensity towards isomerization.¹⁵ Hoveyda-Grubbs 1st generation catalyst (HG1) has a higher stability and is slightly more active than G1, although still less active than the 2nd generation catalysts.¹² Grubbs 2nd

generation catalyst (G2) is quite active and stable but it can lead to significant isomerization of the double bond.^{15,17,18} Hoveyda-Grubbs 2nd generation catalyst (HG2) scores highest in all of the metrics above, being the most stable and active, but also having the greatest tendency for isomerization.^{13,19,20} Isomerization of the double bond in olefin metathesis has been attributed to the formation of ruthenium hydride (Figure 2 - 1).^{36,76}

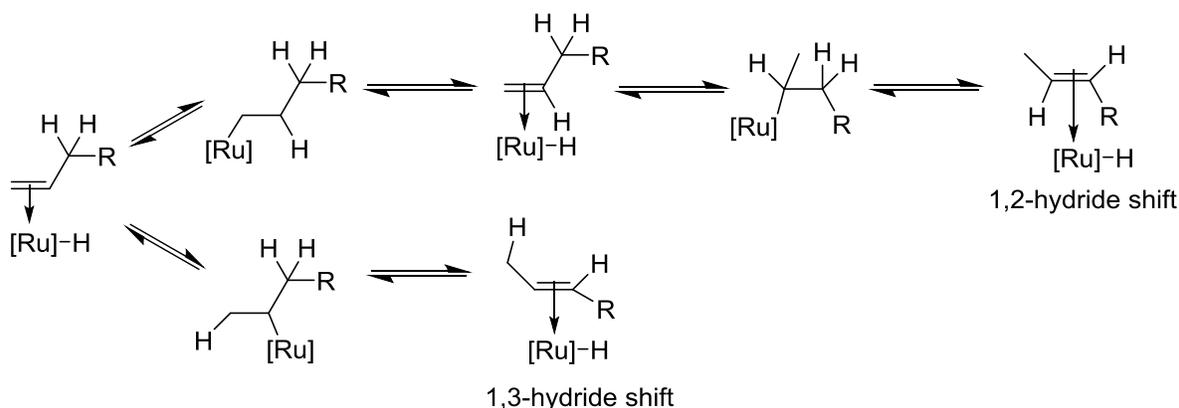


Figure 2 - 1. Two paths of hydride isomerization mechanism. Top: Isomerization via 1,2-hydride shift. Bottom: Isomerization via 1,3-hydride shift.¹⁶

Metal-centered Lewis acids and protic acids reduce isomerization in reactions involving Grubbs 2nd generation type catalysts.^{66,77-79} Lewis acids have been shown to activate molybdenum nitride catalysts leading to increased yields and rates of alkyne metathesis.^{80,81} Vedrenne *et al.* studied how Lewis acids, including some containing boron, facilitate the CM of certain olefins having functional groups that interfere with the catalyst or undergo some other side reaction. In these cases, the Lewis acids are thought to coordinate with the functional group, leaving the metathesis catalyst unencumbered.⁸²

2.2 Results and Discussion

Lewis acids that contain boron were chosen for this study due to the wide range of acid strengths that are available. Recently boron-containing moieties have been used extensively in organic synthesis^{83–85}, pharmaceuticals^{86–88}, and polymers^{89–91}.

Understanding boron's effect on common synthetic and polymerization techniques can open many doors in these fields. The calculated values for fluorine affinities were used as a measure of Lewis acidity as shown in Figure 2 - 2, triphenyl borane (PhenB) displays the highest Lewis acidity to boric acid (OHB), which is the weakest and pinacol phenyl borate (PinB) in the middle.^{92–94} These Lewis acids were studied for their impact on yield and olefin isomerization tendency of a variety of Hoveyda and Grubbs type metathesis catalysts. As the model system, we used the cross metathesis (CM) of 1-hexene (Figure 2 - 3) monitored by GC and NMR. Deuterated chloroform was chosen as solvent to aid in NMR analysis and to solvate the Lewis acid. Chlorinated solvents have also been shown to facilitate olefin metathesis.^{95–97}

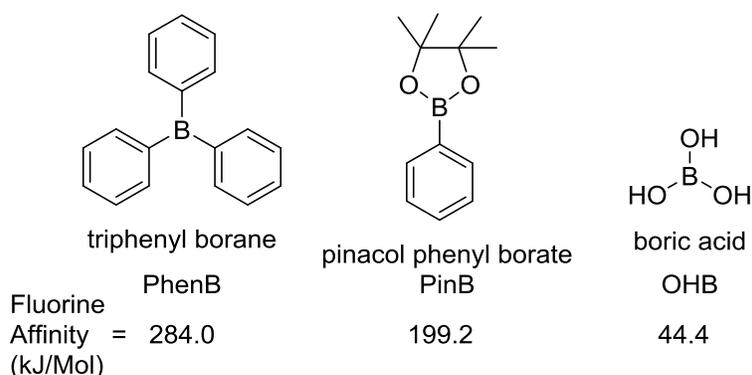
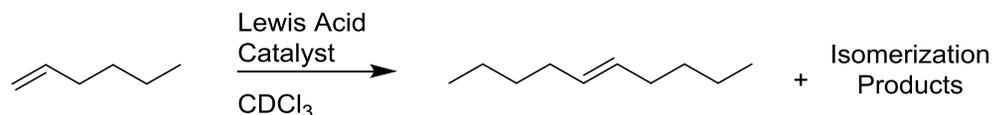


Figure 2 - 2. Boron-containing Lewis acids which exhibit a range of Lewis acidities. Fluorine affinity is used as a metric of Lewis acidity, PhenB being the strongest Lewis acid and OHB being the weakest.^{92–94}



Lewis Acid= PhenB, PinB, OHB
 Catalyst= G1, HG1, G2, HG2

Figure 2 - 3. Model reaction used to study the effects of Lewis acids on olefin metathesis. Reaction conditions: 100mg (1.2 mmol) of 1-hexene, 20 mol% Lewis acid, 1 mol% catalyst reacted at 45 °C in CDCl₃ for 15 hours.

The yields were studied for all four catalysts with each of the boron-containing Lewis acids. As shown in Table 2 - 1, HG1 provided similar yields when used with PhenB, PinB, and OHB.

Table 2 - 1. CM conversion of 1-hexene

Catalysts	HG1	G1	HG2	G2
Lewis Acids	yield ^a (%)	yield ^a (%)	yield ^a (%)	yield ^a (%)
Control ^b	84	29	99+	63
OHB	78	71	24	60
PinB	74	62	33	69
PhenB	81	5	50	5

a. Yields determined by NMR. b. Control reactions were performed without Lewis acids. Reaction conditions: 100mg 1-hexene, 20 mol% Lewis acid, 1 mol% catalyst reacted at 45 °C in CDCl₃ for 15 hours. The standard deviation was found to be 7.9%.

For Grubbs 1st generation (G1) catalyst the control reaction yielded 29% CM, but addition of OHB and PinB significantly increased the yields to 71% and 62%

respectively (Table 1). G1 and G2 are phosphine containing catalysts; the first step in their initiation is the dissociation of the tricyclohexylphosphine ligand which is the rate limiting step (Figure 2 -4).

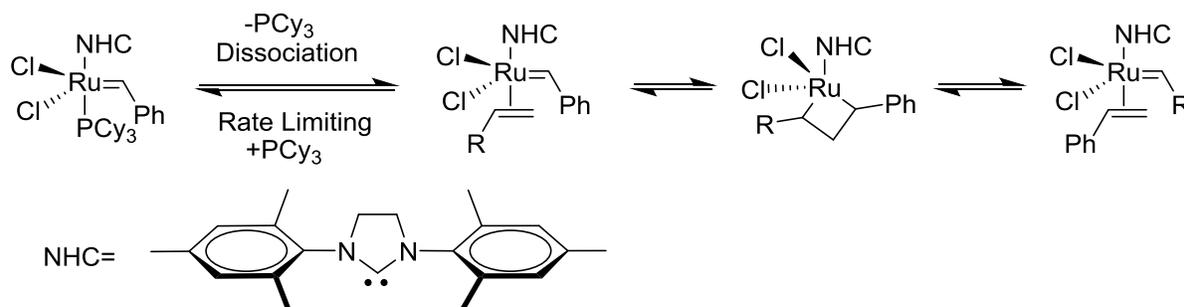


Figure 2 - 4. Phosphine dissociation mechanism for activation of Grubbs-type olefin metathesis catalysts

In these cases, the Lewis acid behaves as a phosphine sponge. It removes the tricyclohexyl phosphine ligand from the catalyst and, presumably, increases the rate of the initiation step (Figure 2 - 5).

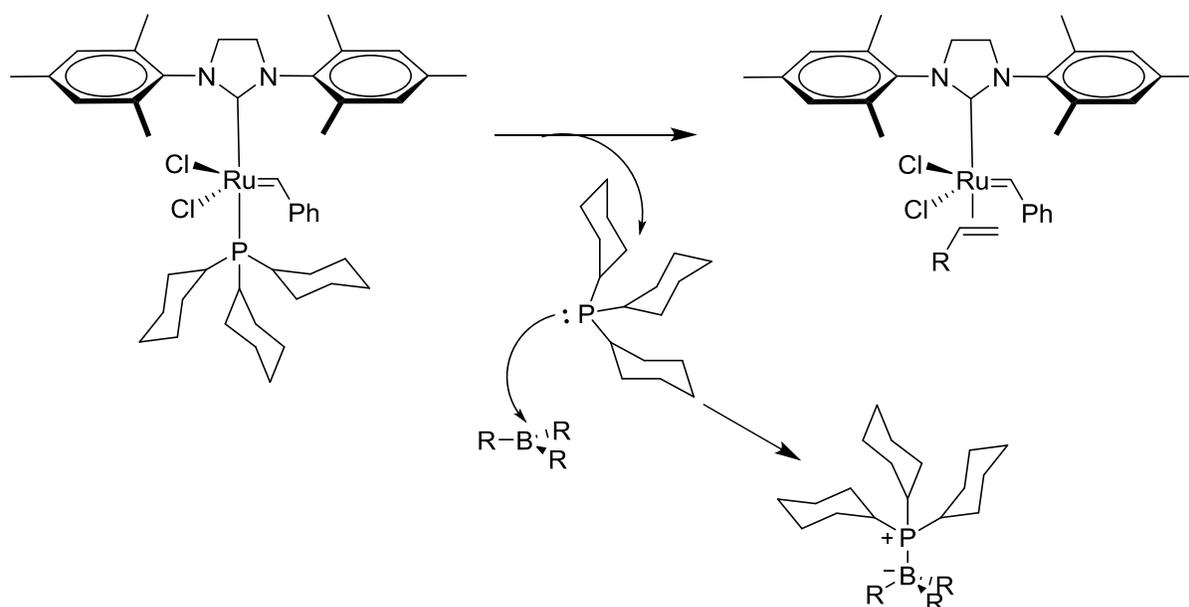


Figure 2 - 5. Proposed mechanism for the increase in conversion observed in the presence of boron-containing Lewis acids. The boron-containing Lewis acid behaves as a phosphine sponge, removing the tricyclohexyl phosphine (PCy₃) ligand from the equilibrium.

This capture of phosphine ligands has been shown with a variety of boron-containing and metal-containing Lewis acids, these include; triphenyl borane⁹⁸, tris(pentafluoro phenyl) borane⁹⁹, 9-borabicyclo[3.3.1]nonane¹⁰⁰, and copper iodide¹⁰¹. Furthermore, metal-containing Lewis acids such as tin(III) chloride⁷⁷ and copper iodide¹⁰², have displayed yield and rate increases in metathesis reactions, presumably from the phosphine sponge effect. This effect is supported by a shift in the ³¹P NMR of G1 in the presence of PinB presumably caused by the complexation of the phosphine ligand with the Lewis acid (Figure 2 – 18). This effect was not observed for the HG1 catalyst because the isopropyl phenyl ether ligand does not undergo a dissociative mechanism, limiting the effect of the Lewis acid. The PhenB Lewis acid surprisingly led to only about 5% conversion. Similar results with PhenB were found with Grubbs 2nd generation catalyst (G2) and will be discussed in more detail below.

The trend in yields for Hoveyda Grubbs 2nd generation catalyst (HG2) was expected to be similar to that of HG1, but this was not the case. As seen in Table 1, the control reaction achieved nearly quantitative conversion, but the addition of a Lewis acid dramatically decreased the yields in the order; PhenB at 50%, PinB at 33%, and OHB at 24%. This is contrary to current thought, since the HG2 catalyst is expected to show increased stability compared to G1 and G2. The yields follow the trend in acid strength; the stronger Lewis acids causing the catalyst to decay more slowly. When studying the effects of Lewis acids on hard to metathesize olefins, Vedrenne *et al.* showed that chloro catachol borane at 10 mol% enhanced the cross metathesis reaction using HG2 of methyl vinyl ketone and BOC protected 2-propene-1-amine, but at 40mol% borane the reaction was retarded.⁸² These results indicate that there is an optimal concentration of Lewis acid before it causes decomposition of HG2 catalyst.

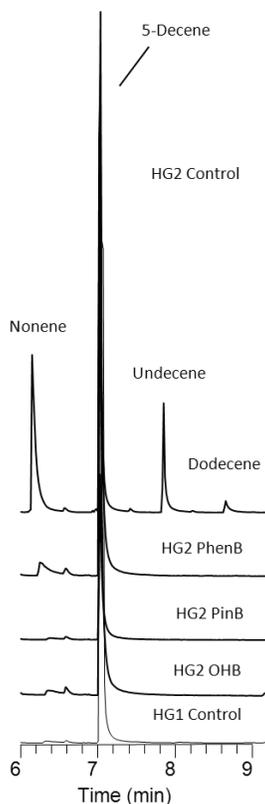


Figure 2 - 6. GC traces show a reduction in isomerization with the addition of Lewis acids¹⁰³

The results for HG2 were not entirely negative. When the isomerization was studied by GC-MS, it was found that the addition of any of the Lewis acids led to an significant reduction in isomerization. When compared to the GC traces from the HG1 reactions, which show only very minimal isomerization, the traces with Lewis acids and HG2 are almost identical (Figure 2 - 6). The boron-containing Lewis acid presumably reacts with any hydride formed to shut down that isomerization path.

Grubbs 2nd generation catalyst (G2) behaves as a hybrid of HG2 and G1. The control reaction yielded 63% conversion. With OHB and PinB added to the reaction, the yields were 61% and 69%, respectively, indicating that there was a competition between the decomposition tendency of HG2 and the phosphine sponge effect observed with G1. This competition was also observed when the concentration of the Lewis acid was

varied. Figure 2 - 7 displays the CM yields as a function of Lewis acid concentration. PinB was used for this study because it displayed the greatest effect in terms of yield enhancement and isomerization reduction. When PinB was added at 5 mol%, the yield increased to 97%, a dramatic change from the 63% control experiment. When the concentration of PinB was increased to 10-20%, the yields dropped to about 68%. At 30-50% Lewis acid the yields further decreased to about 50-55%. These results demonstrate a competition between the increase in the rate of initiation and the decomposition of the catalyst. At low concentrations the PinB only removes the phosphine from the catalyst, causing an increase in yield. However, once the concentration of PinB is increased, the catalyst begins to decompose.

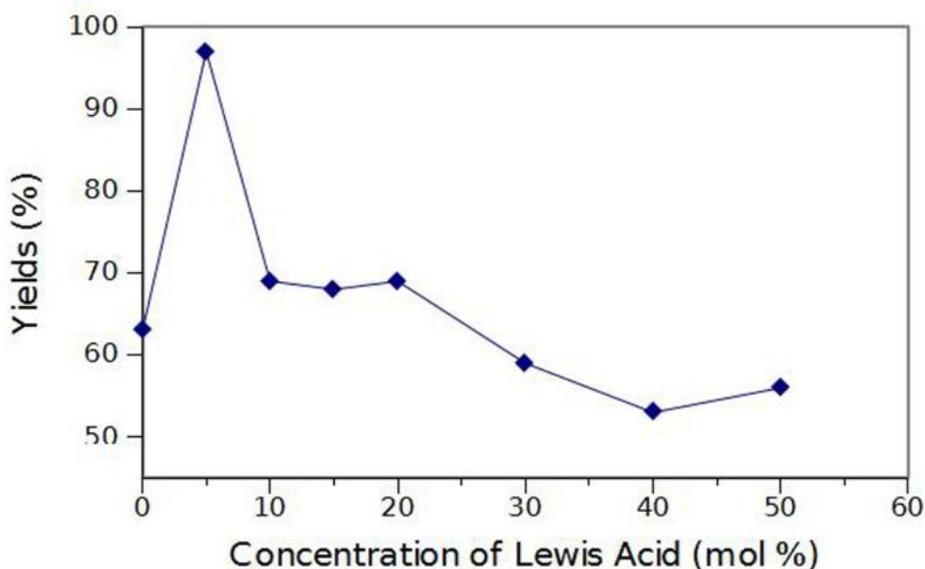


Figure 2 - 7. Concentration effects of PinB Lewis acid on CM reaction using G2. The standard deviation was found to be 7.9%.¹⁰³

With PhenB and either G1 or G2, small amounts of the CM product were observed. But with HG1 or HG2, PhenB was one of the better Lewis acids. To further investigate this behavior the reaction was run neat. The control experiments for G1 and

G2 resulted in yields of 76% and 55% respectively. However, in the experiments containing BPhen, the G1 and G2 yields were 93% and 68%, respectively, an increase in conversion of 122% and 124% for G1 and G2, respectively, from the control reactions. These results lead to the conclusion that BPhen is good Lewis acid choice, but it is sensitive to the solvent impurities when using Grubbs 1st and 2nd generation catalysts. When compared to the increases in conversion from control experiments observed with OHB and PinB for G1, 245% and 214%, respectively, PhnB is not as effective at increasing the yield of the CM reaction.

2.3 Conclusions

This work has demonstrated the effect of boron-containing Lewis acids on olefin metathesis yield and isomerization tendency. Grubbs series of catalysts show improvements in both yield and isomerization tendency in the presence of boron-containing Lewis acids, while the Hoveyda type catalysts show no change in yield for HG1 and a decrease in both yield and isomerization with HG2. These results have implications for olefin metathesis reactions in chemistry, polymer synthesis and polymerization, and pharmaceutical science.

2.4 Experimental

2.4.1 Materials and Instrumentation

All materials were purchased from Aldrich and used without further purification unless noted. Grubbs 1st and 2nd generation catalyst (G1 and G2) as well as Hoveyda-Grubbs 1st and 2nd generation catalyst (HG1 and HG2) were kindly provided by Materia, Inc. The deuterated chloroform solvent was used from a freshly opened bottle and stored under nitrogen in a desiccator. All ¹H NMR, ¹³C, and ³¹P were obtained on a Varian Mercury 300MHz spectrometer and recorded in CDCl₃. All Gas Chromatography-

Mass Spectrometry (GC-MS) were obtained using a Thermo Scientific Trace GC DSQ equipped with a 60m-AT-5ms column, heating from 40°C to 280°C at 20 °C/min.

2.4.2 Procedures

General procedure for olefin cross metathesis of 1-hexene with no Lewis acid in CDCl₃ (Table 1, Control). A test tube equipped with a magnetic stirrer was charged with 100mg of 1-hexene (.149mL, 1.19mmol), and 1mL of CDCl₃. 1 mol% of catalyst (G1, G2, HG1, or HG2) was then added. The reaction was then capped with a septum and stirred under a constant argon atmosphere at 45°C for 15 hours.

General procedure for olefin cross metathesis of 1-hexene with Lewis acids in CDCl₃ (Table 1). A test tube equipped with a magnetic stirrer was charged with 100mg of 1-hexene (.149mL, 1.19mmol), 20 mol% of boron-containing Lewis acid (FPB, PhenB, PinB, or OHB) (237µmol), and 1mL of CDCl₃. 1 mol% of catalyst (G1,G2, HG1, or HG2) was then added. The reaction was then capped with a septum and stirred under constant argon atmosphere at 45°C for 15 hours.

Bulk olefin cross metathesis 1-hexene. A test tube equipped with a magnetic stirrer was charged with 250mg of 1-hexene. 1 mol% of catalyst (G1 or G2) was then added. The reaction was then capped with a septum and stirred under constant argon atmosphere at 45°C for 15 hours.

Bulk olefin cross metathesis 1-hexene with PhenB. A test tube equipped with a magnetic stirrer was charged with 250mg of 1-hexene (.149mL, 1.19mmol), 20 mol% of triphenyl borane (PhenB) (30µmol). 1 mol% of catalyst (G1 or G2) was then added. The reaction was then capped with a septum and stirred under constant argon atmosphere at 45°C for 15 hours.

General procedure for Lewis acid optimization (Figure 4). A test tube equipped with a magnetic stirrer was charged with 100mg of 1-hexene (.149mL, 1.19mmol) and 1mL CDCl_3 . The amount of pinacol phenylboronate (PinB) was varied (5, 10, 15, 20, 30, 40, or 50 mol%) and added to the test tube. 1 mol% of Grubbs 2nd generation catalyst was then added. The reaction was then capped with a septum and stirred under constant argon atmosphere at 45°C for 15 hours.

2.5 Representative Spectra

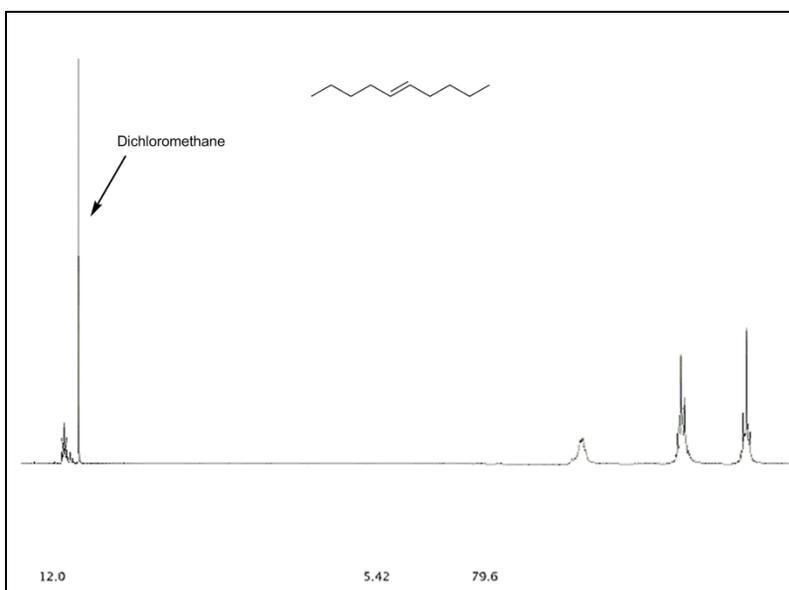


Figure 2 - 8. ¹H NMR of cross metathesis reaction. 5-decene is produced from control experiment using Hoveyda-Grubbs 1st generation catalyst.

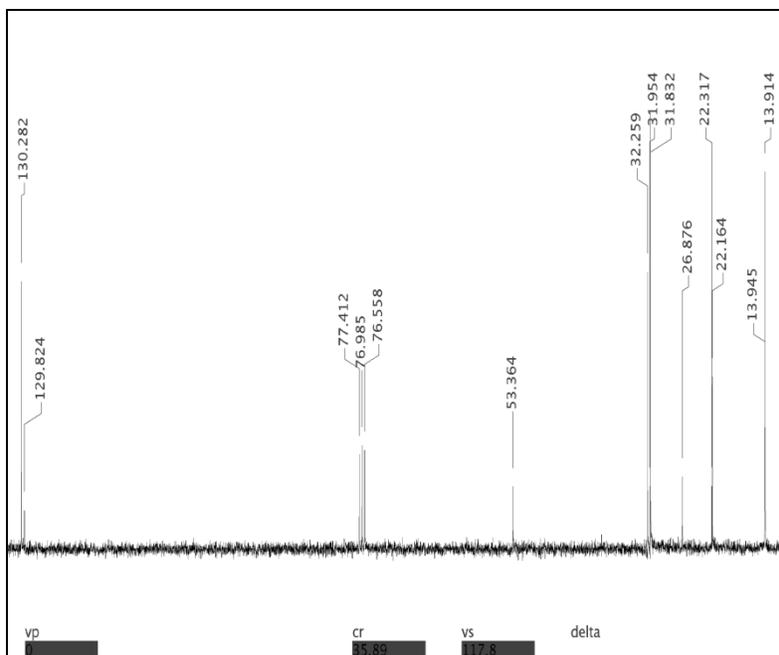


Figure 2 - 9. ^{13}C NMR of cross metathesis reaction. 5-decene is produced from control experiment using Hoveyda-Grubbs 1st generation catalyst.

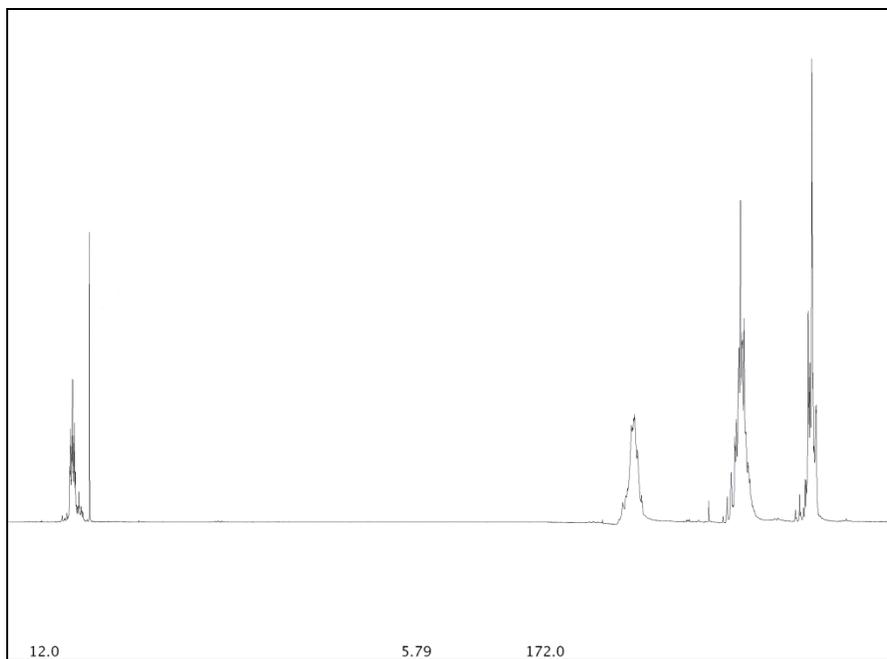


Figure 2 - 10. ^1H NMR of cross metathesis reaction. 5-decene is produced from control experiment using Hoveyda-Grubbs 2nd generation catalyst.

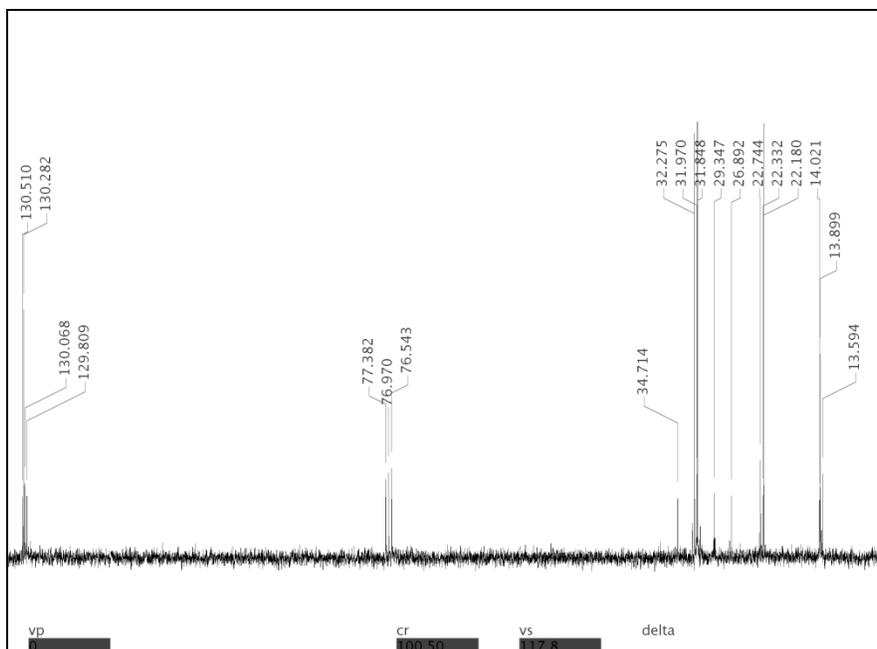


Figure 2 - 11. ^{13}C NMR of cross metathesis reaction. 5-decene is produced from control experiment using Hoveyda-Grubbs 2nd generation catalyst.

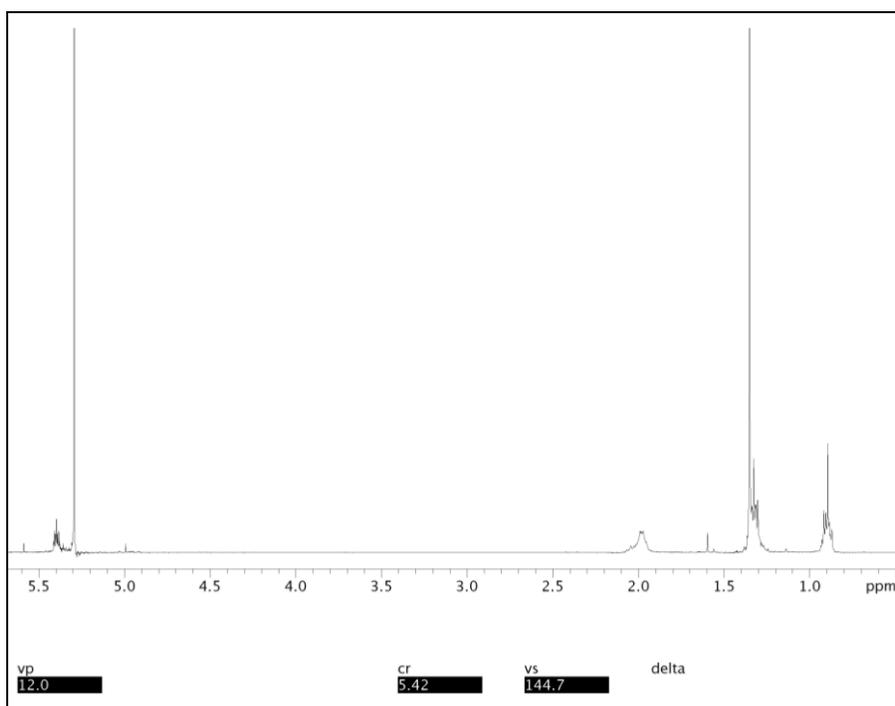


Figure 2 - 12. ^1H NMR of cross metathesis reaction. 5-decene is produced using Hoveyda-Grubbs 2nd generation catalyst, residual pinacol phenylboronate is still observed in the NMR.

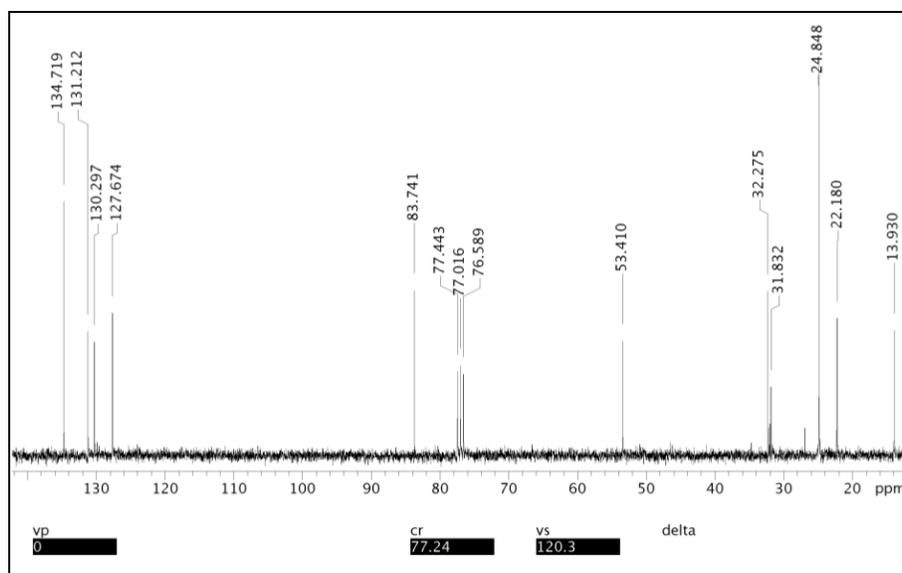


Figure 2 - 13. ^{13}C NMR of cross metathesis reaction. 5-decene is produced using Hoveyda-Grubbs 2nd generation catalyst, residual pinacol phenylboronate is still observed in the NMR.

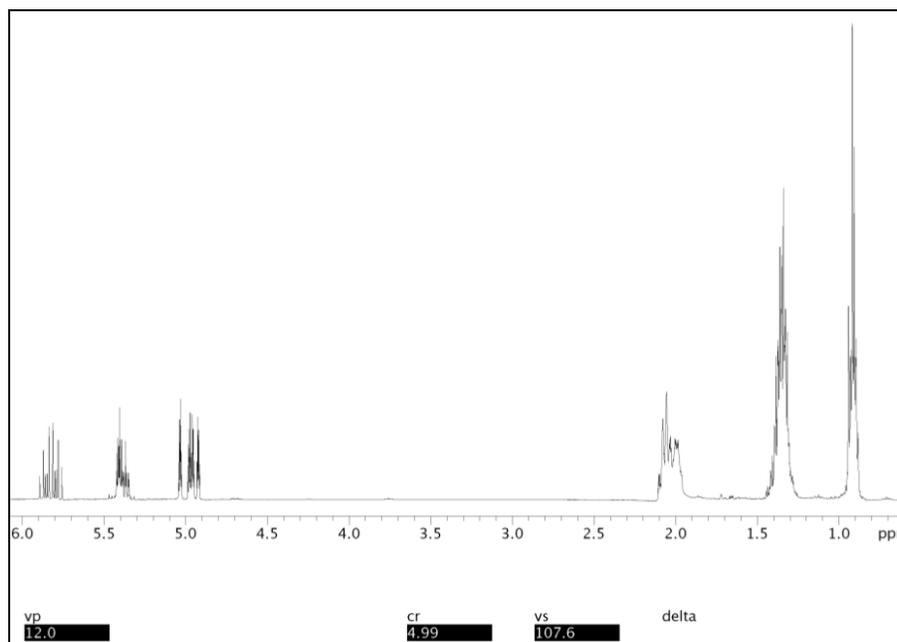


Figure 2 - 14. ^1H NMR of cross metathesis reaction. 5-decene is produced from control experiment using Grubbs 2nd generation catalyst, residual 1-hexene is observed.

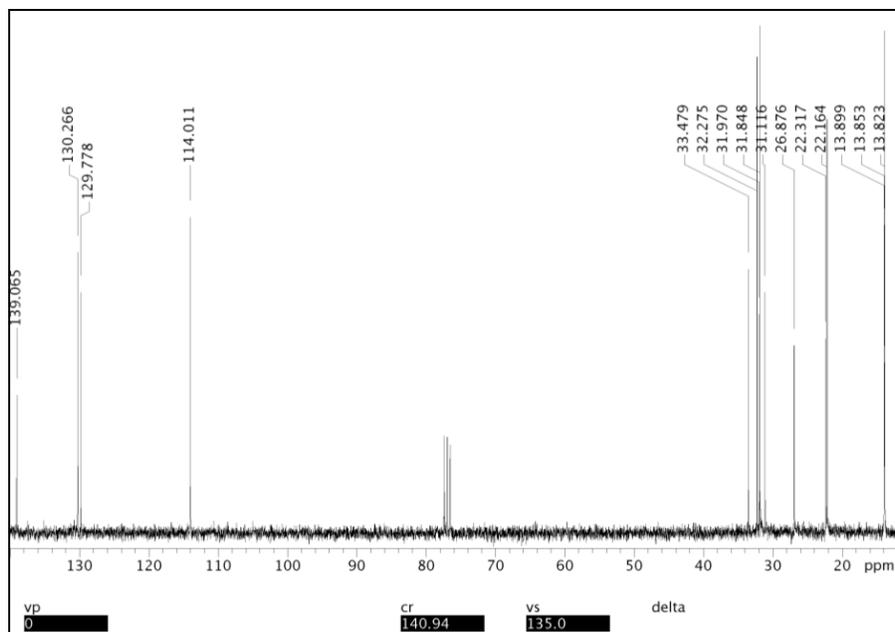


Figure 2 - 15. ^{13}C NMR of cross metathesis reaction. 5-decene is produced from control experiment using Grubbs 2nd generation catalyst, residual 1-hexene is observed.

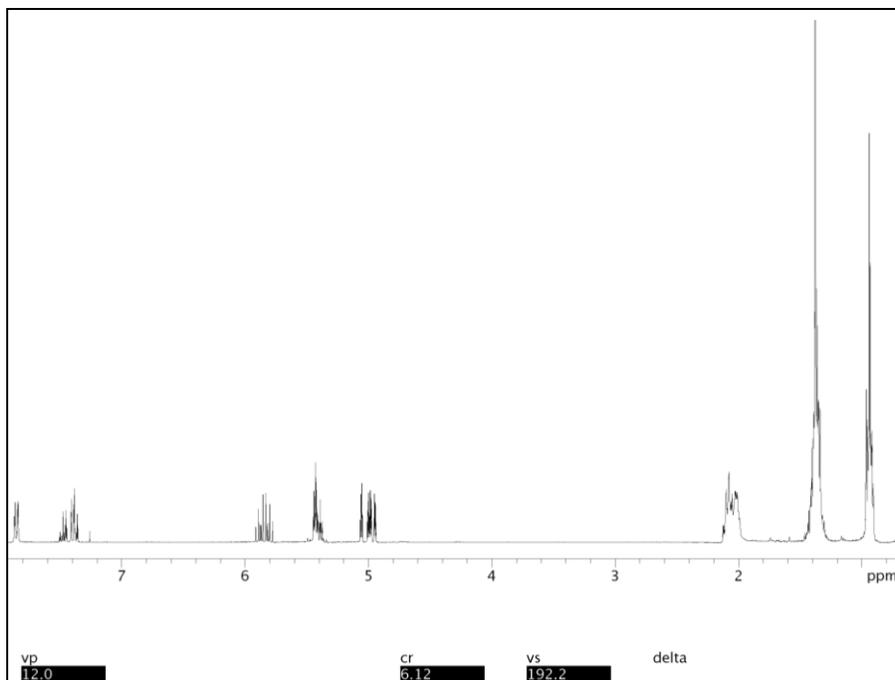


Figure 2 - 16. ^1H NMR of cross metathesis reaction. 5-decene is produced using Grubbs 2nd generation catalyst, residual 1-hexene and pinacol phenylboronnate are observed.

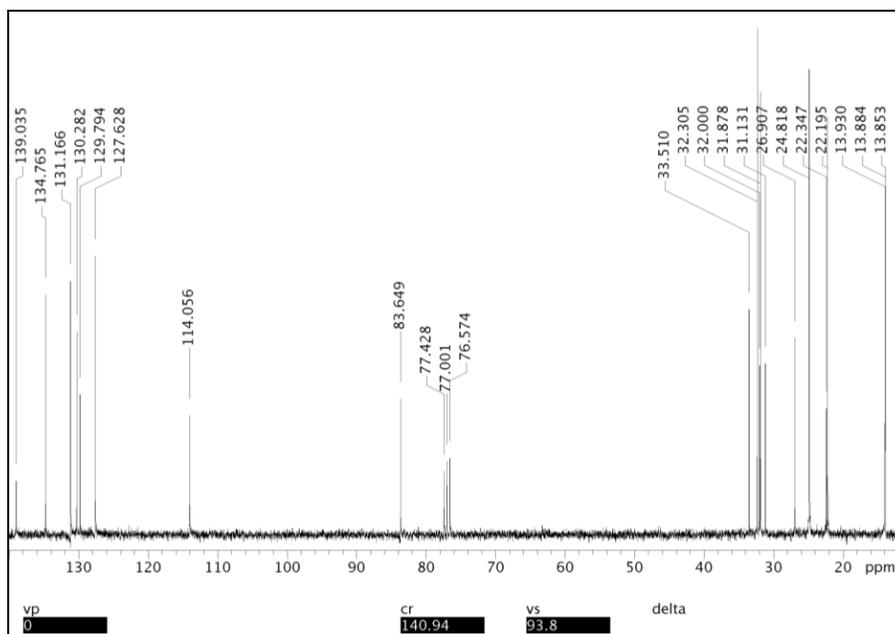


Figure 2 - 17. ^{13}C NMR of cross metathesis reaction. 5-decene is produced using Grubbs 2nd generation catalyst, residual 1-hexene and pinacol phenylboronate are observed.

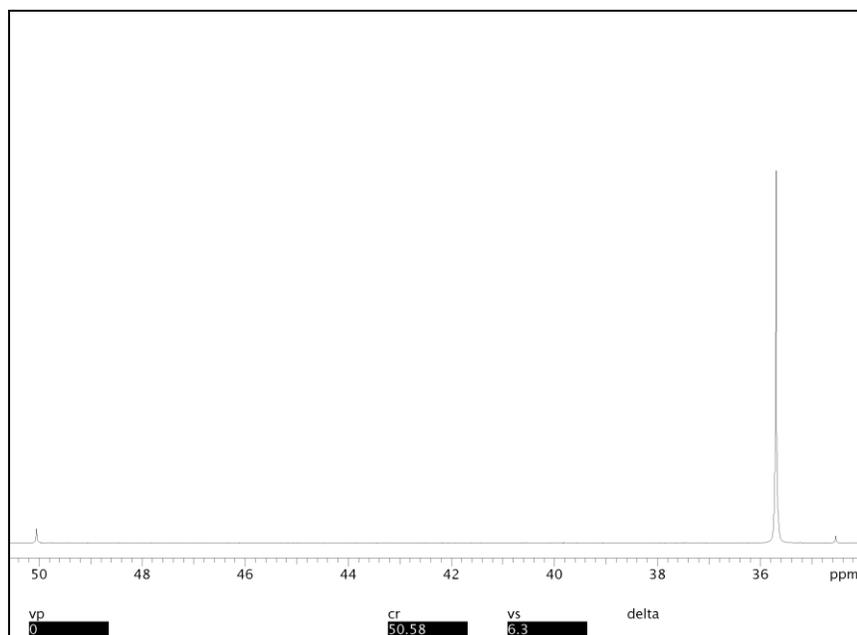


Figure 2 - 18. ^{31}P NMR of Grubbs 1st generation catalyst in the presence of Bpin Lewis acid.

CHAPTER 3
Use of Ionic Liquids as a Medium for ADMET Polymerization

3.1 Background

ADMET has the ability to create high molecular weight polymer. However, this is not a favorable reaction since the equilibrium constant is very low. Fortunately, the polymerization can be driven forward by removal of ethylene which is formed as a byproduct of olefin metathesis (Figure 3 - 1). Several methods have been developed accomplish this task and, as a result, high molecular weight polymers have been made via ADMET.

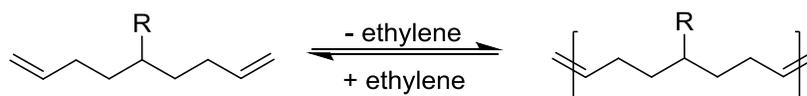


Figure 3 - 1. ADMET equilibrium reaction

The earliest and most widely employed method of ethylene removal is the use of high vacuum conditions.⁶³ This technique proves to be extremely versatile, easy to set up, and minimizes impurities in the system. Though widely used successfully, bulk ADMET polymerization has several drawbacks. In a bulk system, only liquid monomers can be used effectively. Investigations into solid-state ADMET polymerization have shown to be successful, however reaction times are generally on the order of weeks.^{104,105} Another drawback is viscosity; as the polymerization proceeds, the viscosity of the reaction medium increases, making removal of the ethylene inefficient. Finally, ADMET monomers are largely non-polar. Non-polar solvents have been shown to reduce the effectiveness of olefin metathesis catalyst.⁹⁵⁻⁹⁷ This is because non-polar solvents don't effectively solvate or stabilize the active catalyst. Non-coordinating polar solvents, on the other hand, tend to increase the rate of olefin metathesis. So while

bulk polymerization is the simplest to set up and most widely used, there are some areas of improvement.

The next ADMET polymerization method that is widely used doesn't rely on a vacuum system to remove the ethylene. This technique utilizes a fairly high boiling solvent, such as toluene, to dissolve the monomer and catalyst followed by purging the reaction with a neutral atmosphere during the polymerization.¹⁰⁶ This method allows for solid monomers to polymerized, keeps the viscosity low, and provides a solvent that both dissolves and stabilizes the olefin metathesis catalyst. However this technique has some drawbacks as well. The use of solvent introduces another possible source of impurities to contaminate the reaction, so only solvents that have been extensively purified and degassed can be used. Another problem is that the solvent evaporates due to being constantly purged, so more has to be added, risking exposing the reaction to air and other impurities. Most importantly the removal of ethylene by this method is not always the most efficient. Fortunately, this problem can be solved using a slight modification.

The final method for ADMET polymerization is known as the high-boiling solvent method.¹⁰⁷ As the name suggests a high boiling solvent is used, generally 1,2-dibromobenzene with a boiling point of 224°C. The polymerization is then held under a gentle vacuum, around 40 torr, while simultaneously purging with a neutral atmosphere. This method benefits from many of the same advantages as seen in the previous, neutral atmosphere method. However, it also comes with many of the same drawbacks. Fortunately, ethylene removal is more efficient than by purging with neutral atmosphere alone.

By using ionic liquids (ILs) as an ADMET solvent, it is possible to combine many of the advantages of previous methods. This method was first attempted in the dissertation of Yong Yang in Dr. Timothy Swager's group at the Massachusetts Institute of Technology, but was never optimized.¹⁰⁸ Ionic liquids are ideal solvents for ADMET polymerization. ILs have very low vapor pressure making them perfect for high vacuum applications. They are known to dissolve metal catalysts and many organic molecules, but are generally immiscible with many organic solvents. ILs provide polar, non-coordinating environments that can enhance catalyst activity, and they are stable over a wide range of temperatures.¹⁰⁹ However, despite all of these advantages, using ILs as a reaction medium for ADMET remained elusive. Yong Yang observed that only oligomers were formed when attempting to polymerize triptycene containing dienes (Figure 3 - 2). However, at high catalyst loading, 11 mol%, and long polymerization times, moderate molecular weight polymer was obtained. The goal of this project, in collaboration with the Swager group, is to optimize the use of ILs for use in ADMET polymerization and study the cause of the low conversions observed.

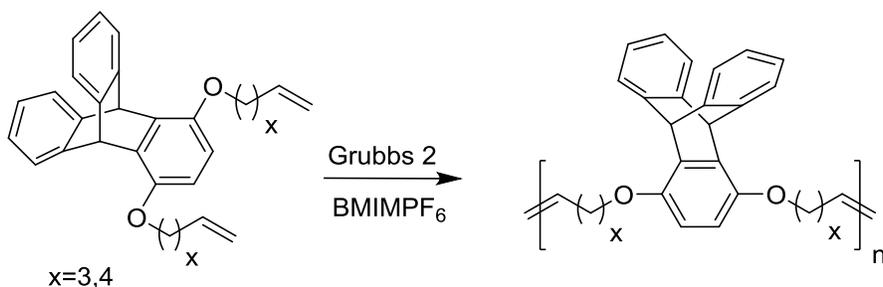


Figure 3 - 2. Polymerization of triptycene monomers with Grubbs 2nd generation catalyst in ionic liquid¹⁰⁸

3.2 Results and Discussion

A simple model polymerization was used to optimize the use ionic liquids in ADMET polymerization. 1,9 decadiene was polymerized at 50°C using G1 catalyst (Figure 3 - 3).

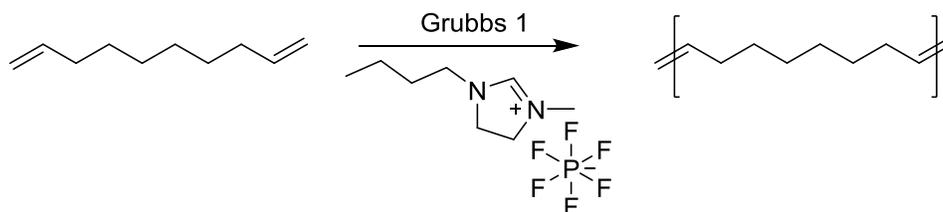


Figure 3 - 3. Model polymerization of 1,9 decadiene to optimize ionic liquid polymerization techniques

1-butyl-3-methylimidazolium hexafluorophosphate was chosen as the ionic liquid to study as it has shown to be highly compatible with small molecule olefin metathesis. G1 was chosen as the catalyst since it doesn't have the propensity to isomerize the olefin, but the results can translate to other ruthenium centered olefin metathesis catalysts. The first concern with using ILs is their purity. Purity of ILs varies greatly depending on the batch and supplier. ILs can come in a range of colors from colorless to orange, indicating more or less impurities. Common impurities found in 1-butyl-3-methylimidazolium hexafluorophosphate include water, 1-butyl-3-methylimidazolium chloride, and 1-butyl-3-methylimidazole (Figure 3 - 4).⁹⁵

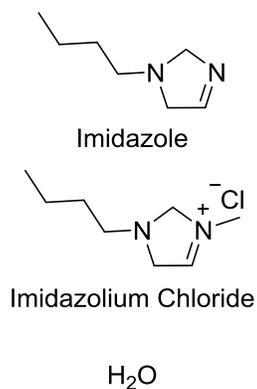


Figure 3 - 4. Common impurities found in 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆)⁹⁵

The IL was purified via a neutral alumina plug; this caused the IL to go from yellow to nearly colorless. ILs are also extremely proficient at dissolving gases, some of which, such as oxygen, can inhibit the ADMET polymerization. To remove these gases the solvent is freeze-pump-thawed in triplicate. The IL is then handled using dry techniques to avoid absorption of water or non-neutral gasses.

Table 3 - 1. Polymerization of 1,9 decadiene at various catalyst concentrations

[G1] (mol%)	M _n (g/mol)	M _w (g/mol)	PDI
.25	5554	8649	1.56
.5	18454	41790	2.27
1	12746	26656	2.09
2	10717	24676	2.3
3	12457	26664	2.14
4	9541	22851	2.4
7	8847	20379	2.28
11	8737	19177	2.2

The first studies that were conducted with the purified IL were catalyst concentration experiments (Table 3 – 1). Polymerizations were run with the concentration of catalysts at .25, .5, 1, 2, 3, 4, 7, and 11 mol%. Low catalyst concentrations, .25 mol%, resulted in fairly low molecular weight polymer. At .5 mol% catalyst, however, the molecular weight sharply increased to over 18000 g/mol. As the catalyst concentration was increase past this point, the molecular weights decreased. For the purpose of these studies .5 mol% was selected. This catalyst concentration is comparable to the amount of catalyst used in both bulk and high-boiling solvent polymerization techniques.

A kinetic study was then run to determine the optimal duration of the polymerization. Polymerizations were conducted and stopped at intervals of 6, 18, 24, 48, 72, and 96 hours (Figure 3 - 5).

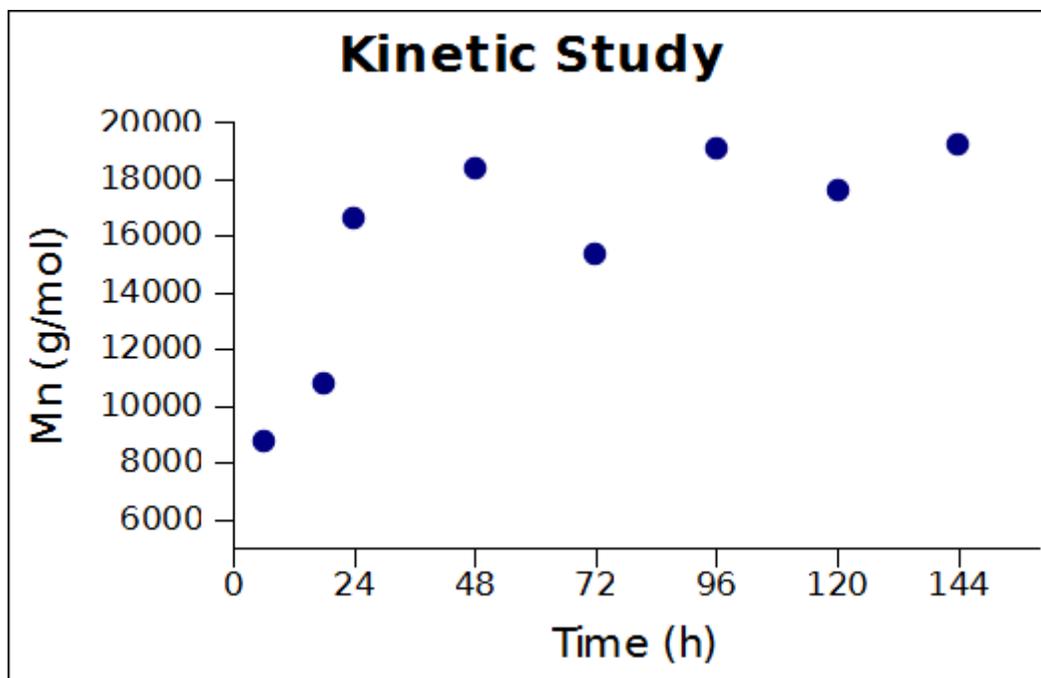


Figure 3 - 5. Kinetics of ADMET polymerization of 1,9 decadiene in ionic liquid, maximum molecular weights were achieved after 48 hours.

Maximum molecular weights were reached after only 48 hours, significantly shorter than many of the reported polymerizations using the bulk and high-boiling solvent methods.

With the purified IL, the high catalyst loading and long reaction times were no longer needed. To study the effects of known IL impurities on ADMET polymerization, a number of test reactions were run and small amounts of impurities were added (Figure 3 – 6, blue bar). The control reaction obtained a M_n of about 11900 g/mol. Upon addition of water and the imidazolium chloride, no reduction in molecular weight was observed. Addition of the imidazole compound resulted in no polymer formation. Imidazole is a known Grubbs catalyst poison. In fact, it poisons the catalysts in a catalytic manner. This means that an almost undetectable amount of imidazole can completely disrupt the ADMET polymerization.^{66,79}

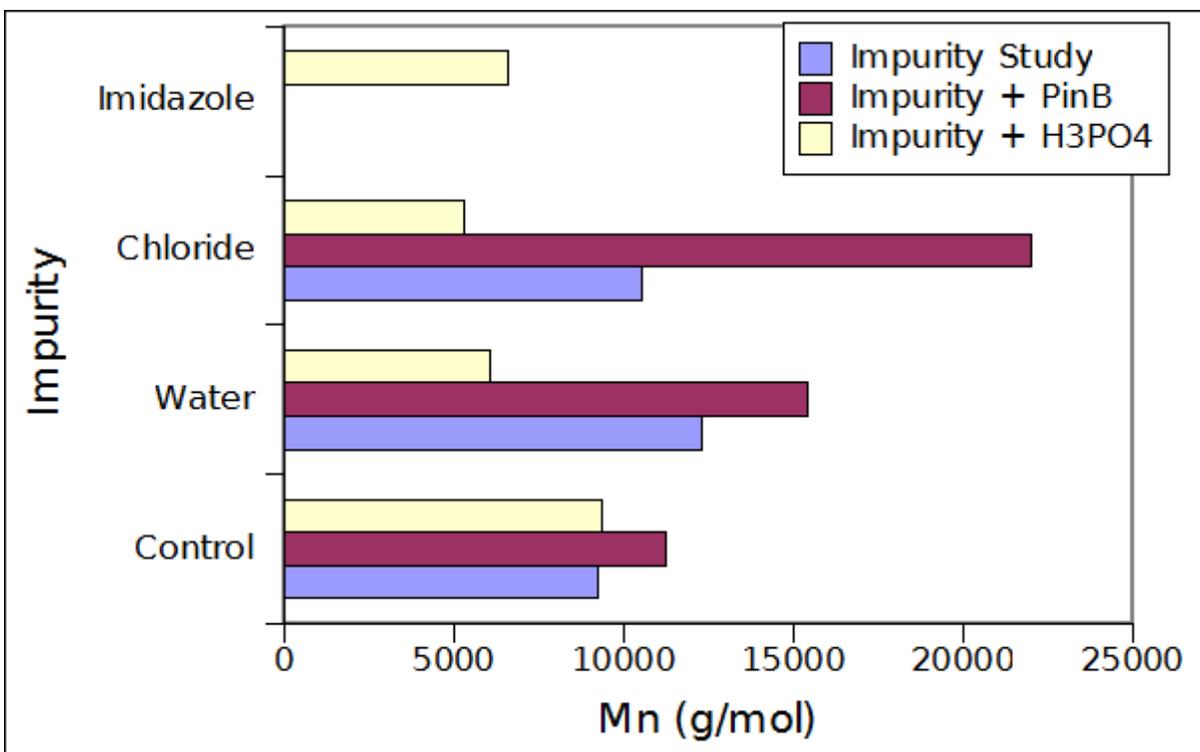


Figure 3 - 6. The effects of common ionic liquid impurities on ADMET polymerization. Blue bar: Polymerization was run with only the impurity stated. Maroon bar: Polymerization was run with impurity as well as pinacol phenyl borate (PinB). Yellow bar: Polymerization was run with impurity and phosphoric acid (H₃PO₄).

In an attempt to neutralize the effects of the impurities, several additives were tested. The first additive was phenyl pinacol borate (PinB), this Lewis acid has been shown to increase the activity of phosphine containing Grubbs catalysts.¹⁰³ In the control reaction molecular weights involving PinB were slightly higher, as expected (Figure 3 – 6, maroon bar). Similar results were seen for both the water and the imidazolium chloride experiments. Unfortunately, imidazole still prevented any polymer from being formed.

The other additive investigated was phosphoric acid, which has also been shown to be compatible with olefin metathesis.^{66,79} In the control experiment no difference in molecular weight was seen (Figure 3 – 6, off-white bar). The molecular weights

decreased slightly in the presence of both water and imidazolium chloride. However, in the imidazole containing experiment, polymer was formed. This is believed to be due to the protination of the imidazole, shutting down the pathway of catalyst poisoning. So while the phosphoric acid resulted in slightly lower molecular weights in the water and imidazolium chloride polymerization, it allowed the formation of polymer in the presence of the imidazole compound.

These optimizations were applied to a well studied system and compared to the high-boiling solvent method. First 1,4-bis(undec-10-en-1-yloxy)-tritycene (**T9**) was synthesized following the procedure described by Delgado *et al.*¹¹⁰ **T9** was then polymerized using G1(Figure 3 - 7).

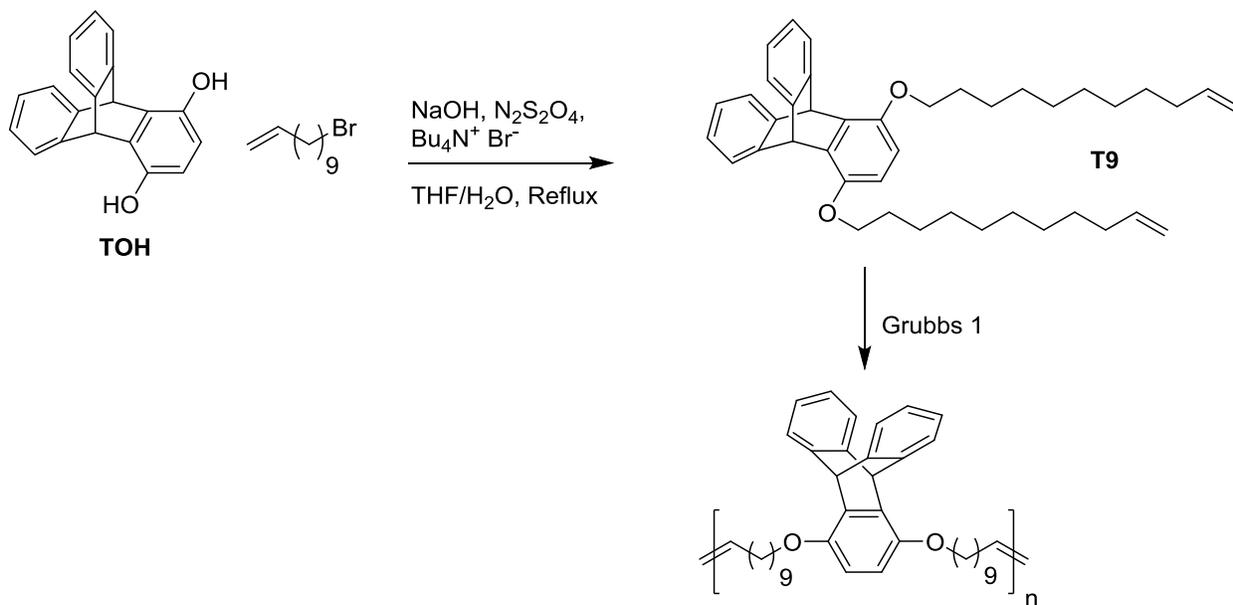


Figure 3 - 7. Synthesis of triptycene monomer (**T9**) and polymerization with Grubbs 1st generation catalyst

Three polymerizations were conducted at different temperatures: 50, 80, and 100°C for 48 hours in BMIMPF₆ (Table 3 - 2).

Table 3 - 2. Polymerization of **T9** and **T3**

Monomer	Temperature (°C)	Catalyst	M _n (g/mol)	M _w (g/mol)	PDI	DP _n	DP _w
T9	50	G1	2511	5966	2.38	4.5	10.6
T9	80	G1	1814	5087	2.8	3.2	9.1
T9	100	G1	2209	6362	2.9	3.9	11.3
T3	100	G1	1482	2271	1.53	3.8	5.8
T3	100	G2	2079	3621	1.74	5.28	9.2

At low temperatures, 50°C, the monomer **T9** was minimally soluble in the ionic liquid so only oligomers were formed, M_n of 2511 g/mol. As the temperature increases the monomer begins to melt and dissolve in the ionic liquid however no increase in molecular weights are observed. At 100°C the monomer is a liquid, and was miscible with the ionic liquid solvent but still no increase in molecular weights. These results lead to the conclusion that the molecular weight of **T9** is determined by the solubility of the polymer, which in this case only leads to oligomers.

The next study compared the optimized polymerization methods to the technique used by Yang *et al.*¹⁰⁸ The 1,4-bis(pent-5-en-1-yloxy)-tritycene (**T3**) was synthesized following the reported procedure and polymerized via G1 and G2 (Figure 3 - 8)

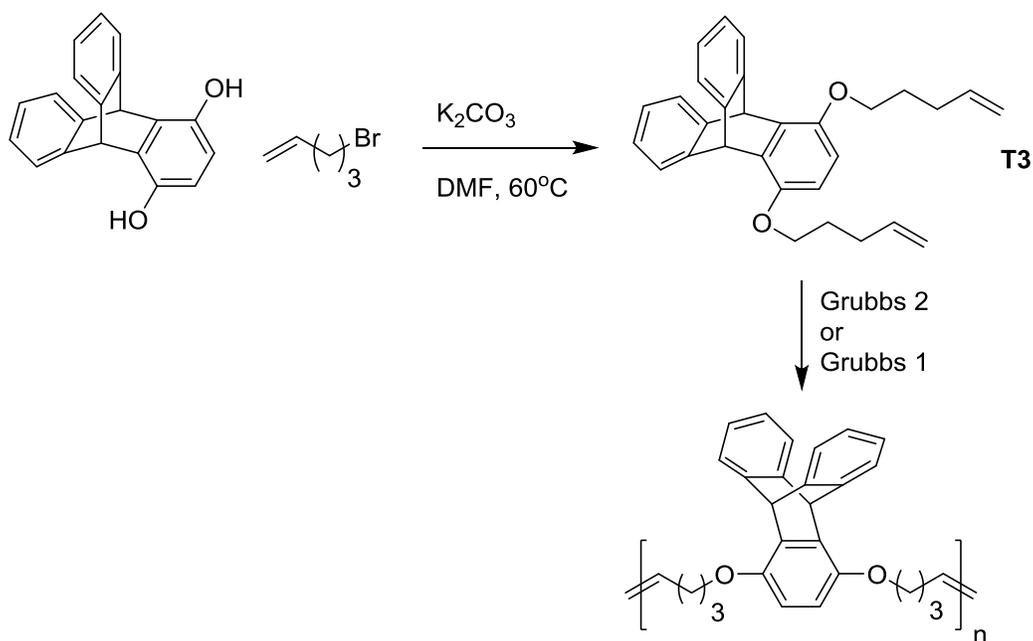


Figure 3 - 8. Synthesis of triptycene monomer (**T3**) and polymerization with Grubbs 1st and 2nd generation catalyst

Using the optimization reactions above, **T3** was polymerized for 48 hours at $100^\circ C$ using both G1 and G2 at .5 mol% catalyst (Table 3 – 2). The shorter alkyl chain length leads to an increase in crystallinity of the monomer and lower solubility. As a result, low molecular weights were observed; similar to the polymer created from **T9**.

3.3 Conclusion

This study has optimized the use of ionic liquids in ADMET polymerization. It has demonstrated that ILs are compatible with catalyst loading level comparable to that of both bulk and high-boiling solvent polymerization methods. Polymerization times were significantly shorter than many reported ADMET polymerization techniques. Impurities can be detrimental to the polymerization; however some impurities such as water and imidazolium chloride have shown to have no effect on molecular weight. Imidazole impurities completely shut down the polymerization, but can be neutralized using a protic acid. Solubility played an important role in the polymerization of triptycene-

containing monomers. Higher temperatures resulted in no increase in molecular weights due to insolubility of the polymer. All of these studies demonstrate that ionic liquids are a viable medium for ADMET polymerization.

3.4 Experimental

3.4.1 Materials and Instrumentation

1,9 decadiene was purchased from Sigma Aldrich and purified via silica plug. It was then degassed in triplicate. 1-Butyl-3-methylimidazolium hexafluorophosphate was purchased from AK Scientific and purified via a neutral alumina plug followed by degassing via freeze-pump thaw in triplicate. All other materials were purchased from Aldrich and used without further purification unless noted. Grubbs 1st and 2nd generation catalyst (G1 and G2) as well as Hoveyda-Grubbs 1st and 2nd generation catalyst (HG1 and HG2) were kindly provided by Materia, Inc. The deuterated chloroform solvent was used from a freshly opened bottle and stored under nitrogen in a desiccator. All ¹H NMR, and ¹³C NMR were obtained on a Varian Mercury 300MHz spectrometer and recorded in CDCl₃.

3.4.2 Procedures

General procedure for catalyst concentration study. Under constant argon flow, .25g of 1,9 decadiene was added to flame-dried Schlenk flask equipped with a magnetic stir bar. Also under constant argon flow 1.5mL of 1-butyl-3-methylimidazolium hexafluorophosphate was added. Grubbs 1st generation catalyst was then added to the reaction mixture. The amount was varied between .25, .5, 1, 2, 3, 4, 7, and 11mol%. The reaction was then placed under high vacuum at 50°C while stirring. After 48 hours the reaction quenched with a solution of 2mL of ethyl vinyl ether in 10mL of toluene. The toluene layer was separated from the ionic liquid via pipette and the solvent removed

under vacuum. The polymer was then dissolved in a minimal amount of toluene and precipitated into 250mL of cold ethanol. The polymer was filtered out and NMR was used to determine molecular weights.

General procedure for kinetic study. Under constant argon flow, .25g of 1,9 decadiene was added to flame-dried Schlenk flask equipped with a magnetic stir bar. Also under constant argon flow 1.5mL of 1-butyl-3-methylimidazolium hexafluorophosphate was added. .5 mol% of Grubbs 1st generation catalyst was then added to the reaction mixture. The reaction was then placed under high vacuum at 50°C while stirring. The polymerization was run for 6, 18, 24, 48, 72, and 96 hours. After the requisite time hours the reaction quenched with a solution of 2mL of ethyl vinyl ether in 10mL of toluene. The toluene layer was separated from the ionic liquid via pipette and the solvent removed under vacuum. The polymer was then dissolved in a minimal amount of toluene and precipitated into 250mL of cold ethanol. The polymer was filtered out and NMR was used to determine molecular weights.

General procedure for the control impurity study. Under constant argon flow, .25g of 1,9 decadiene was added to flame-dried Schlenk flask equipped with a magnetic stir bar. Also under constant argon flow 1.5mL of 1-butyl-3-methylimidazolium hexafluorophosphate was added. .5 mol% of Grubbs 1st generation catalyst was then added to the reaction mixture. Finally, .5 mol% of the impurity; water, 1-butyl-3-methylimidazolium bromide, or 1-butyl imidazole was added to the reaction mixture. The reaction was then placed under high vacuum at 50°C while stirring. After 48 hours the reaction quenched with a solution of 2mL of ethyl vinyl ether in 10mL of toluene. The toluene layer was separated from the ionic liquid via pipette and the solvent removed

under vacuum. The polymer was then dissolved in a minimal amount of toluene and precipitated into 250mL of cold ethanol. The polymer was filtered and NMR was used to determine molecular weights.

General procedure for impurity study with phenyl pinacol borate. Under constant argon flow, .25g of 1, 9 decadiene and 20 mol% of phenyl pinacol borate were added to flame-dried Schlenk flask equipped with a magnetic stir bar. Also under constant argon flow 1.5mL of 1-butyl-3-methylimidazolium hexafluorophosphate was added. .5 mol% of Grubbs 1st generation catalyst was then added to the reaction mixture. Finally, .5 mol% of the impurity; water, 1-butyl-3-methylimidazolium bromide, or 1-butyl imidazole was added to the reaction mixture. The reaction was then placed under high vacuum at 50°C while stirring. After 48 hours the reaction quenched with a solution of 2mL of ethyl vinyl ether in 10mL of toluene. The toluene layer was separated from the ionic liquid via pipette and the solvent removed under vacuum. The polymer was then dissolved in a minimal amount of toluene and precipitated into 250mL of cold ethanol. The polymer was filtered and NMR was used to determine molecular weights.

General procedure for impurity study with phosphoric acid. Under constant argon flow, .25g of 1, 9 decadiene and 20 mol% of solid phosphoric acid were added to flame-dried Schlenk flask equipped with a magnetic stir bar. Also under constant argon flow 1.5mL of 1-butyl-3-methylimidazolium hexafluorophosphate was added. .5 mol% of Grubbs 1st generation catalyst was then added to the reaction mixture. Finally, .5 mol% of the impurity; water, 1-butyl-3-methylimidazolium bromide, or 1-butyl imidazole was added to the reaction mixture. The reaction was then placed under high vacuum at 50°C while stirring. After 48 hours the reaction quenched with a solution of 2mL of ethyl

vinyl ether in 10mL of toluene. The toluene layer was separated from the ionic liquid via pipette and the solvent removed under vacuum. The polymer was then dissolved in a minimal amount of toluene and precipitated into 250mL of cold ethanol. The polymer was filtered and NMR was used to determine molecular weights.

Synthesis of 1,4-bis(undec-10-en-1-yloxy)-tritycene (T9). A round-bottom flask equipped with a magnetic stirbar was charged with 50mL of water and 50mL of THF. To this solution 4g (14 mmol) of triptycene-1,4-diol, 13.25g (57 mmol) of 11-bromo-1-undecene, 1.35g (4.2 mmol) of tetrabutyl ammonium bromide, 7.26g (182 mmol) of sodium hydroxide, and 2.18g (14 mmol) of sodium dithionite and refluxed overnight. The reaction was then cooled to room temperature and diethyl ether was added. The solution was separated and the aqueous phase was then extracted once more with diethyl ether. The organic phases were combined and washed with a 3M solution of sodium hydroxide and dried over magnesium sulfate. The solvent was evaporated *in vacuo*. The resulting residue was then dissolved in the minimum amount of dichloromethane and precipitated twice into cold ethanol to give 2.5g of **T9**.

Yield: 30% ^1H NMR (300 MHz, CDCl_3 , ppm): δ = 7.40 (t, 4H), 6.99 (t, 4H), 6.45 (s, 2H), 5.92-5.79 (m, 4H), 5.10-4.9 (m, 4H), 3.95 (t, 4H), 2.15-2.00 (q, 4H), 1.90-1.79 (m, 4H), 1.70-1.20 (m, 24H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ = 148.44, 145.82, 139.23, 135.65, 124.88, 123.73, 114.18, 110.64, 69.65, 47.49, 29.66, 29.51, 29.45, 29.21, 28.98, 26.23.

Polymerization of 1,4-bis(undec-10-en-1-yloxy)-tritycene. Under constant argon flow, .5g of **T9** was added to flame-dried Schlenk flask equipped with a magnetic stir bar. Also under constant argon flow 1.5mL of 1-butyl-3-methylimidazolium

hexafluorophosphate was added. .5 mol% of Grubbs 1st generation catalyst was then added to the reaction mixture. The reaction was then placed under high vacuum and polymerized for 48 hours. The temperature was kept at 50, 80, or 100°C. After the requisite time hours the reaction quenched with a solution of 2mL of ethyl vinyl ether in 10mL of toluene. The toluene layer was separated from the ionic liquid via pipette and the solvent removed under vacuum. The polymer was then dissolved in a minimal amount of toluene and precipitated into 250mL of cold ethanol. The polymer was filtered out and NMR was used to determine molecular weights.

Synthesis of 1,4-bis(pent-5-en-1-yloxy)-tritycene (T3). A flame-dried 3-neck flask charged with a magnetic stir bar was charged with 4.3g (15 mmol) of triptycene-1,4-diol, 4.35g (31.5 mmol) of potassium carbonate, .and .33g (2 mmol) of potassium iodide was suspended in anhydrous DMF. The suspension was heated to 65°C for 30 minutes, then 4.65 mL (37.5 mmol) 5-bromo-1-pentene was added dropwise. The reaction was heated overnight at 65°C. It was then cooled to room temperature and the solvent was removed via vacuum distillation. The remaining residue was dissolved in dichloromethane washed three times with 1M HCl, and twice with deionized water. The solvent was removed *in vacuo* and the residue was then dissolved in the minimum amount of dichloromethane and precipitated into cold methanol. The product was filtered and then purified via column chromatography (hexane:ethyl acetate 8:1) yielding 4.07g of **T3**.

Yield: 65% ¹H NMR (300 MHz, CDCl₃, ppm): δ= 7.40 (m, 4H), 6.99 (m, 4H), 6.50 (s, 2H), 6.02-5.85 (m, 4H), 5.20-5.03 (m, 4H), 3.95 (t, 4H), 2.35 (q, 4H), 1.95 (m, 4H).

^{13}C NMR (75 MHz, CDCl_3 , ppm): δ = 148.55, 145.92, 138.23, 135.87, 125.12, 123.92, 115.37, 110.80, 68.98, 47.67, 30.56, 28.92

Polymerization of 1,4-bis(pent-5-en-1-yloxy)-tritycene. Under constant argon flow, .5g of **T3** was added to flame-dried Schlenk flask equipped with a magnetic stir bar. Also under constant argon flow 1.5mL of 1-butyl-3-methylimidazolium hexafluorophosphate was added. .5 mol% of Grubbs 1st generation catalyst was then added to the reaction mixture. The reaction was then placed under high vacuum and polymerized for 48 hours at 100°C. After the requisite time hours the reaction quenched with a solution of 2mL of ethyl vinyl ether in 10mL of toluene. The toluene layer was separated from the ionic liquid via pipette and the solvent removed under vacuum. The polymer was then dissolved in a minimal amount of toluene and precipitated into 250mL of cold ethanol. The polymer was filtered out and NMR was used to determine molecular weights.

CHAPTER 4
Boronic Acid Chemistry: Synthesis of Boronic Acid Monomer

4.1 Background

The chemistry of boron is unique and different from that of carbon chemistry. The most striking difference between carbon and boron is that many boron compounds naturally form planar trivalent species (Figure 4 - 1).¹¹¹

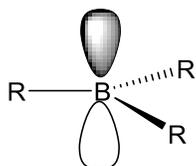


Figure 4 - 1. Planar boron compound with empty p orbitals

Due to this, boron contains an empty P-orbital so is naturally sp^2 hybridized. Another consequence of having an empty P-orbital is boron's propensity towards Lewis acidity. In the presence of a nucleophile, boron will accept the electrons and adopt a charged sp^3 hybridized conformation (Figure 4 - 2).¹¹¹

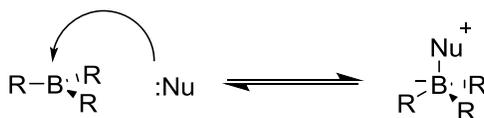


Figure 4 - 2. Nucleophilic attack on a planar boron compound to yield the tetrahedral boron species

The Lewis acidity of boron can easily be tuned from some of the weakest Lewis acids, such as boric acid, to one of the strongest, boron tribromide (Figure 4 - 3).¹¹² This is done by altering the substituents attached to the boron. Substituents that have the ability to donate electrons into the empty π -orbital yield weaker Lewis acids, while substituents that are unable to donate electron lead to very strong Lewis acids.

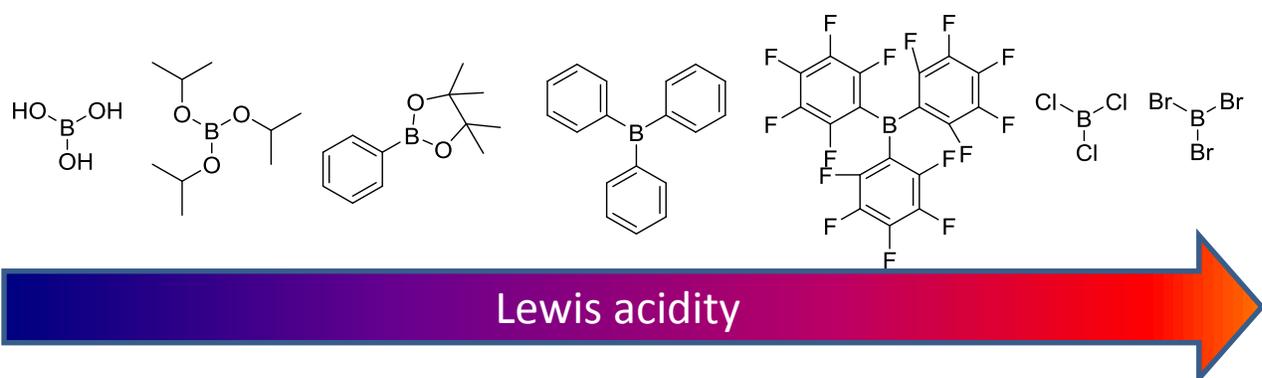


Figure 4 – 3. Lewis acidity as a function of boron substitution, by changing substituent on the boron a wide range of Lewis acidities can be achieved.

Alkyl boron compounds are known to undergo deboronation (Figure 4 - 4).¹¹¹

This is where the boron is cleaved from the alkyl branch with the addition of water, or other oxidative process, across the bond.



Figure 4 – 4. Deboronation of alkyl boron compounds in the presence of water or other nucleophilic oxygen compounds.

This can be explained if we look at the bond strengths of an alkyl C-B bond and a C-O bond. A carbon-boron bond has a bond dissociation energy of about 107 kcal/mol. When compared to the boron-oxygen bond, which has bond dissociation energy of 192 kcal/mol, deboronation is thermodynamically very favorable, but generally kinetically slow.¹¹¹ The reason for the difference in bond energies is explained in Figure 4 – 5 and Figure 4 - 6.

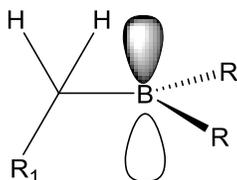


Figure 4 – 5. Alkyl carbon-boron bond. The carbon is unable to donate electrons into the boron's empty p orbital, this results in a weak C-B bond.

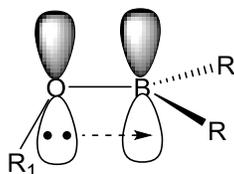


Figure 4 – 6. The oxygen in a B-O bond is capable of donating electrons to the empty p orbital of boron, this leads to partial double bond character.

In an alkyl carbon-boron system, the sp^3 hybridized carbon has no free electrons to donate into the boron's empty π -orbital. In the boron-oxygen bond, the lone pair from the oxygen is able to donate into the empty π -orbital of the boron, lending some double bond character to the system (Figure 4 – 6). This is also seen in the boron oxygen bond lengths which are around 135 pm.¹¹¹ These bonds length are indicative of some double bond character.

A stable boron-carbon bond can be made by taking advantage of the same effect that strengthens the boron-oxygen bond; specifically electrons donated into boron's empty π orbital cause formation of the stable bonds. This is found to be true with vinyl and aryl carbon-boron bonds (Figure 4 - 7).¹¹¹

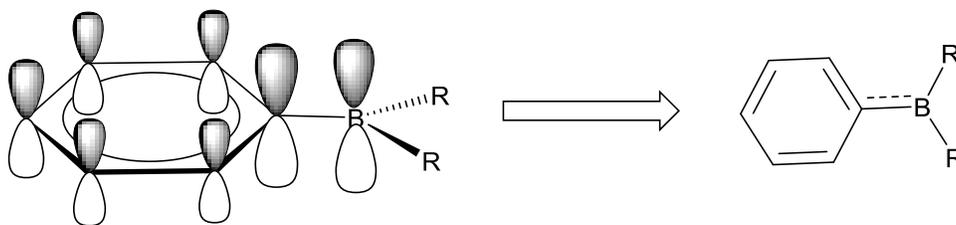


Figure 4 – 7. An aryl C-B bond is much more stable than the alkyl B-C bond due to donation of electron density from the pi system of the aryl system into the boron p orbital, increasing the strength of the B-C bond.

In an aryl boron-carbon bond, the conjugated system donates electrons into the boron's π -orbital and strengthens the bond. This forms boron-carbon bonds that are comparable in strength to the boron-oxygen bond. Keeping these facts in mind will be necessary to successfully synthesize boronic acid ADMET monomers.

Boronic acids are unique because the acidity does not come from its protons, but instead from the boron's own Lewis acidity.¹¹¹ At low pH, boronic acids are sp^2 hybridized and adopt a trigonal planar conformation; however as the pH increases they become sp^3 hybridized and conform to a tetrahedral geometry (Figure 4 - 8). The pK_a of boronic acids is defined by when there is an equal concentration of both the planar and tetrahedral species present.¹¹¹

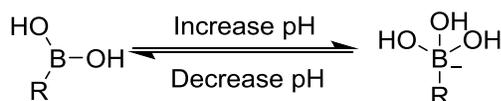


Figure 4 – 8. Boronic acids are trigonal planar at low pH, but as the pH increase they assume a charged tetrahedral configuration

Boronic acids do share some similarities with other organic acids. They have the ability to form boronic acid anhydrides. These are created when two or more boronic acids condense together and expel water. Unlike carboxylic acids, boronic acids are not limited to dimer formation, they can form cyclical boroxines and other boronic anhydride systems (Figure 4 - 9).¹¹¹

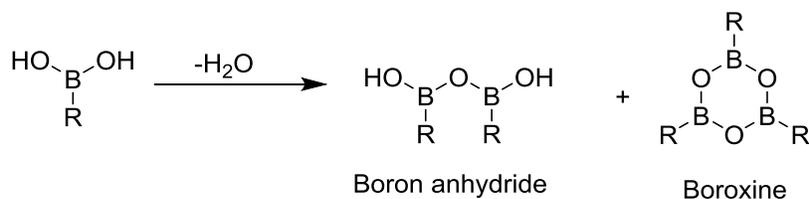


Figure 4 – 9. Formation of boron anhydride and boroxine. These compounds can be formed simply by applying vacuum to a boronic acid solution or recrystallization from a dry solvent.

By keeping the unique chemistry of boron in mind, the following chapter will describe a number of methods used to attempt and finally succeed in creating boronic acid monomers. This chapter will discuss monomer synthesis, and boronic acid deprotection both which provide a unique challenge when applied to boron chemistry.

4.2 Synthesis of Alkyl Boronic Acid Monomers

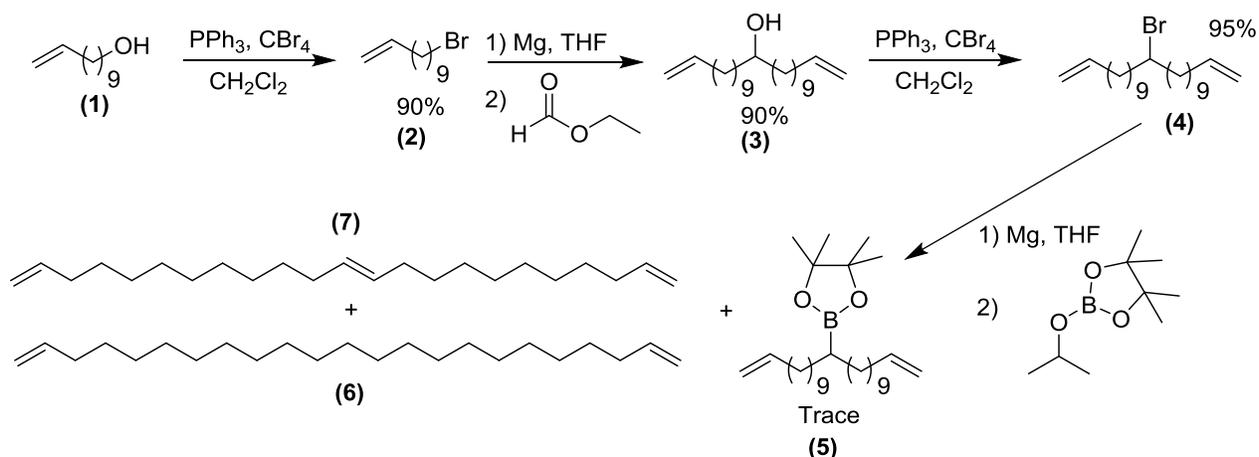


Figure 4 – 10. Synthesis of 4,4,5,5-tetra-methyl-2-(tricoso-1,22-dien-12-yl)-1,3,2-dioxaborolane (5) via borylation by grignard reaction

4.2.1 Synthesis of 4,4,5,5-tetra-methyl-2-(tricoso-1,22-dien-12-yl)-1,3,2-dioxaborolane (5) monomer.

As shown in Figure 4 - 10, the 9-spacer alcohol **1** was reacted with triphenyl phosphine and carbon tetrabromide to form the 9-spacer bromide **2**. This reaction was nearly quantitative; the loss in yield is a result of the distillation to remove the bromoform side product which cannot be removed via chromatography. The 9-spacer bromide was then reacted with Mg to form a Grignard reagent followed by the addition of ethyl formate to form the 9,9 alcohol **3**. The 9,9 alcohol **3** was then reacted with triphenyl phosphine and carbon tetrabromide to make the 9,9 bromide **4**. This proceeded in excellent yield. The bromoform could be removed via flash chromatography instead of having to be distilled off as in the synthesis of compound **2**.

A Grignard reagent was used to perform the boronation since lithiation reactions do not proceed to high conversion on sp^3 hybridized carbons. Lithium reagents are also more basic than Grignard reagents, which could lead to more elimination of the

secondary bromide **4**. After formation of the Grignard reagent, 2-isopropoxy-4,4,5,5-tetra-methyl-1,3,2-dioxaborolane was added to the reaction. Unfortunately, even using the less basic Grignard reagent, the elimination product predominated. The 9,9, boronic ester **5** was made but only in about 5% yield. The major products of the reaction were **6** and **7**. After trying a number of conditions there was no improvement of yield, so this line of synthesis was reconsidered.

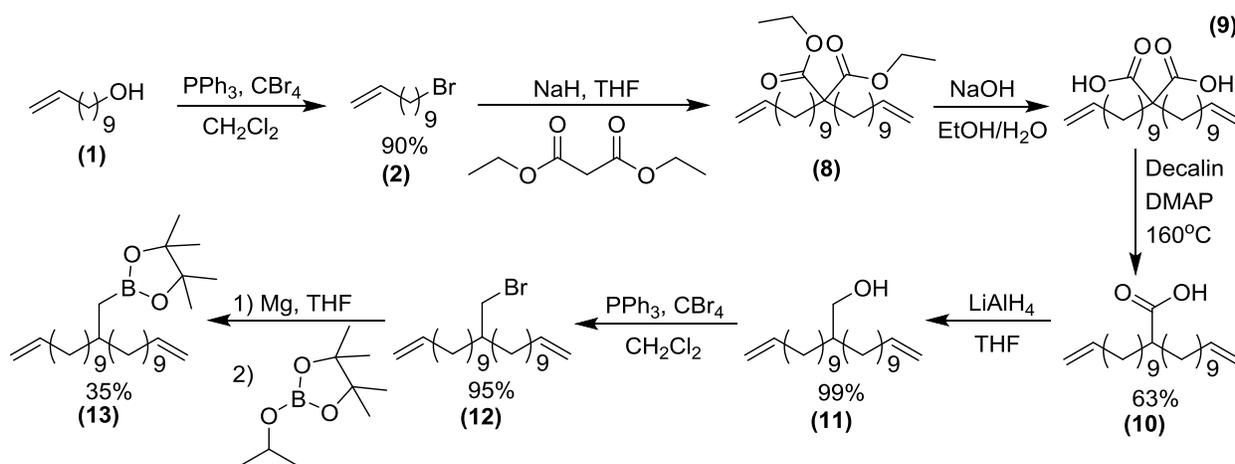


Figure 4 – 11. Synthesis of 4,4,5,5-tetra-methyl-2-(2-(undec-10-enyl)tridec-12-enyl)-1,3,2-dioxaborolane (**13**) via Grignard addition of boronic ester to a primary bromide

4.2.2 Synthesis of 4,4,5,5-tetra-methyl-2-(2-(undec-10-enyl)tridec-12-enyl)-1,3,2-dioxaborolane (**13**).

The next line of synthesis was designed to form a primary bromide compound in an effort to curb the elimination reaction seen in Figure 4 - 10. To a slurry of NaH in THF, diethyl malonate was slowly added. Compound **2** was then added and the reaction was allowed to reflux for several days, until no monoalkylation product was seen via TLC. This forms the 9,9-diester **8**. Upon saponification of the crude product the diester is converted into the 9,9-diacid **9**. The crude product of that reaction is then dissolved in a minimal amount of decalin with a catalytic amount of N,N-Dimethyl aminopyridine and

heated to 160°C to undergo the decarboxylation. Once the decalin is removed via flash chromatography and solvent evaporated the crude mixture of compound **10** was reacted with lithium aluminum hydride to form the 9, 9-methyl alcohol **11**. Compound **11** was purified via column chromatography and reacted with triphenyl phosphine and carbon tetrabromide to form **12**. **12** was reacted with Mg to form a Grignard reagent. 2-isopropoxy-4,4,5,5-tetra-methyl-1,3,2-dioxaborolane is added and the substitution reaction takes place to form compound **13**. **13** was purified via flash chromatography, and then reacted with Grubbs 1st generation catalyst to form the polymer **14**. Unfortunately the polymer only reached a molecular weight of 2500 g/mol, about 5-6 repeat units. The overall yield of this synthetic approach we rather low due to the number of steps and the low yielding boronation reaction. Also, as mentioned earlier the alkyl boronic ester was unstable, and it is believed that decomposition products lead to the low molecular weights obtained after polymerization. To prevent this decomposition, the next synthetic scheme was designed for aryl boronic acids and esters.

4.3 Aryl Boronic Acid Monomer Synthesis

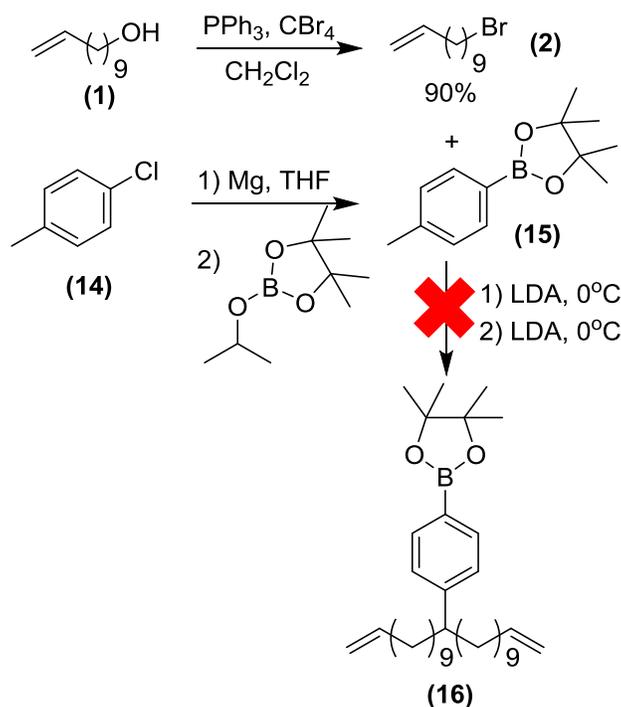


Figure 4 – 12. Synthesis of 2-(4-(heptacosyl)phenyl)-4,4,5-trimethyl-1,3,2-dioxaborolane (**16**) via dialkylation of **15**.

4.3.1 Synthesis of 2-(4-(heptacosyl)phenyl)-4,4,5-trimethyl-1,3,2-dioxaborolane (**16**)

The synthesis of the aryl boronic ester **16** is shown in Figure 4 - 12. The 9-spacer alcohol **1** is converted into the 9-spacer bromide **2**. Then *para*-chlorotoluene (**17**) is converted to the Grignard reagent with Mg and reacted with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to form *para*-toluene boronic ester (**18**). The di-alkylation reaction is attempted by reacting LDA and compound **2** with the boronic ester **18**. Unfortunately, under the reaction conditions attempted, 0°C reacted for 6 hours, the alkylation was unsuccessful.

By modifying the method used to make the 9,9 alcohols, it was hypothesized that a boronic acid/ester monomer could be made the same way. In this case the ethyl ester

of a protected boronic acid was used instead of the ethyl formate. The Grignard was formed from the 9-spacer bromide **2**, which then would react twice with the ester to form a carbon center with both an alcohol and the protected boronic acid. The next step would then be to remove the tertiary alcohol, resulting in the desired protected boronic acid monomer. Unfortunately this was not the case. As shown in Figure 4 – 13, the Grignard reaction failed to produce the desired product, in fact no reaction was observed even though the Grignard reagent did form. This is thought to be caused by the electrophilicity of the boronic ester. Instead of the Grignard reagent attacking at the carbonyl, it instead binds to the boron. Upon aqueous work up the alkyl group is cleaved, recreating the starting ester.

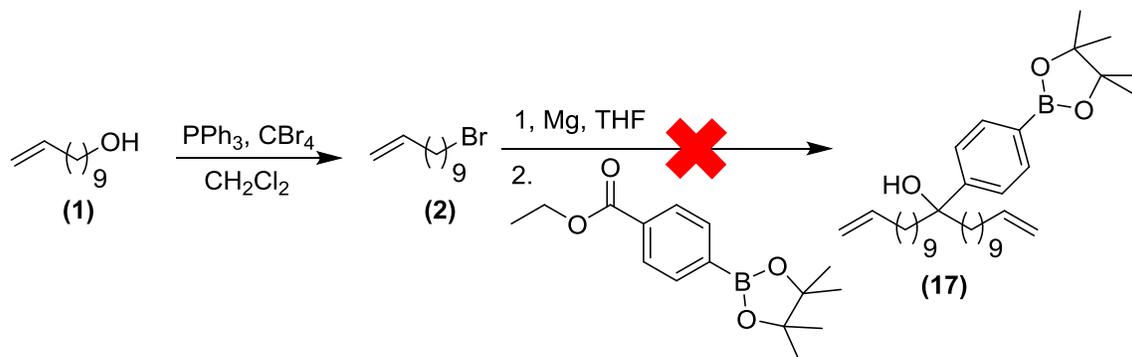


Figure 4 – 13. Synthesis of 12-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)tricoso-1,22-dien-12-ol (**17**) using a boron-containing electrophile

In an attempt to circumvent the electrophilicity problem, the reaction was reversed. The boron-containing compound would become the nucleophile and the alkyl substrate would be the electrophile (Figure 4 - 14). The hypothesis behind this approach was that by creating a Grignard reagent that was conjugated with boron, the increased electron density of the system would be enough to reduce the electrophilicity of boron. The 9,9 ketone **18** was made from reacting the 9,9 alcohol **3** with pyridinium

chlorochromate (PCC). This reaction progressed well, creating the ketone **18** in 90+% yields. The 9,9 ketone **18** was then reacted with **19** in a Grignard reaction with the goal of forming **20**. Unfortunately, no reaction appeared to take place yet the Grignard reagent was formed. Most likely the boron was still too electrophilic to allow any useful nucleophilic reaction to take place.

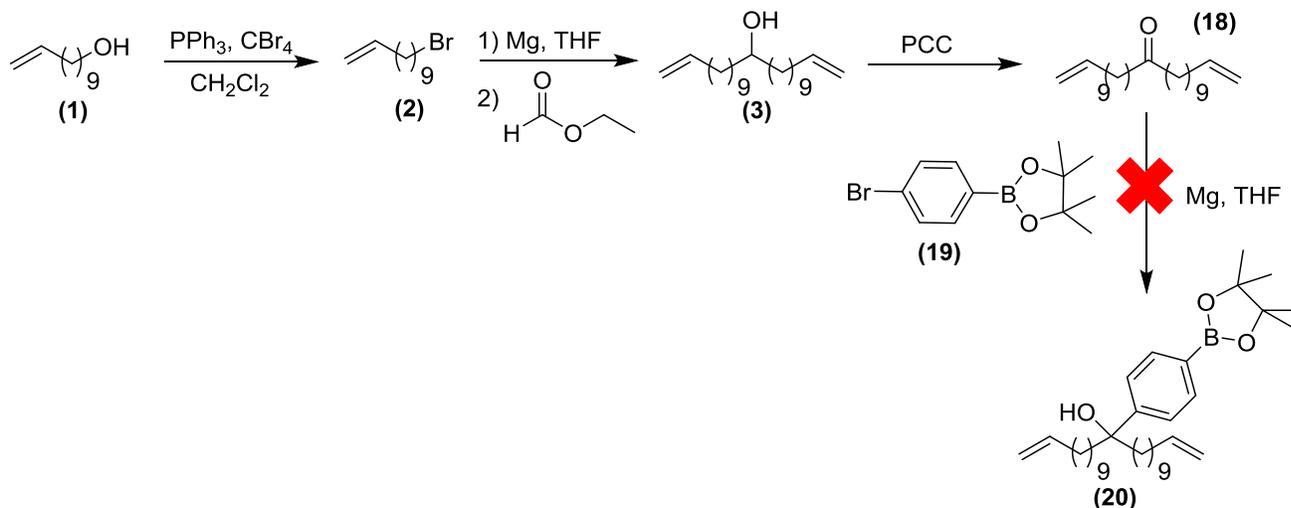


Figure 4 – 14. Synthesis of 12-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)tricos-1,22-dien-12-ol (**17**) using a boron-containing nucleophile

To avoid complications with the boron compound, a synthetic scheme was designed to synthesize a substrate that could then have the boronic acid or ester attached in the final step (Figure 4 - 15). This was carried out much the same way as the reaction above, except **19** was replaced with 1,4 dibromobenzene as the Grignard reagent. By controlling the stoichiometry of the magnesium, it can be assured that 1,4 dibromobenzene will only form one Grignard reagent. This was found to be the case in fairly good yields, about 80%. The next step was to removal of the tertiary alcohol.

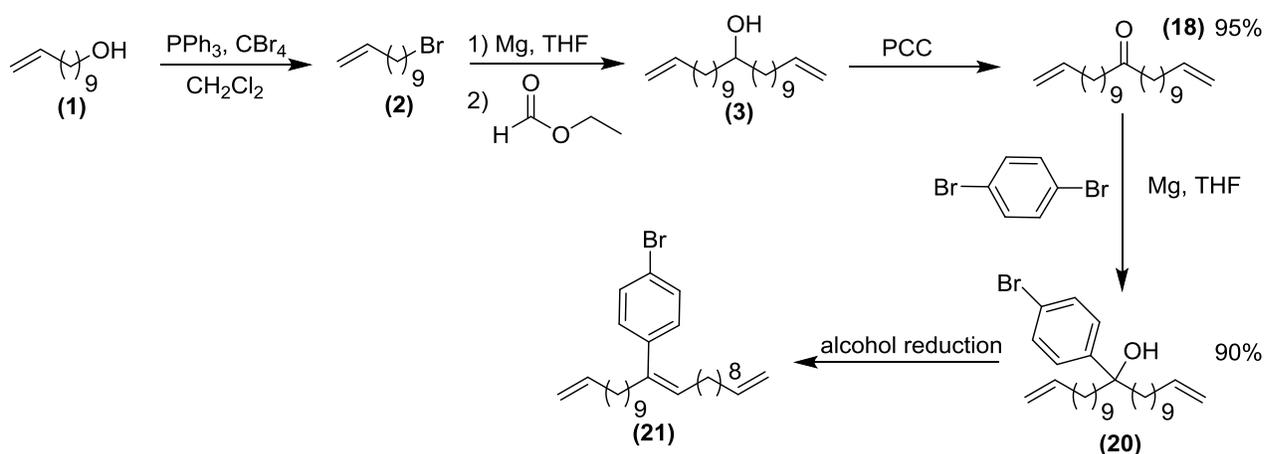


Figure 4 – 15. Synthesis of 12-(4-bromophenyl)tricoso-1,22-dien-12-ol (**21**) via Grignard reaction.

Reduction of tertiary alcohols has traditionally been a difficult proposition. Methods that work for primary and secondary alcohols, such as substitution with lithium aluminum hydride, seldom work on their tertiary counterparts. This is because many of these techniques rely on a $\text{S}_{\text{N}}2$ type mechanism, which don't occur on the more sterically hindered tertiary carbons. Figure 4 - 16 demonstrates a number of techniques attempted to reduce the alcohol.

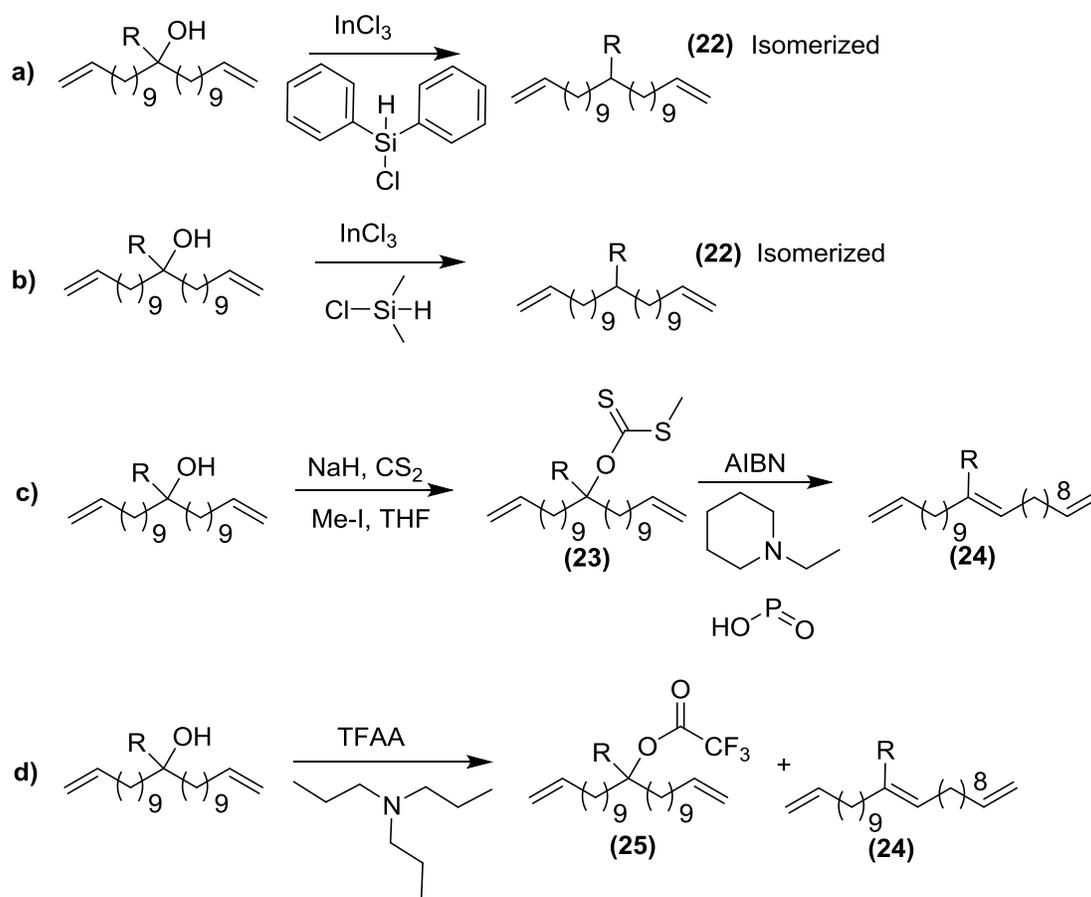


Figure 4 – 16. Reduction of tertiary alcohols a) Reduction with InCl_3 and chloro diphenylsilane resulting alcohol reduction but also olefin isomerization. b) Reduction with InCl_3 and chloro dimethylsilane no improvement was seen. c) Barton-McCombie radical deoxygenation results in elimination of the alcohol instead of reduction. d) Using trifluoroacetyl as a method for reduction of the tertiary alcohol; results in elimination and acylation.

The first method attempted was reported by *Yasuda et al.*¹¹³ This technique uses an indium trichloride as a catalyst and diphenyl chlorosilane as a mild hydride source.

The reported reaction demonstrates good conversion even at low temperatures for both tertiary and secondary alcohols. Tertiary alcohols seem to react more quickly, indicative of a $\text{S}_{\text{N}}1$ type reaction mechanism. Unfortunately, these reaction conditions cause the isomerization of the terminal double bonds. When studied, neither reagent alone produced isomerization but it was hypothesized that the electronics of the phenyl rings

lead to the silane behaving more as a proton source than a hydride source, allowing for isomerization. To prevent this dimethyl chlorosilane, which is a stronger hydride source, was used. Unfortunately, the isomerization was still present.

The next method attempted was Barton-McCombie radical deoxygenation.¹¹⁴ First the xanthate was formed from the alcohol by deprotonation with sodium hydride, which then reacted with carbon disulfide and methyl iodide to form **23**. Azobisisobutyronitrile (AIBN) was used as a radical source which causes the xanthate to decompose to carbon oxide sulfide, leaving a tertiary radical which reacts with a hydride source to form the final product. Unfortunately, tertiary Barton-McCombie reactions can form the elimination product **24** instead of the reduction product. One method to prevent elimination, reported by *Holbert et al.*, is to form the trifluoroacetyl species instead of the xanthate.¹¹⁵ This was done by reacting the alcohol with trifluoroacetic anhydride in the presence of tripropyl amine as a proton sponge to form **25**. Unfortunately, the trifluoroacetyl functional group is also an excellent leaving and even a gentle workup caused elimination and formation of **24**. With these oxygen reduction techniques exhausted, a new method was needed to attach the phenyl boronic acid or ester functionality.

4.3.2 Synthesis of 4,4,5,5-tetramethyl-2-(4-(tricoso-1,22-dien-12-yloxy)phenyl)-1,3,2-dioxaborolane

To avoid the problems associated with removal of the tertiary alcohol, the use of an ether linkage to attach the phenyl boronic acid or ester was evaluated. Ethers are versatile, stable, and there exists a large number of ways to synthesize them. To this end, synthesis of **27** was attempted (Figure 4 -17).

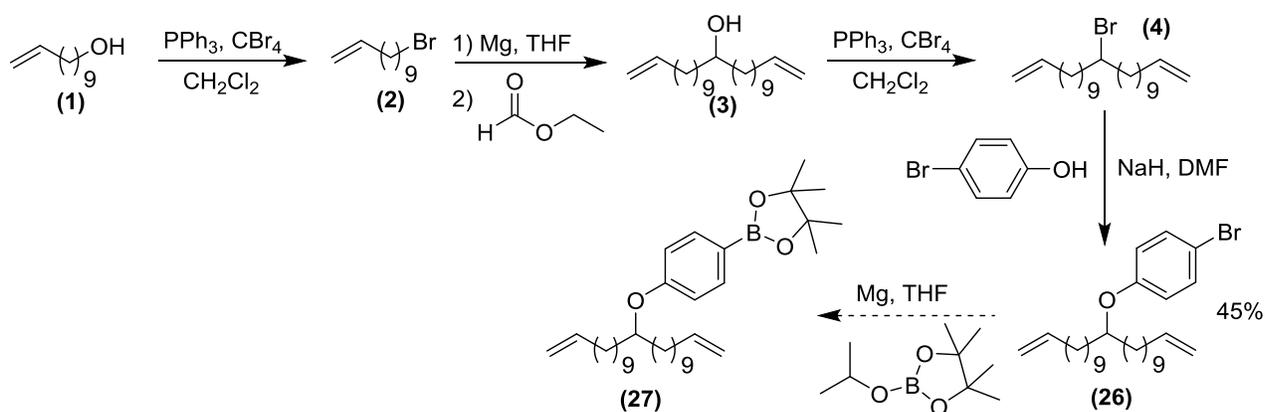


Figure 4 – 17. Synthesis of 4,4,5,5-tetramethyl-2-(4-(tricoso-1,22-dien-12-yloxy)phenyl)-1,3,2-dioxaborolane (**27**) via ether synthesis of **4** with 4-bromo phenol

This reaction scheme began with the synthesis of the 9, 9 bromide **4**, as mentioned earlier, this series of reactions is facile and high yielding. The next step was the synthesis of the ether. This was done using 4-bromo phenol as the nucleophile and sodium hydride as the base in DMF. This reaction proceeded, but in fairly low yields of only about 45%. This is due to the nature of the using a secondary bromide as the leaving group, it can easily undergo elimination, which was seen here. Changing reaction condition to using sodium hydroxide, and tetrabutyl ammonium bromide in a biphasic water/THF reaction did not improve the yields. While this reaction scheme did work, the yields were rather low so another monomer synthesis was attempted below.

4.3.3 Synthesis of 4,4,5,5-tetramethyl-2-(4-((tricoso-1,22-dien-12-yloxy)methyl)phenyl)-1,3,2-dioxaborolane

In an attempt to increase the overall yield of the ether synthesis and cut down on the number of steps, the compounds used for the nucleophile and the electrophile were reversed (Figure 4 - 18).

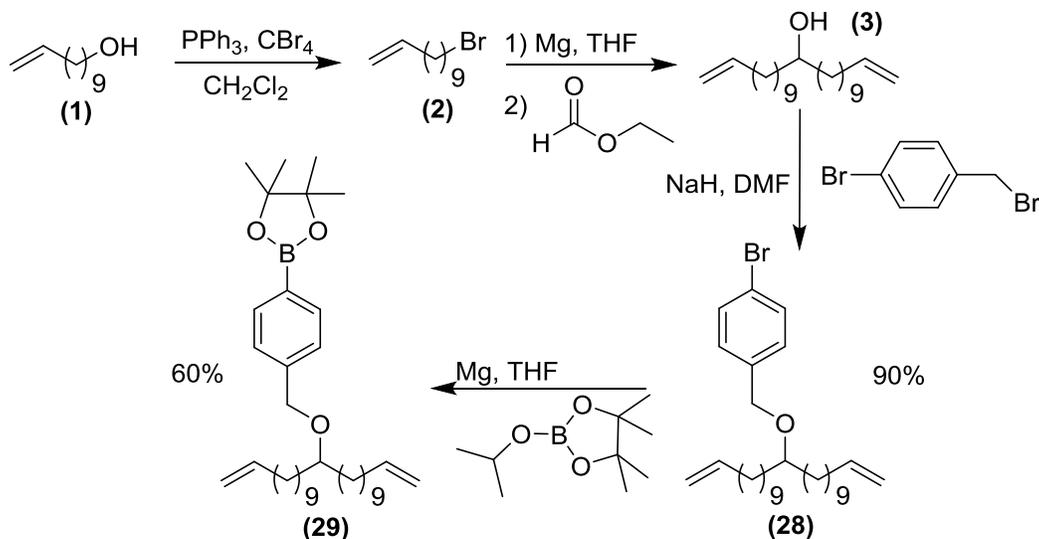


Figure 4 – 18. Synthesis of 4,4,5,5-tetramethyl-2-(4-((tricoso-1,22-dien-12-yloxy)methyl)phenyl)-1,3,2-dioxaborolane (**29**) via ether synthesis of **3** with 4-bromobenzyl bromide followed by a Grignard reaction to attach the boronic ester

Instead of synthesizing the 9,9 bromide **4** and using it as the electrophile, the 9,9 alcohol **3** was used. This increased yields in several ways; first it cut down on the number of steps, and second it allowed the electrophile to be a primary bromide. In this case the electrophile was chosen to be 4-bromobenzyl bromide. When reacted under the same conditions as above a 90% yield was achieved. Finally, a Grignard reaction was used to attach the boronic ester. This reaction progressed at about 60% yield with fresh reagent, but the yield was drastically reduced in the presence of any hydrolyzed 2-isopropoxy-4,4,5,5-tetra-methyl-1,3,2-dioxaborolane. This is a common problem when using Grignard reactions to produce boron compounds. While the presence of isopropanol (or water) would be expected to lower the yields of a Grignard reaction in a stoichiometric fashion, when in the presence of boronic ester, the yields are reduced in a more catalytic fashion. This indicates a different mechanism is at work that deactivated the Grignard reagent. This method proved effective in the synthesis of

boronic ester monomers. However, upon polymerization this monomer proved challenging. These difficulties will be discussed in the next chapter.

4.3.4 Synthesis of in-chain boronic acid monomer

The final synthetic route was another variation using an ether synthesis, combining the stability of phenolic ether with reactivity of a primary electrophile (Figure 4 - 19). This reaction began with the the alkenyl bromide with carbon spacers of 3, 6, or 9, **34**, **35**, or **2** respectively. This was then reacted with 1-bromo-3,5-hydroxybenzene to form **36**, **37**, or **38** in good yields. Due to the excessive cost of 1-bromo-3,5-hydroxybenzene, it was synthesized by reacting the much cheaper 1-bromo-3,5-methoxybenzene (**30**) with boron tribromide. Boron tribromide is an extremely strong Lewis acid that is commonly used to cleave phenolic ethers. In this case the reaction proceeded splendidly, in about 80% yield. The final step is to introduce the boronic acid to the monomer. This is done using a lithiation procedure as to avoid the problems mentioned with use of Grignard reagents. Triisopropyl borate was used since under standard aqueous work up conditions yield the free boronic acid. Purification of the lithiation reaction also made it an attractive option. A simple silica plug followed by recrystallization in hexanes resulted in unoptimized yields of 60% for **39** and 53% for **41**.

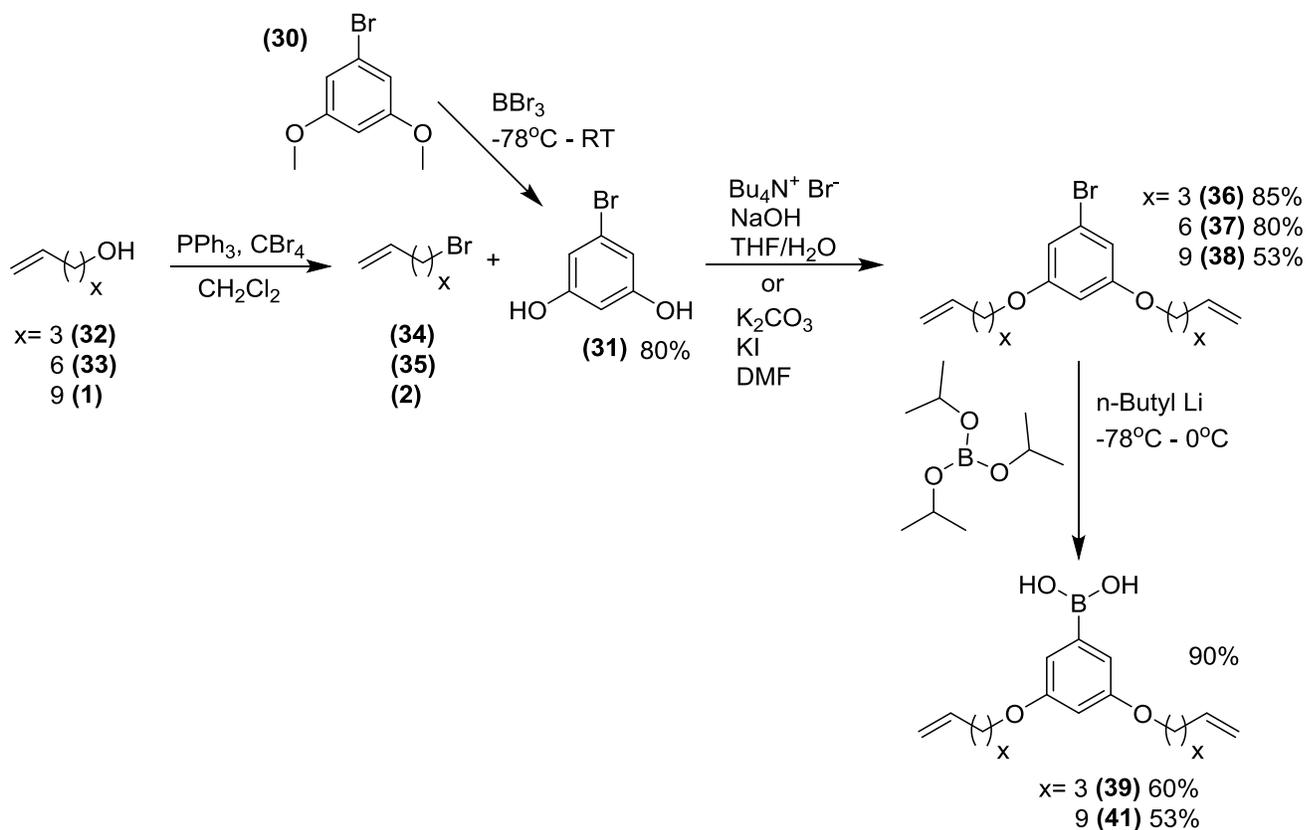


Figure 4 – 19. Synthesis of in-chain boronic acid monomer (**39-41**). The alkenyl groups are attached via ether synthesis then the boronic acid is added using a standard lithiation reaction.

4.4 Deprotection of Boronic Acids

Deprotecting the boronic esters to the acids has presented difficulties. Figure 4 - 21 shows several different techniques that have been attempted.

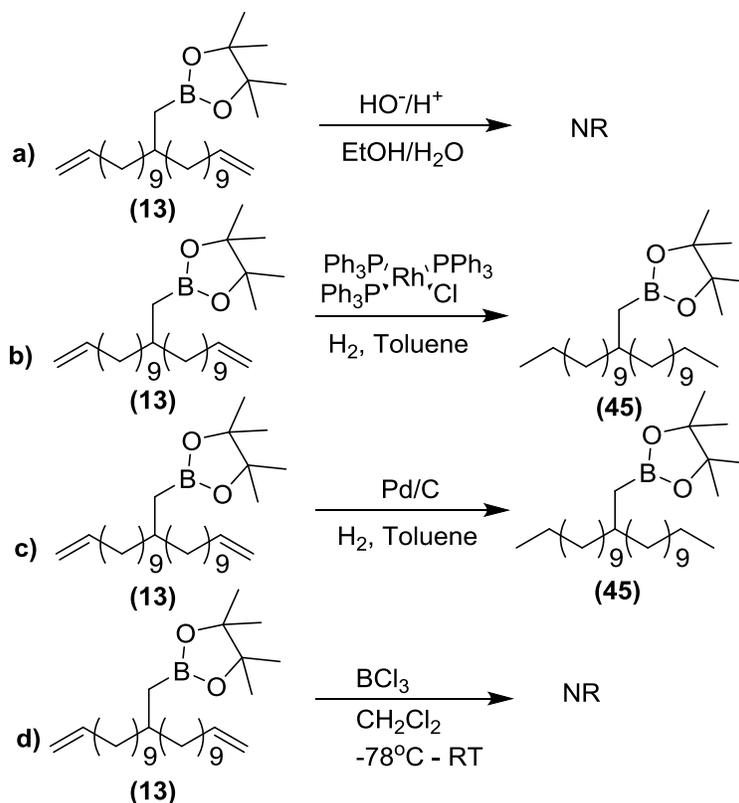


Figure 4 – 21. Deprotection of alkyl boronic esters a) Acid/base hydrolysis yielded no reaction b+c) Use of hydrogenation techniques only reduced the terminal alkenes d) Use of boron trichloride also resulted in no reaction

All of the deprotections were done on the monomer for test purposes, once promising deprotection conditions are found it would be attempted on the polymer. The first attempt at deprotections was a simple hydrolysis. Both acid and base hydrolysis were attempted in a refluxing water/ethanol solution. Unfortunately, no reaction occurred, presumably due to the sterics of the pinacol methyl groups. Next hydrogenation conditions were attempted to remove the pinacole protective group. This would be ideal, as the finished ADMET polymer gets hydrogenated to remove the residual double bonds. Unfortunately, neither the Wilkinson's catalyst or the Pd/C accomplished nothing more than hydrogenation of the double bond. The final attempt

was to use boron trichloride to cleave the boron oxygen bond. This is then converted back to the acid upon aqueous work up. This attempt also yielded no useful reaction.

Benzylic boronic esters have been shown to be cleaved in a similar fashion to benzylic ethers.¹¹⁶ To this end a series of protecting groups were synthesized and studied (Figure 4 - 22).

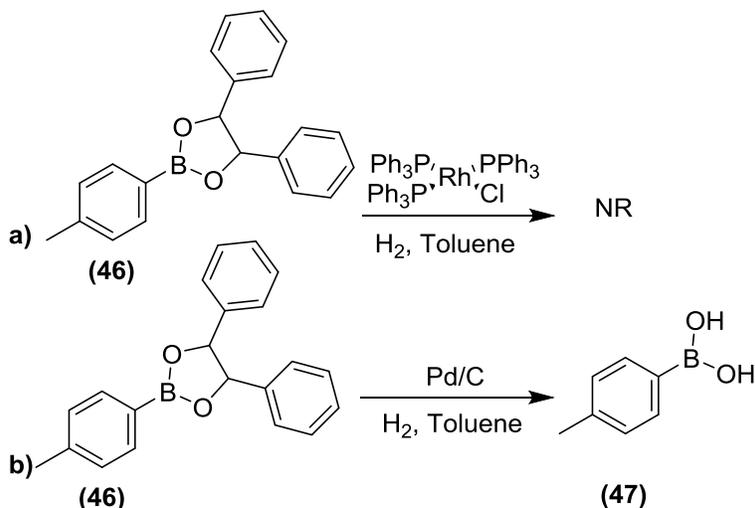


Figure 4 – 22. Deprotection of aryl boronic esters via hydrogenation. Changing the protection group to one containing benzylic oxygens allow for their removal with hydrogenation via Pd/C (a) but not with with Wilkinson's catalyst (b)

The model compound **46** was used for these experiments. Since many ADMET polymers are hydrogenated with Wilkinson's catalyst, this was the first system tested. Unfortunately, the catalyst did not remove the protecting group. In an attempt to replicate the published procedure, Pd/C was used as the hydrogenation catalyst. This system worked flawless, demonstrating that the protecting groups can be removed under hydrogenation procedures. This study demonstrated that the correct protecting group could be removed using mild hydrogenation conditions.

Shortly after these studies were concluded, other work (Chapter 2) demonstrated that free boric acid did not hinder olefin metathesis, in fact, can even enhance it. This result leads to the conclusion that protection of the boronic acid is unnecessary.

4.5 Conclusions

This chapter discusses many important aspects of boron chemistry. The instability of alky boronic esters was demonstrated; both by the decomposition of monomer, and the difficulty of the synthesis. Aryl boronic acids were proven to be the synthetic target of choice. Numerous methods were demonstrated to synthesize these compounds. Use of boron-containing compounds in nucleophilic reactions was proven to be fruitless. This is caused by the Lewis acidity of the boron species interfering with free electrons of the nucleophile. Finally, boronic acid and ester monomers were synthesized using ether linkages.

Protection and deprotection of boronic acid compounds were also studied. The pinacol protection groups were found to be extremely stable but difficult to remove, however the diphenyl protection group was easily cleaved via hydrogenation yielding the free boronic acid. With these discoveries in hand, precision boronic acids polymers can be synthesized and their morphologies studied.

4.6 Experimental

4.6.1 Materials and Instrumentation

1-Butyl-3-methylimidazolium hexafluorophosphate was purchased from AK Scientific and purified via a neutral alumina plug followed by degassing via freeze-pump thaw in triplicate. All other materials were purchased from Aldrich and used without further purification unless noted. Grubbs 1st and 2nd generation catalyst (G1 and G2) as well as Hoveyda-Grubbs 1st and 2nd generation catalyst (HG1 and HG2) were kindly

provided by Materia, Inc. Anhydrous solvents were obtained from an anhydrous solvent system. All ^1H NMR, and ^{13}C NMR were obtained on a Varian Mercury 300MHz spectrometer and recorded in CDCl_3 . ^1H and ^{13}C chemical shifts were referenced to signals from CDCl_3 . Mass spectrograms were carried out on a Thermo Scientific DSQ MS. Elemental analyses were carried out by Atlantic Microlab, Inc. Thermogravimetric analysis (TGA) was performed on TA Instruments TGA Q1000 Series using dynamic scans under nitrogen. Differential scanning calorimetry (DSC) analysis was performed using a TA Instruments Q1000 series equipped with a controlled cooling accessory (refrigerated cooling system) at $10\text{ }^\circ\text{C}/\text{min}$. Differential scanning calorimetry (DSC) analysis was performed using a TA Instruments Q1000 series equipped with a controlled cooling accessory (liquid nitrogen cooling system) at $10\text{ }^\circ\text{C}/\text{min}$. Gel permeation chromatography (GPC) was performed at $40\text{ }^\circ\text{C}$ using a Waters Associates GPCV2000 liquid chromatography system with an internal differential refractive index detector and two Waters Styragel HR-5E columns ($10\text{ }\mu\text{m}$ PD, 7.8 mm i.d., 300 mm length) using HPLC grade THF as the mobile phase at a flow rate of $1.0\text{ mL}/\text{min}$.

4.6.2 Procedures

Synthesis of 11-bromo-1-undecene (2) 40.00g of undecene-11-ol and 93.52g of carbon tetrabromide were dissolved in 350mL of dichloromethane in a round bottom flask with a stir bar. The mixture was chilled to 0C . Triphenyl Phosphine was added slowly, keeping the temperature cold. The reaction was allowed to stir overnight at room temperature under argon. The solid triphenyl phosphine oxide was then filtered out of solution and washed with hexane. The solvent was then removed under vacuum, and the solid was recrystallized in ether. The solid was filtered off, and filtrate was run through a silica plug to remove the remaining triphenyl phosphine oxide. The collected

product is a mixture of bromoform and desired 11-bromo-1-undecene. The bromoform was distilled off under vacuum.

Yield: 90% ^1H NMR (300MHz, CDCl_3 , ppm): δ = 5.9-5.7 (m, 1H); 5.05-4.85 (m, 2H); 3.45-3.35 (t, 2H); 2.10-2.00 (m, 2H); 1.92-1.80 (m, 2H); 1.50-1.20 (m, 12H)

Synthesis of tricoso-1,22-dien-12-ol (3) A flame dried three neck flask with a stir bar was charged with 40mL of THF and 1.90g Mg under argon. The flask was chilled in an ice bath, and 1.7mL of 1,2 Dibromoethane was added to the solution and stirred at RT for 30 minutes. 10 g of 11-bromo-1-undecene was added to drop wise to the reaction mixture and refluxed for 2 hours. The reaction was then cooled to RT and 1.44g of ethyl formate was added to the reaction. The mixture was then refluxed overnight, still under argon. The reaction is then cooled in an ice bath and neutralized with 1M HCl. The mixture was then extracted with ether. The solvent was removed under vacuum and the resulting solid was recrystallized in acetone.

Yield: 90% ^1H NMR (300MHz, CDCl_3 , ppm): δ = 5.9-5.73ppm (m, 2H); 5.05-4.85ppm (m, 4H); 3.6-3.5ppm (s, 1H); 2.1-2.0ppm (q, 4H) 1.6-1.1ppm (m, 41H) (grease impurity overlaps alkyl peaks)

Synthesis of 12-bromotricos-1,22-diene (4) The same bromination procedure was followed as outlined in the synthesis of 11-bromo-1-undecene. 5.92g of **(3)**, 6.96g carbon tetrabromide, and 6.82g triphenyl phosphine. The work up was the same as outlined above except the bromoform was removed via flash chromatography in hexane.

Yield: 95% ¹H NMR (300MHz, CDCl₃, ppm): δ= 5.9-5.73 (m, 2H); 5.05-4.85 (m, 4H); 4.1-3.95 (m, 1H); 2.10-2.00 (m, 4H); 1.85-1.75 (m, 4H); 1.6-1.1 (m, 30H) (grease impurity overlaps alkyl peaks)

Synthesis of 2-(undec-10-enyl)tridec-12-enoic acid (10) 3.1g of NaH was added to a three necked flask with a stir bar along with 30mL of dry THF. 6.88g of diethyl malonate was added slowly drop wise, and stirred for 30 minutes. 25 g of compound **(2)** was added dropwise and refluxed under argon for 48 hours. The reaction was then cooled and 1g of NaH and compound **(2)** were added and refluxed for another 24 hours. The reaction was then cooled in an ice bath and neutralized with 1M HCl. The reaction mixture was then extracted with ether. The ether was removed under reduced pressure. The recovered oil was then dissolved in 250mL of 6M NaOH solution and ethanol. This was then refluxed under argon for 24 hours. The reaction mixture was chilled in the ice bath, neutralized with concentrated HCl, and extracted with ether. The ether was removed under vacuum and the crude mixture was dissolved in 30mL of hot decalin. A catalytic amount, about 20mg, of DMAP was added to the reaction and heated to 160C for 4 hours. The reaction was then cooled and the decalin removed via flash chromatography in hexane, the solvent was then changed to a 3:1 hexane/ ethyl acetate mixture to remove the desired 2-(undec-10-enyl)tridec-12-enoic acid in a 63% yield.

Synthesis of 2-(undec-10-enyl)tridec-12-en-1-ol (11) 1.9g of lithium aluminum hydride was added to dry THF to make a slurry and then chilled in an ice bath. Then 5.5g of compound **(10)** dissolved in THF was added slowly to the slurry. This was allowed to react over night at room temperature. The reaction was chilled in an ice bath

and slowly neutralized with water followed by 1M HCl. The mixture was then extracted with ether, and condensed under vacuum. The desired product was recovered in near quantitative yields.

Synthesis of 12-(bromomethyl)tricos-1,22-diene (12) The same bromination procedure was followed as outlined in the synthesis of 11-bromo-1-undecene. 4.94g of (11), 5.6g carbon tetrabromide, and 5.25g triphenyl phosphine. The work up was the same as outlined above except the bromoform was removed via flash chromatography in hexane. The desired product was isolated in 95% yield.

Synthesis of 4,4,5,5-tetramethyl-2-(2-(undec-10-enyl)tridec-12-enyl)-1,3,2-dioxaborolane (13). A flame dried three neck flask with a stir bar was charged with 20mL of THF and .95g Mg under argon. The flask was chilled in an ice bath, and .89mL of 1,2 Dibromoethane was added to the solution and stirred at RT for 30 minutes. 4.05g of compound (12) was then added drop wise and refluxed for 3 hours under argon. The reaction was cooled and 2.75g of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added drop wise and refluxed overnight still under argon. The reaction was the cooled and quenched with water in an ice bath. The mixture was extracted with ether and condensed under vacuum. The recovered oil was then purified by flash chromatography, starting with hexane then moving to a 20% ethyle acetate and 80% hexane eluent to recover desired product in about 80% yield.

Synthesis of 4,4,5,5-tetramethyl-2-p-tolyl-1,3,2-dioxaborolane (18) A flame dried three neck flask with a stir bar was charged with 50mL of THF and 2.13g Mg under argon. The flask was chilled in an ice bath, and 2.53mL of 1,2 Dibromoethane was added to the solution and stirred at RT for 30 minutes. 5.00g of 1-chloro-4-methyl

benzene was then added drop wise and refluxed for 3 hours under argon. The reaction was cooled and 6.53g of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added drop wise and refluxed overnight still under argon. The reaction was the cooled and quenched with water and 1M HCl in an ice bath. The mixture was extracted with ether and condensed under vacuum. The crude oil was then separated using flash chromatography using a 5:1 hexane/ethyl acetate as the eluent. Solvent was removed under vacuum and the desired product was isolated in 60% yield.

Synthesis of 8-bromo-1-octene (26) 462.25g of 1,8 dibromo octane, 1.25L of THF, and 1.25L of toluene were added to a 5L round bottom flask. The mixture was chilled in an ice bath and 407.1g of potassium tert-butoxide was added over the course of an hour. The reaction was removed from the ice bath and allowed to react for another 2 hours at RT. The reaction was then chilled again in an ice bath and quenched with water and HCl. Once the solution was neutralized and the water removed. The organic solution was washed with water in a 2:1 water/toluene ratio. This was repeated until the THF was removed. The toluene solution was the washed with brine. The toluene was then removed by vacuum distillation. The unreacted 1,8 dibromo octane was distilled under vacuum using azeotropic distillation. A mixture of water and ethanol was used to form an azeotrope with the 1,8 dibromo octane, allowing for its removal.

Synthesis of 2,2-di(oct-7-enyl)malonic acid (28) 10.00g of NaH was added to a three necked flask with a stir bar along with 100mL of dry THF. 12.01g of diethyl malonate was added slowly drop wise, and stirred for 30 minutes. 31.9 g of compound (26) was added dropwise and refluxed under argon for 48 hours. The reaction was then cooled and 2g of NaH and 3g compound (26) were added and refluxed for another 48

hours. The reaction was then cooled in an ice bath and neutralized with 1M HCl. The reaction mixture was then extracted with ether. The ether was removed under reduced pressure. The recovered oil was then dissolved in 100mL of 6M NaOH solution and 50mL ethanol. This was then refluxed under argon for 24 hours. The reaction mixture was chilled in the ice bath, neutralized with concentrated HCl, and extracted with ether. The ether was removed and the crude oil was separated via flash chromatography using 5% methanol/ 95% hexane eluent. The solvent was removed and the desired product was recovered.

Yield: 45% ¹H NMR (300MHz, CDCl₃, ppm): δ= 5.9-5.73 (m, 2H); 5.05-4.90 (m, 4H); 2.10-2.00 (q, 4H); 2.00-1.88 (m, 4H); 1.6-1.1 (m, 16H)

General synthesis of 12-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)tricoso-1,22-dien-12-ol via boronic ester electrophile (17). A flame dried three neck flask with a stir bar was charged with dry THF and 4 equiv. of Mg under argon. The flask was chilled in an ice bath, and 1 equiv. of 1,2 dibromoethane was added to the solution and stirred at RT for 30 minutes. 2.2 equiv. of 11-bromo-1-undecene was added to drop wise to the reaction mixture and refluxed for 2 hours. The reaction was then cooled to RT and 1 equiv. of ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate was added to the reaction. The mixture was then refluxed overnight under argon. The reaction is then cooled in an ice bath and neutralized with 1M HCl. The aqueous solution was extracted three times with ether. The organic phases were combined and the solvent was removed under vacuum. An NMR of the resulting residue indicated no product had been formed.

General synthesis of 12-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)tricoso-1,22-dien-12-ol via boronic ester nucleophile (17). A flame dried three neck flask with a stir bar was charged with dry THF and 2.5 equiv. Mg under argon. The flask was chilled in an ice bath, and 1 equiv. of 1,2 dibromoethane was added to the solution and stirred at RT for 30 minutes. 1.2 equiv. of 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**19**) was added to the reaction mixture and refluxed for 2 hours. The reaction was then cooled to RT and 1 equiv. of tricoso-1,22-dien-12-one was added to the reaction. The mixture was then refluxed overnight under argon. The reaction is then cooled in an ice bath and neutralized with 1M HCl. The aqueous solution was extracted three times with ether. The organic phases were combined and the solvent was removed under vacuum. An NMR of the resulting residue indicated no product had been formed.

Synthesis of tricoso-1,22-dien-12-one (18). In a flame dried 1L flask equipped with a stir bar 15.5g pyridinium chlorochromate and 15.5g of celite were suspended in 100mL of dry dichloromethane. 16g of tricoso-1, 22-dien-12-ol was dissolved in in 30mL of dichloromethane and added drop wise to the slurry. The reaction was stirred overnight and quenched with addition of 200mL of diethyl ether. The slurry was then filtered through a silica plug and the solvent was evaporated under vacuum. The crude ketone was then recrystallized in acetone to yield 13.5g of (**18**).

Yield: 85% ¹H NMR (300MHz, CDCl₃, ppm): δ= 5.9-5.7 (m, 2H); 5.05-4.85 (m, 4H); 2.41-2.32 (t, 4H); 2.10-1.95 (q, 4H); 1.61-1.49 (m, 4H); 1.91-1.70 (m, 24H)

General synthesis of 12-(4-bromophenyl)tricoso-1,22-dien-12-ol (20). A flame dried three neck flask with a stir bar was charged with dry THF and 1.5 equiv. Mg

under argon. The flask was chilled in an ice bath, and .1 equiv. of 1,2 dibromoethane was added to the solution and stirred at RT for 30 minutes. 1.5 equiv. of 1,4 dibromobenzene was added to the reaction mixture and refluxed for 2 hours. The reaction was then cooled to RT and 1 equiv. of tricos-1,22-dien-12-one was added to the reaction. The mixture was then refluxed overnight under argon. The reaction is then cooled in an ice bath and neutralized with 1M HCl. The aqueous solution was extracted three times with ether. The organic phases were combined and the solvent was removed under vacuum.

Yield: 80% ^1H NMR (300MHz, CDCl_3 , ppm): δ = 7.65 (m, 2H); 7.25 (m, 2H); 5.9-5.7 (m, 2H); 5.05-4.85 (m, 4H); 2.35-2.10 (q, 4H); 1.91-1.70 (m, 4H); 1.60-1.20 (m, 28H)

Tertiary alcohol reduction via indium trichloride and diphenyl chlorosilane.

In a flame dried flask equipped with a stir bar, .05 equiv. of InCl_3 was added to 1.0 equiv. of tertiary alcohol in dichloromethane. 2.0 equiv. of diphenyl chlorosilane was added under argon. The reaction was refluxed for 4 hours then poured into a mixture of diethyl ether:water (5:3). The mixture was extracted with diethyl ether three times and the organic phases were combined. The solvent was evaporated under vacuum. The crude residue was analyzed via NMR and found the while the alcohol was reduced, the terminal olefins were also isomerized.

Tertiary alcohol reduction via indium trichloride and dimethyl chlorosilane.

In a flame dried flask equipped with a stir bar, .05 equiv. of InCl_3 was added to 1.0 equiv. of tertiary alcohol in dichloromethane. 2.0 equiv. of diethyl chlorosilane was added under argon. The reaction was refluxed for 4 hours then poured into a mixture of diethyl ether:water (5:3). The mixture was extracted with diethyl ether three times and

the organic phases were combined. The solvent was evaporated under vacuum. The crude residue was analyzed via NMR and found that while the alcohol was reduced, the terminal olefins were also isomerized.

Tertiary alcohol reduction via Barton-McCombie radical deoxygenation. In a flame-dried three-neck round bottom flask equipped with a flask, 1 equiv. of tertiary alcohol was added to a slurry of THF (3.5mL of solvent per mmol of tertiary alcohol), 1.6 equiv. of sodium hydride, and .05 equiv. of imidazole. The slurry was stirred for 2 hours at RT, then cooled to 0°C and 3 equiv. of carbon disulfide was added. The reaction was stirred overnight at RT, then cooled to 0°C and 1.5 equiv. of methyl iodide was added. The reaction was stirred for 2 hours then quenched with water and extracted three times with diethyl ether. The solvent was removed under vacuum, and the residue was purified via column chromatography using 95:5 hexane:ethyl acetate. The purified product was then added to a flame dried flask, with 5 equiv. of N-ethylpiperidine hypophosphite in dioxane. The reaction was refluxed for 2-3 hours. Aliquots of 2,2-azobisisobutyronitrile (.1 equiv.) dissolved in dioxane was added over the course of the reaction. The solvent was removed under vacuum, and the crude product was purified via column chromatography in pure hexane. The pure product was analyzed via NMR and found that while the tertiary alcohol was removed, it formed the elimination product not the pure reduction product.

Tertiary alcohol reduction via trifluoroacetic anhydride. A flame-dried flask was charged with 1 equiv. of tertiary alcohol and 1 equiv. of tripropyl amine in dichloromethane. 1.2 equiv. of trifluoroacetic anhydride was added to the solution drop wise and the reaction was stirred overnight under argon. The reaction was quenched

with water and extracted three times with diethyl ether. The solvent was removed under vacuum and the crude product was analyzed via NMR. The isolated product was found to contain some of trifluoro acylated product, but also large amount of the elimination product as well.

Synthesis of 1-bromo-4-(tricoso-1,22-dien-12-yloxy)benzene (26). .46g of 4-bromophenol dissolved in dry DMF was added drop wise to a slurry of .12g sodium hydride in DMF at 0°C. The reaction was stirred at RT for 30 minutes, then 1g of 12-bromotricoso-1,22-diene (**4**) was added. The reaction was heated to 65°C overnight then cooled to 0°C and quenched with water. The reaction was extracted three times with diethyl ether. The organic phases were combined and washed three times with 1M HCl followed by three washes with 3M NaOH solution. The organic phase was dried of magnesium sulfate and the solvent was removed *in vacuo* The product was purified via silica column chromatography.

Yield: 45% ¹H NMR (300MHz, CDCl₃, ppm): δ= 7.35 (m, 2H); 6.75 (m, 2H); 5.9-5.7 (m, 2H); 5.05-4.85 (m, 4H); 3.45 (d, 1H); 2.15-2.00 (q, 4H); 1.85-1.10 (m, 32H) ¹³C NMR (75 MHz, CDCl₃, ppm): δ= 154.96, 139.46, 132.67, 117.41, 114.32, 112.99, 39.95, 39.72, 34.03, 32.78, 29.98, 29.92, 29.77, 29.70, 29.35, 29.15, 26.76

Synthesis of 1-bromo-4-((tricoso-1,22-dien-12-yloxy)methyl)benzene (28). In a flame-dried three neck flask, a slurry was made of 1.43g (60 mmol) of sodium hydride in DMF and cooled to 0°C. 5.0g (14.85 mmol) of (**3**) was added drop wise and stirred at room temperature for 30 minutes. 4.08g (16.3 mmol) of 1-bromo-4-(bromomethyl)benzene was then added. The reaction was heated to 60°C and stirred overnight. The reaction was quenched with water and extracted three times with ether.

The organic phase was washed with 1M HCl and dried over magnesium sulfate. The solvent was evaporated under vacuum. The crude product was then purified via column chromatography with hexanes as the eluent.

Yield: 90% HRMS: Actual $[M+NH_4]^+$ =522.3314 Theory $[M+NH_4]^+$ =522.3305 1H NMR (300MHz, $CDCl_3$, ppm): δ = 7.45 (d, 2H); 7.25 (d, 2H); 5.9-5.75 (m, 2H); 5.05-4.85 (m, 4H); 4.5 (s, 2H); 3.4 (m, 1H); 2.15-2.00 (q, 4H); 1.75-1.10 (m, 32H) ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 139.46, 138.42, 131.50, 129.45, 121.32, 114.32, 79.44, 70.08, 34.00, 33.98, 30.01, 29.91, 29.82, 29.76, 29.69, 29.34, 29.13, 25.12.

Synthesis of 4,4,5,5-tetramethyl-2-(4-((tricoso-1,22-dien-12-yloxy)methyl)phenyl)-1,3,2-dioxaborolane (29). A flame dried three neck flask with a stir bar was charged with THF and 4 equiv. of magnesium under argon. The flask was chilled in an ice bath, and 1 equiv. of 1,2 dibromoethane was added to the solution and stirred at RT for 30 minutes. 1 equiv. of 1-bromo-4-((tricoso-1,22-dien-12-yloxy)methyl)benzene (**28**) was added to drop wise to the reaction mixture and refluxed for 2 hours. The reaction was then cooled to RT and 1.3 equiv. of Isopropoxyboronic acid pinacol ester was added to the reaction. The mixture was then refluxed overnight, still under argon. The reaction was then cooled in an ice bath and neutralized with 1M HCl. The mixture was then extracted three times with ether. The solvent was removed under vacuum and crude product was purified via column chromatography in 19:1 hexane:ethyl acetate eluent.

Yield: 60% HRMS: Actual $[M+NH_4]^+$ =570.5087 Theory $[M+NH_4]^+$ =570.5059 Elemental Analysis: Theory C:78.23 H:11.12 Actual C:78.45 H:11.16 1H NMR (300MHz, $CDCl_3$, ppm): δ = 7.80 (d, 2H); 7.40 (d, 2H); 5.9-5.75 (m, 2H); 5.05-4.90 (m, 4H); 4.55 (s,

2H); 3.4 (m, 1H); 2.10-2.00 (q, 4H); 1.75-1.10 (m, 44H) ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ = 142.67, 139.37, 134.97, 127.01, 114.30, 83.84, 79.22, 70.70, 34.02, 33.99, 30.04, 29.81, 29.76, 29.69, 29.34, 29.14, 25.17, 25.04.

Synthesis of 5-bromobenzene-1,3-diol (31). In a flame-dried three neck flask, 25.0g (115.3 mmol) of 5-bromo-1,3-dimethoxybenzene (**30**) was added to dry dichloromethane. The reaction was cooled to -78°C and 86.6g (345 mmol) tribromobenzene was added slowly with stirring. The reaction was allowed to stir overnight at room temperature. The mixture was then chilled to 0°C and quenched with water. The reaction was extracted three times with ethyl acetate, and the solvent was then removed under vacuum. The crude product was purified via silica plug in 1:1 hexane:ethyl acetate. Once the solvent was removed, the residue was dissolved in toluene which was then removed under vacuum. This yielded a pure off-white solid.

Yield: 80% ^1H NMR (300MHz, CDCl_3 , ppm): δ = 6.64 (s, 2H); 6.35 (s, 1H) ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ = 160.67, 122.95, 110.35, 100.72

General procedure for alkylation of 5-bromobenzene-1,3-diol via biphasic reaction. In a single neck round bottom flask, 1 equiv. of 5-bromobenzene-1,3-diol (**30**), 1 equiv. of $\text{Na}_2\text{S}_2\text{O}_4$, 13 equiv. of sodium hydroxide, and .3 equiv. of tetrabutyl ammonium bromide was dissolved in a 1:1 mixture THF: H_2O . 4 equiv. of alkenyl bromide was then added drop wise to the reaction mixture. The reaction was refluxed overnight then cooled to RT and quenched with diethyl ether. The aqueous phase was extracted three times with diethyl ether. The solvent was removed under vacuum and the crude product was then purified via a column chromatography.

General procedure for alkylation of 5-bromobenzene-1,3-diol via potassium carbonate in DMF. A flame-dried 3-neck flask charged with a magnetic stir bar was charged with 1 equiv. of 5-bromobenzene-1,3-diol, 3 equiv. of potassium carbonate, and .25 equiv. of potassium iodide was suspended in anhydrous DMF. The suspension was heated to 65°C for 30 minutes, then 2.5 equiv. of 5-bromo-1-pentene was added dropwise. The reaction was heated overnight at 65°C. It was then cooled to room temperature and the solvent was removed via vacuum distillation. The remaining residue was dissolved in dichloromethane washed three times with 2M NaOH, and dried over magnesium sulfate. The solvent was removed *in vacuo* and the residue was then purified via column chromatography in hexanes.

Synthesis of 1-bromo-3,5-bis(undec-10-en-1-yloxy)benzene (38). 3g (15.9 mmol) of 5-bromobenzene-1,3-diol (**30**), 2.48g (15.9 mmol) Na₂S₂O₄, 8.25g (206.3 mmol) of sodium hydroxide, 1.54g (4.76mmol) of tetrabutyl ammonium bromide, and 14.8g (63.5 mmol) of 11-bromo-1-undecene purified via column chromatography in hexanes.

Yield: 3.91g, 52.5% ¹H NMR (300MHz, CDCl₃, ppm): δ= 6.64 (s, 2H); 6.40 (s, 1H); 5.9-5.75 (m, 2H); 5.05-4.90 (m, 4H); 3.95-3.85 (t, 4H); 2.10-2.00 (q, 4H); 1.82-1.70 (m, 4H); 1.50-1.10 (m, 24H) ¹³C NMR (75 MHz, CDCl₃, ppm): δ= 160.90, 139.34, 122.99, 114.33, 110.37, 100.74, 68.44, 34.02, 29.71, 29.63, 29.53, 29.33, 29.13, 26.19.

Synthesis of 1-bromo-3,5-bis(oct-7-en-1-yloxy)benzene (37). 3g (15.9 mmol) of 5-bromobenzene-1,3-diol (**30**), 6.58g (47.6 mmol) of potassium carbonate, .66g (4 mmol) of potassium iodide, 6.66mL (7.58g, 39.7 mmol) of 5-bromo-1-pentene.

Yield: 5.15, 79.3% ^1H NMR (300MHz, CDCl_3 , ppm): δ = 6.65 (s, 2H); 6.35 (s, 1H); 5.9-5.75 (m, 2H); 5.05-4.90 (m, 4H); 3.95-3.85 (t, 4H); 2.15-2.00 (q, 4H); 1.55-1.70 (m, 4H); 1.50-1.20 (m, 12H) ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ = 160.84, 139.08, 122.95, 114.84, 110.34, 100.70, 68.35, 33.87, 28.97, 26.10.

Synthesis of 1-bromo-3,5-bis(pent-4-en-1-yloxy)benzene (36). 3g (15.9 mmol) of 5-bromobenzene-1,3-diol (**30**), 6.58g (47.6 mmol) of potassium carbonate, .66g (4 mmol) of potassium iodide, 4.70mL (5.91g, 39.7 mmol) of 5-bromo-1-pentene.

Yield: 4.42, 85.8% ^1H NMR (300MHz, CDCl_3 , ppm): δ = 6.70 (s, 2H); 6.40 (s, 1H); 5.9-5.75 (m, 2H); 5.05-4.90 (m, 4H); 3.95-3.85 (t, 4H); 2.35-2.15 (q, 4H); 1.95-1.80 (m, 4H) ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ = 160.80, 137.77, 123.00, 115.52, 110.44, 100.80, 67.61, 30.23, 28.47.

General procedure for boronation of benyl bromide (36-38). In a flame dried 3-neck round-bottom flask, 1 equivalent of phenyl bromide was dissolved in dry THF under argon. The solution was cooled to -78°C and 1.1 equivalent of n-butyl lithium was added slowly. The solution was allowed to stir at -78°C for 1 hour than 1.1 equivalents of triisopropyl borate was added all at once. The reaction was allowed to rise to room temperature over 2 hours, then quenched with 1M HCl. The aqueous phase was extracted three times with diethyl ether. The organic phase was then dried over magnesium sulfated and the solvent was removed via rotary evaporation. The crude produce was then purified via silica plug, hexanes were used to remove all impurities then the product was flushed of the silica with diethyl ether. The solvent was removed, first under vacuum to remove the bulk of the ether, then under argon flow to remove the

remaining ether. The resulting solid was recrystallized from hexane. This yields pure boronic acid monomer in good yields.

Synthesis of (3,5-bis(undec-10-en-1-yloxy)phenyl)boronic acid (41). 2g (4.05mmol) of **36**, 1.78mL (4.46mmol) n-butyl lithium), .84g (1.03mL, 4.46mmol) triisopropyl borate.

Yield: .98g, 53% HRMS: Actual $[M+H]^+=459.3654$ Theory $[M+H]^+=459.3645$ ^1H NMR (300MHz, d6-DMSO, ppm): $\delta= 7.95$ (bs, 2H) 6.905 (s, 2H); 6.45 (s, 1H); 5.85-5.75 (m, 2H); 5.00-4.80 (m, 4H); 3.95-3.85 (t, 4H); 2.00-1.90 (q, 4H); 1.75-1.60 (m,4H); 1.50-1.20 (m, 24H) ^{13}C NMR (75 MHz, d6-DMSO, ppm): $\delta= 159.38, 138.88, 114.32, 112.10, 102.20, 67.35, 33.49, 31.13, 29.14, 28.97, 28.90, 28.92, 28.67, 28.45$. FT-IR (ATR, cm^{-1}) 3333, 2920, 2849, 1586, 1350, 1165, 1026, 907, 782.

Synthesis of (3,5-bis(pent-4-en-1-yloxy)phenyl)boronic acid (39). 2g (6.15mmol) of **38**, 2.71mL (6.76mmol) n-butyl lithium), 1.27g (1.56mL, 6.76mmol) triisopropyl borate.

Yield: 1.07g, 60% HRMS: Actual $[M+H]^+=291.1769$ Theory $[M+H]^+=291.1765$ ^1H NMR (300MHz, d6-DMSO, ppm): $\delta= 8.08$ (bs,2H); 6.90 (s, 2H); 6.45 (s, 1H); 5.9-5.75 (m, 2H); 5.05-4.90 (m, 4H); 3.95-3.85 (t, 4H); 2.20-2.10 (q, 4H); 1.80-1.65 (m,4H) ^{13}C NMR (75 MHz, d6-DMSO, ppm): $\delta= 159.36, 138.13, 115.29, 112.15, 103.32, 66.77, 39.78, 28.07$ FT-IR (ATR, cm^{-1}) 3294, 2936, 2872, 1586, 1351, 1162, 1061, 913, 840.

Deprotection of pinacol protected boronic acid via acid/base hydrolysis. In a round bottom flask, .5g of 4,4,5,5-tetramethyl-2-(2-(undec-10-enyl)tridec-12-enyl)-1,3,2-dioxaborolane (**13**) was dissolved in a 6:4 ethanol:water solution. The water portion was either 3M HCl or 3M NaOH. The reaction was refluxed with stirring

overnight, after which it was cooled to RT and neutralized. The solution was extracted three times with diethyl ether and the organic phase was dried with magnesium sulfate. The solvent was removed *in vacuo* and the residue was analyzed via NMR. No reduction in the integration of the methyl peaks associated with the pinacol protecting group was observed.

Deprotection of pinacol protected boronic acid via hydrogenation with Wilkinson's catalyst. In a Parr bomb equipped with a magnetic stir bar, 5g of 4,4,5,5-tetramethyl-2-(2-(undec-10-enyl)tridec-12-enyl)-1,3,2-dioxaborolane (**13**) was dissolved in approximately 30mL of toluene. 5 mol% of Wilkinson's catalyst was added and the Parr bomb was sealed and placed under 600 PSI of hydrogen. The reaction was heated to 90°C and reacted for three days. After three days the toluene was removed under vacuum and residue was analyzed via NMR. No reduction in the integration of the methyl peaks associated with the pinacol protecting group was observed.

Deprotection of pinacol protected boronic acid via hydrogenation with Pd/C. In a Parr bomb equipped with a magnetic stir bar, .5g of 4,4,5,5-tetramethyl-2-(2-(undec-10-enyl)tridec-12-enyl)-1,3,2-dioxaborolane (**13**) was dissolved in approximately 30mL of toluene. 5 mol% of Pd/C was added and the Parr bomb was sealed and placed under 600 PSI of hydrogen. The reaction was heated to 90°C and reacted for three days. After three days the toluene was removed under vacuum and residue was analyzed via NMR. No reduction in the integration of the methyl peaks associated with the pinacol protecting group was observed.

Deprotection of pinacol protected boronic acid via boron trichloride. In a flame-dried three neck flask, .5g of 4,4,5,5-tetramethyl-2-(2-(undec-10-enyl)tridec-12-

enyl)-1,3,2-dioxaborolane (**13**) was dissolved in dry dichloromethane. 4 equiv. of boron trichloride was added drop wise to the reaction at 0°C. The reaction was allowed to warm up to RT and stir overnight under argon. The solvent was then removed *in vacuo* and the resulting residue was analyzed via NMR. No reduction in the integration of the methyl peaks associated with the pinacol protecting group was observed.

Deprotection of 4,5-diphenyl-2-(p-tolyl)-1,3,2-dioxaborolane via hydrogenation with Wilkinson's catalyst. In a Parr bomb equipped with a magnetic stir bar, .5g of 4,5-diphenyl-2-(p-tolyl)-1,3,2-dioxaborolane (**46**) was dissolved in approximately 30mL of toluene. 5 mol% of Wilkinson's catalyst was added and the Parr bomb was sealed and placed under 600 PSI of hydrogen. The reaction was heated to 90°C and reacted for three days. After three days the toluene was removed under vacuum and residue was analyzed via NMR. No reduction in the integration of the methylene peaks associated with the protecting group were observed.

Deprotection of 4,5-diphenyl-2-(p-tolyl)-1,3,2-dioxaborolane via hydrogenation with Pd/C. In a Parr bomb equipped with a magnetic stir bar, .5g of 4,5-diphenyl-2-(p-tolyl)-1,3,2-dioxaborolane (**46**) was dissolved in approximately 30mL of toluene. 5 mol% of Pd/C was added and the Parr bomb was sealed and placed under 600 PSI of hydrogen. The reaction was heated to 90°C and reacted for three days. After three days the toluene was removed under vacuum and residue was analyzed via NMR. The integration of the methylene peaks associated with the protecting group were no longer observed. Complete deprotection was accomplished.

CHAPTER 5 Boronic Acid and Ester Polymers

5.1 Background

Polymeric systems containing boron-centered Lewis acids have are used for a number of applications such as; polymeric Lewis acid catalysts and catalyst support, sensors, stimuli responsive polymers, and as films in lithium ion batteries.^{89–91,112,117–120}

As mentioned in the previous chapter, the Lewis acidity of the boron-containing moiety can be tuned from weakly Lewis acidic boric acid to highly Lewis acidic alky, and aryl boranes.

Jäkle et al. has reported a system for synthesizing well-defined polymers with a variety of boron-containing Lewis acid pendant groups (Figure 5 - 1).¹¹² This method allows access to a wide range of boron-containing polymers via post-polymerization functionalization.

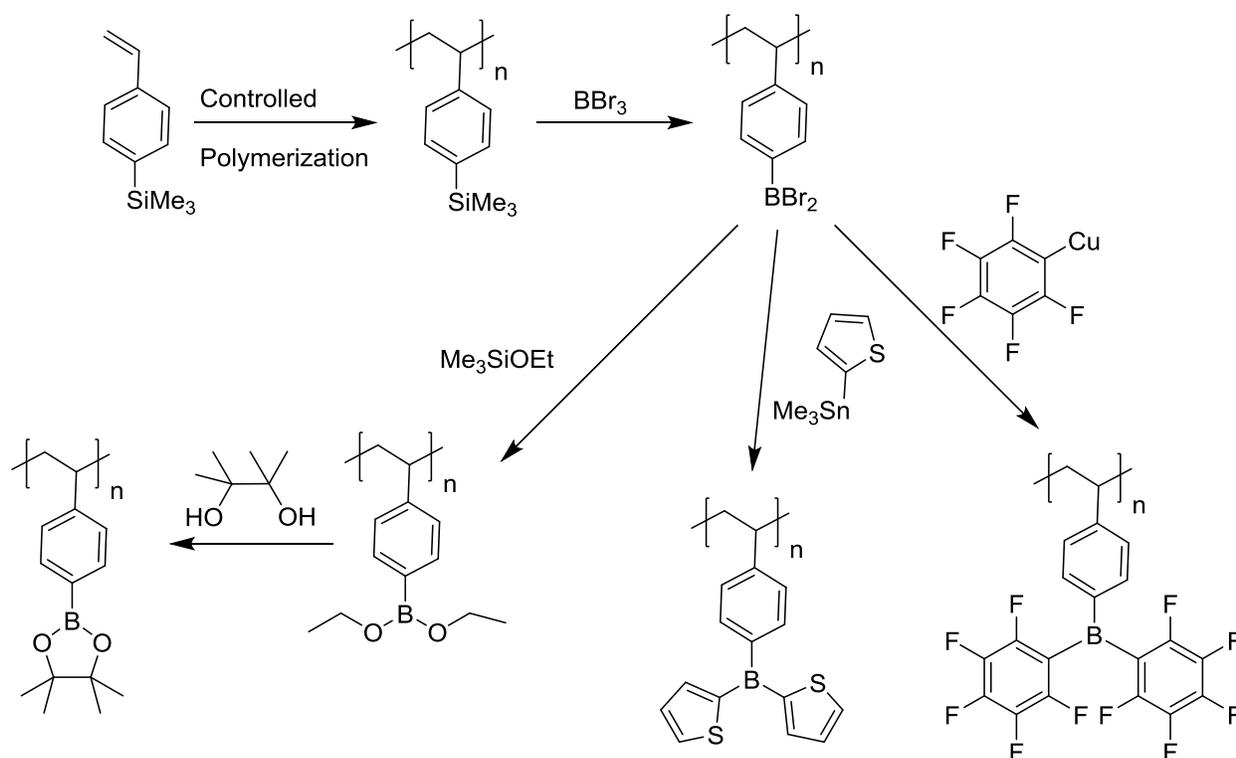


Figure 5 - 1. Synthesis of a variety of boron-containing Lewis acids via post-polymerization modification¹¹²

First, a phenyl trimethyl silane monomer is polymerized using a controlled radical polymerization technique. The resulting silane polymer is then reacted with boron tribromide to yield polyphenyl boron dibromide. By exposing the reactive boron dibromide species to any number of nucleophiles, a catalogue of boron-containing Lewis acid polymers have been synthesized. Moreover, the Lewis acidic sites were shown to be accessible by nucleophiles for potential use as catalyst support.¹¹²

By taking advantage of the unique stability of tetraaryl boronates, highly reactive catalysts can be protected.¹²¹ When tetraaryl boronates are attached to the polymer the stability and processability of the catalyst/boronate complex is increased. One method employed to incorporate boronates onto polystyrene beads was reported by *Frechet et al.*¹²² In this example, a polymeric system was functionalized with covalently bound

ammonium functionality, the counter ion was $[B(C_6F_5)_4]^-$. The polymer bead was then loaded with a metallocene catalyst. The catalyst activity was maintained as demonstrated by copolymerization of ethylene and 1-hexene. Another approach is to attach the tetraaryl boronate covalently to the polymer backbone. *Jäkle et al.* have prepared several amphiphilic block copolymers; poly(styryltriphenylborate-*b*-polystyrene) and poly(styryltris(pentafluorophenyl)borate)-*b*-polystyrene via ATRP. The polymers were loaded with $[Rh(cod)(dppb)]^+(OTf)^-$ (Figure 5 - 2). The degree of loading was approximately 85%, confirmed via 1H NMR.¹²³

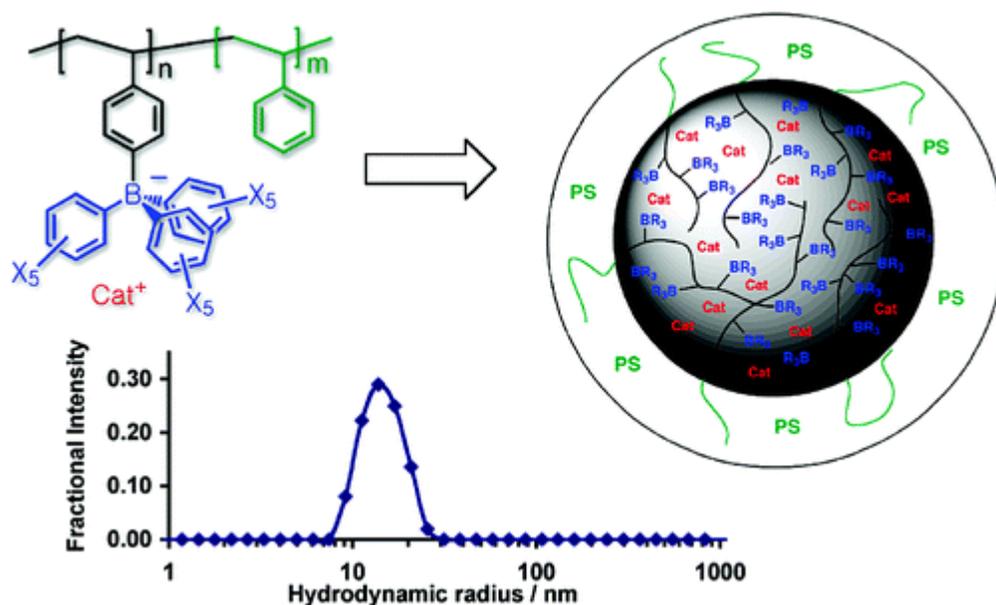


Figure 5 - 2. Tetraaryl boronate polymers used as solid support for catalysts. Reprinted with permission from Cui, C.; Bonder, E. M.; Jäkle, F. *Journal of the American Chemical Society* **2010**, *132*, 1810–2. Copyright 2013 American Chemical Society.¹²³

Borate-containing polymers have also found use as polyelectrolytes in lithium ion batteries. The Bazan group fabricated a bilayer p-n junction of poly(fluorene-co-phenylene) containing a pendant cationic electrolyte with a fluoride counter ion.¹²⁴ The

other layer is a conjugated polymer with a neutral pendant dimesitylborane, which is known to bind fluoride (Figure 5 - 3).

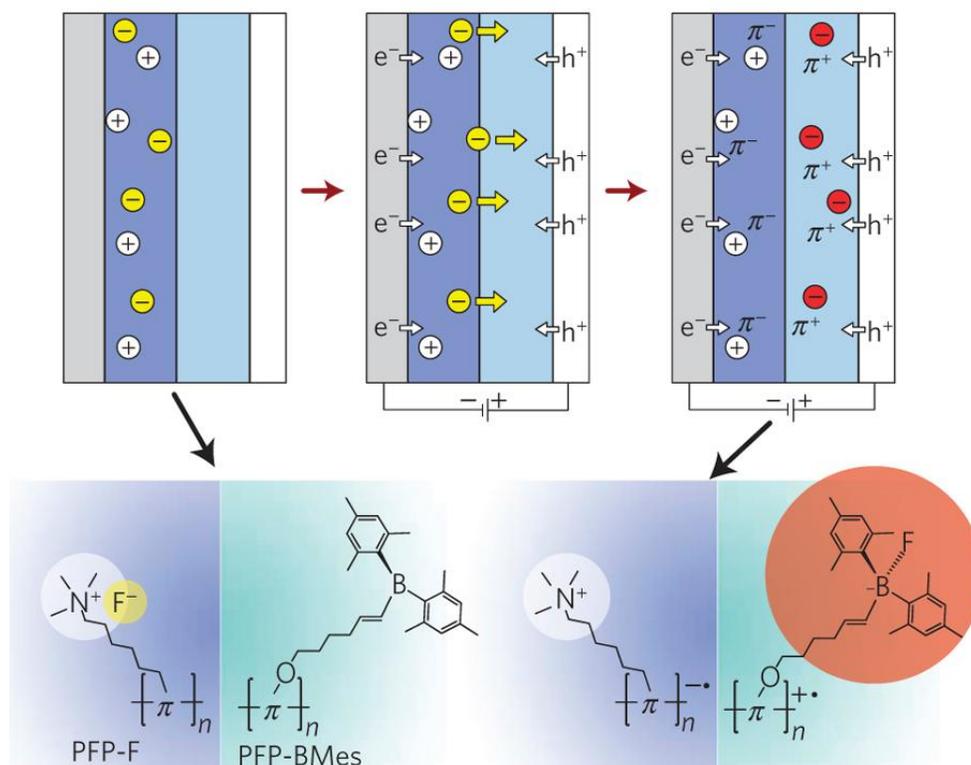


Figure 5 - 3. Boron-containing Lewis acid polymer used for ion conduction, the fluoride anion jumps from the quaternary ammonium to the boron causing a flow of ions. Reprinted by permission from Macmillan Publishers Ltd: *Nature Materials*; Hoven, C. V; Wang, H.; Elbing, M.; Garner, L.; Winkelhaus, D.; Bazan, G. C. *Nature materials* **2010**, 9, 249–52, copyright 2010.¹²⁴

When a current is applied to the system, the fluoride moved from the cationic layer to the neutral layer. This device displayed superior light-emitting and current rectification performance.

Boronic acids have been used in a number of polymers as stimuli responsive moieties for applications such as drug delivery and glucose sensors.^{89,125} In drug delivery applications, diblock copolymers are made via RAFT polymerization. One block

is a hydrophilic poly(dimethylacrylamide) (blue); the other block consists of a boronic acid containing repeat unit (Figure 5 - 4).¹²⁶

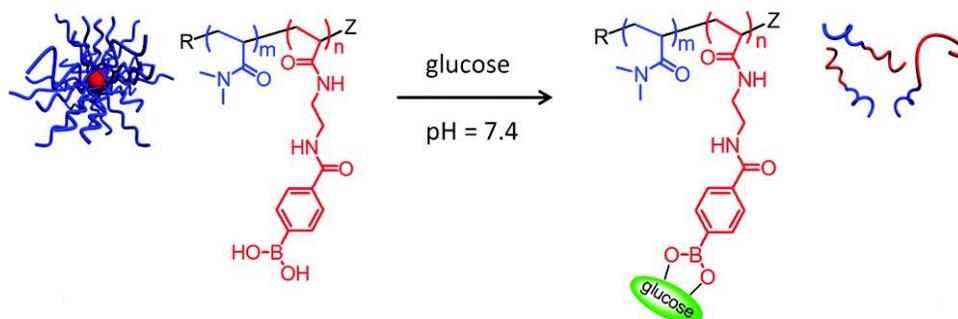


Figure 5 - 4. Stimuli responsive boronic acid polymers for the encapsulation and release of small molecules; at low glucose levels micelles are formed. As the glucose levels increase, the polymer is fully dissolved. Adapted with permission from Roy, D.; Sumerlin, B. S. *ACS Macro Letters* **2012**, 1, 529–532. Copyright 2013 American Chemical Society.¹²⁶

In an aqueous solution at low glucose concentrations the boronic acid is uncharged and hydrophobic. This causes the polymer to form micelles with poly(dimethylacrylamide) block on the outside, and the hydrophobic boronic acid block inside the micelle. As the glucose level increases the boronic acid converts to the tetrahedral charged boronate species and becomes hydrophilic. This causes the polymer micelles to disperse into free polymer chains; releasing the contents of the micelle. Other stimuli can trigger similar results such as temperature and pH.¹²⁵

Gamsey et al. has demonstrated the use of boronic acids as a glucose sensor. This is accomplished by synthesis of a polymer containing an anionic dye and a viologen attached to a boronic acid functional group (Figure 5 - 5).¹²⁷

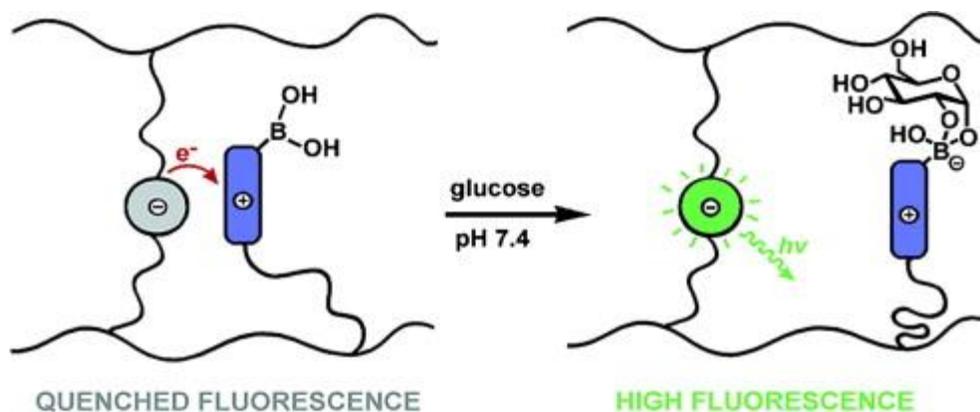


Figure 5 - 5. Use of boronic acid polymers as a glucose sensor; under low glucose conditions the viologen can interact with the anionic dye, preventing fluorescence. However, when glucose binds to the boronic acid it allows the dye to fluoresce. Reprinted with permission from Gamsey, S.; Suri, J. T.; Wessling, R. A.; Singaram, B. *Langmuir : the ACS Journal of Surfaces and Colloids*, **2006**, 22, 9067–74. Copyright 2006 American Chemical Society.¹²³

When the boronic acid is unbound the viologen unit is in close enough proximity to the dye to prevent fluorescence. When bound glucose molecule, the boronic acids becomes negatively charged and repels the anionic dye. This separates the quenching moiety from the dye allowing the polymer to fluoresce. This has shown to be sensitive over a wide range of biologically use glucose concentration, from 2.5-20mM.

All of the uses demonstrated here take advantage of the specific chemistry of boron. Many of the properties displayed by these boron-containing Lewis acid polymers rely heavily on the polymer morphology. By using ADMET, precise boron containing polymers can be made. These precision polymer systems lead to unique morphologies which can elucidate the morphology of existing boron-containing polymer systems, as well as potentially enhance their performance.

5.2 Results and Discussion

5.2.1 Polymerization and Characterization of Poly(4,4,5,5-tetramethyl-2-(4-((tricoso-1,22-dien-12-yloxy)methyl)phenyl)-1,3,2-dioxaborolane) (**29**).

Monomer **29** was first polymerized with **G1** using the bulk polymerization technique, but due to viscosity of the monomer and the resulting oligomers, a M_n of only 2500 was achieved. At this point, ionic liquids were investigated as a polymerization medium (Figure 5 - 6).

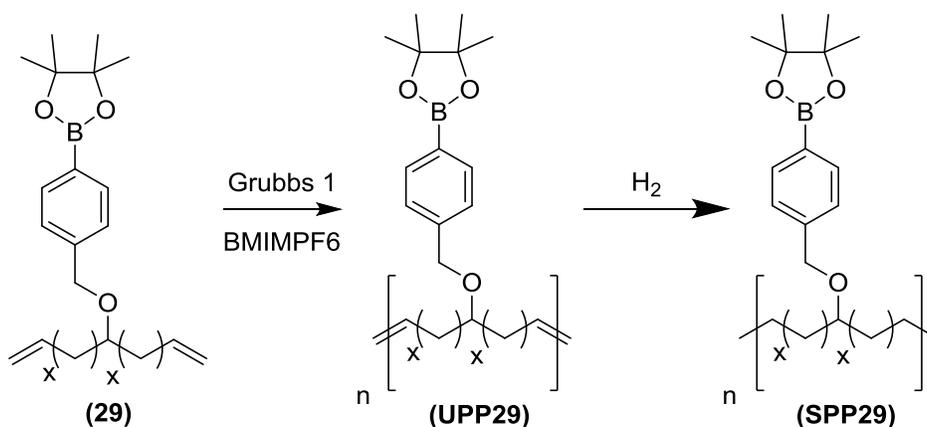


Figure 5 - 6. Polymerization of 4,4,5,5-tetramethyl-2-(4-((tricoso-1,22-dien-12-yloxy)methyl)phenyl)-1,3,2-dioxaborolane (**29**)

In this system, **29** was dissolved in 1-butyl-3-methylimidazolium hexafluorophosphate along with 1 mol% **G1**. The polymerization was run for a total of 96 hours. After precipitation, the polymer was analyzed via GPC resulting in a M_n of 58,000 with a PDI of 1.86. This polymer was then analyzed for thermal characteristics via TGA and DSC (Figure 5 - 7 and Figure 5 - 8).

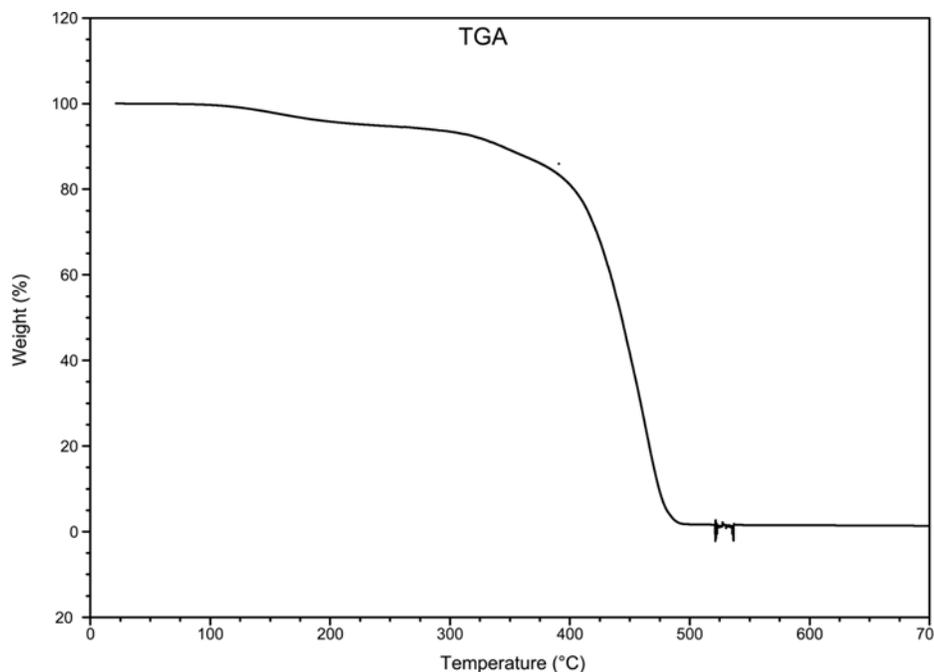


Figure 5 - 7. Poly(4,4,5,5-tetramethyl-2-(4-((tricoso-1,22-dien-12-yloxy)methyl)phenyl)-1,3,2-dioxaborolane) (**UPP29**) is thermally stable up to approximately 350°C

The TGA of the unsaturated polymer **UPP29** demonstrates good thermal stability with no real decomposition until about 350°C followed by complete decomposition starting at about 400°C. The DSC of **UPP29** displays a T_g of about -23°C. When compared to the identically spaced phenyl phosphonic ester polymer produced by ADMET; the T_g is comparable at -28°C.⁴⁷ As expected no T_m was observed, this is due to the unsaturation in the backbone and the bulky, non-interacting pendant group.

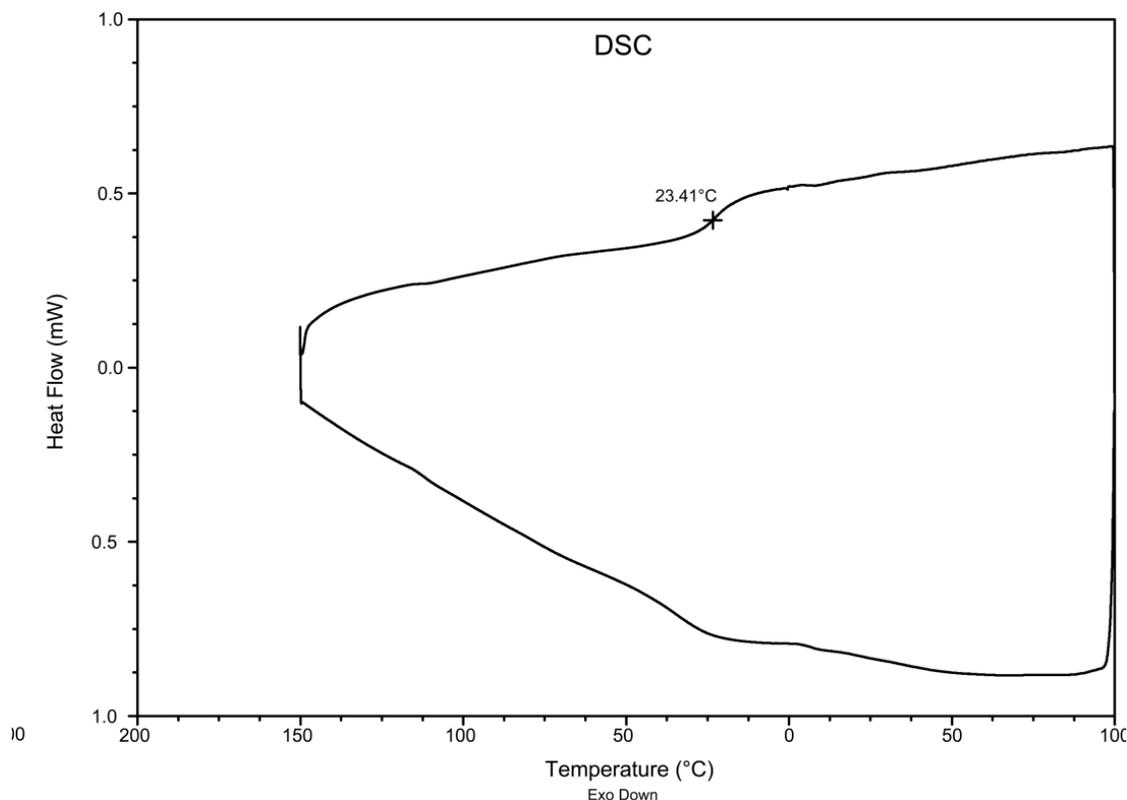


Figure 5 - 8. A T_g for poly(4,4,5,5-tetramethyl-2-(4-((tricoso-1,22-dien-12-yloxy)methyl)phenyl)-1,3,2-dioxaborolane) (**UPP29**) is observed at -23°C but no T_m is seen

Next the remain double bond were hydrogenated the remaining to yield a pure polyethylene backbone (Figure 5 - 9). While Pd/C is traditionally used for hydrogenation of the residual double bonds, it was avoided in this case due to its propensity to cleave benzylic ethers. Instead Wilkinson's catalyst was first used. However, in this case, the catalyst did cause cleavage of the benzylic ether pendant group. This was determined via NMR by observing an increase in the relative number of backbone hydrogens in relation to the benzylic protons. After this was discovered, a more tolerant non-catalytic hydrogenation method was used. This method uses three equivalents of toluenesulfonylhydrazide (TSH) and tripropylamine (TPA) dissolved in *o*-xylene. The reaction is attached to a bubbler and the reaction was refluxed until nitrogen was no

longer observed evolving from the reaction vessel. Another addition of TSH and TPA were added and refluxed until no more nitrogen was released. The solvent was removed and the polymer was analyzed via NMR and IR to determine whether complete saturation was achieved and cleavage of the benzylic ether was avoided. The NMR showed no loss of the pendant group and complete hydrogenation was observed. The IR, however, showed there was remaining internal olefins (observed by the out-of-plane alkene C-H bend near 967cm^{-1})⁴⁸ so the saturation was not complete. The polymer underwent several more rounds of hydrogenation but internal olefins were still observed, albeit in very small amount amounts.

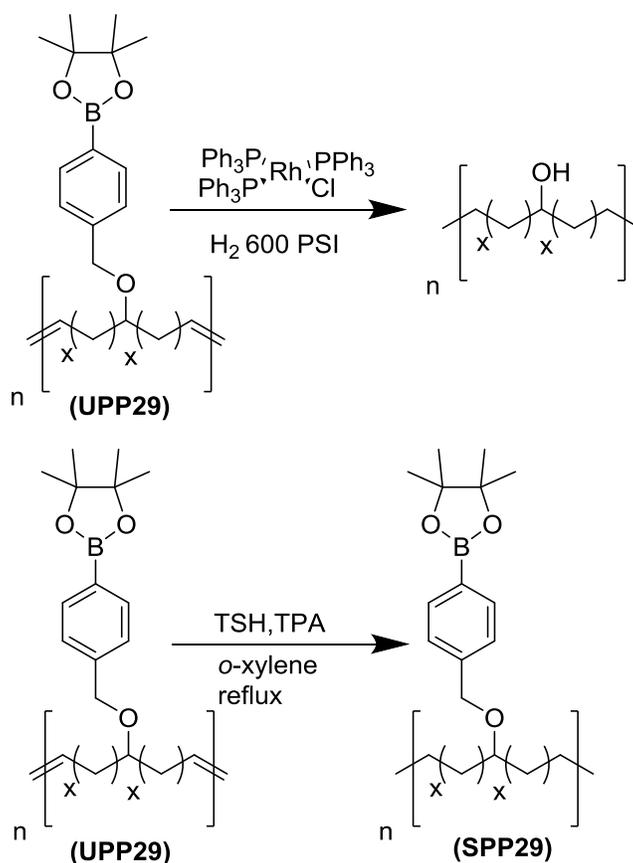


Figure 5 - 9. Hydrogenation of poly(4,4,5,5-tetramethyl-2-(4-((tricoso-1,22-dien-12-yloxy)methyl)phenyl)-1,3,2-dioxaborolane) (**UPP29**). Use of Wilkinson's catalyst caused cleavage of the pendant group. Stoichiometric hydrogenation with TSH, however, preserved the pendant group.

The (mostly) hydrogenated polymer **SPP29** was then analyzed via DSC (Figure 5 - 10). This polymer also displayed no melting temperature; however the glass transition temperature was shown to increase to about -11°C . This is consistent with the T_g of the identically spaced phenyl phosphonic ester polymer.⁴⁷ The endotherm seen at -36°C is not seen in the unsaturated polymer, it is believed to be caused by the precision nature of the polymer. This allows the phenyl boronic ester pendant groups to stack and creating their own melting endotherm. This hypothesis is supported by the work from *Watson et al.*⁶³ They report a precision polymer with a phenyl ring on every 19th carbon displays similar behavior, presumably from the phenyl ring.

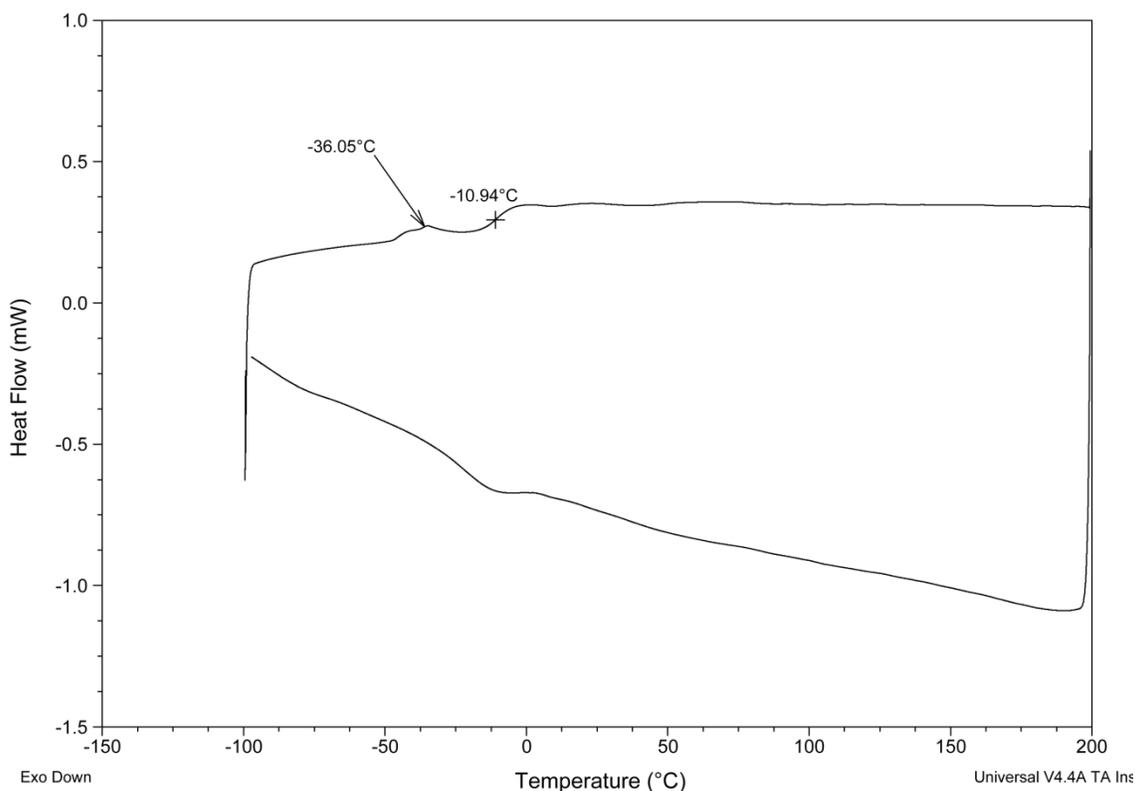


Figure 5 - 10. A T_g observed for hydrogenated poly(4,4,5,5-tetramethyl-2-(4-((tricoso-1,22-dien-12-yloxy)methyl)phenyl)-1,3,2-dioxaborolane) (**SPP29**) at -11°C . Another thermal transition is observed at -36°C most likely caused by the π -stacking from the phenyl rings

5.2.2 Polymerization and Characterization of In-Chain Boronic Acid Polymers (SPP39-41).

While the polymer with pendant phenyl pinacol boronic ester demonstrates some unique thermal properties, the inability to exhaustively hydrogenate the backbone limits the precise nature of the polymer. To solve this, another polymer system was devised (Figure 5 – 11).

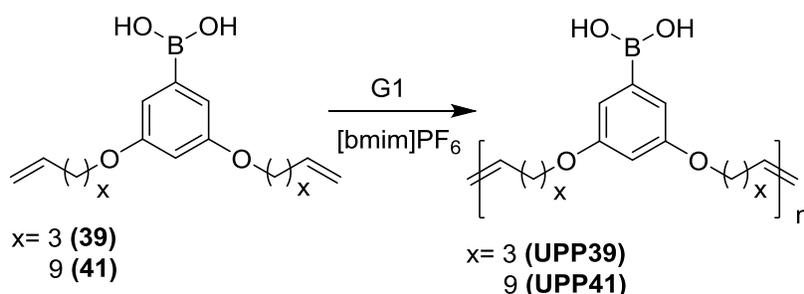


Figure 5 - 11. Precise polymerization of in-chain boronic acid monomers (**39-41**)

The resulting polymers were insoluble, so molecular weights could not be obtained. In an attempt to characterize these polymers, FT-IR with an ATR attachment was employed. Figure 5-12 compares the IR spectra of **41** and **UPP41**.

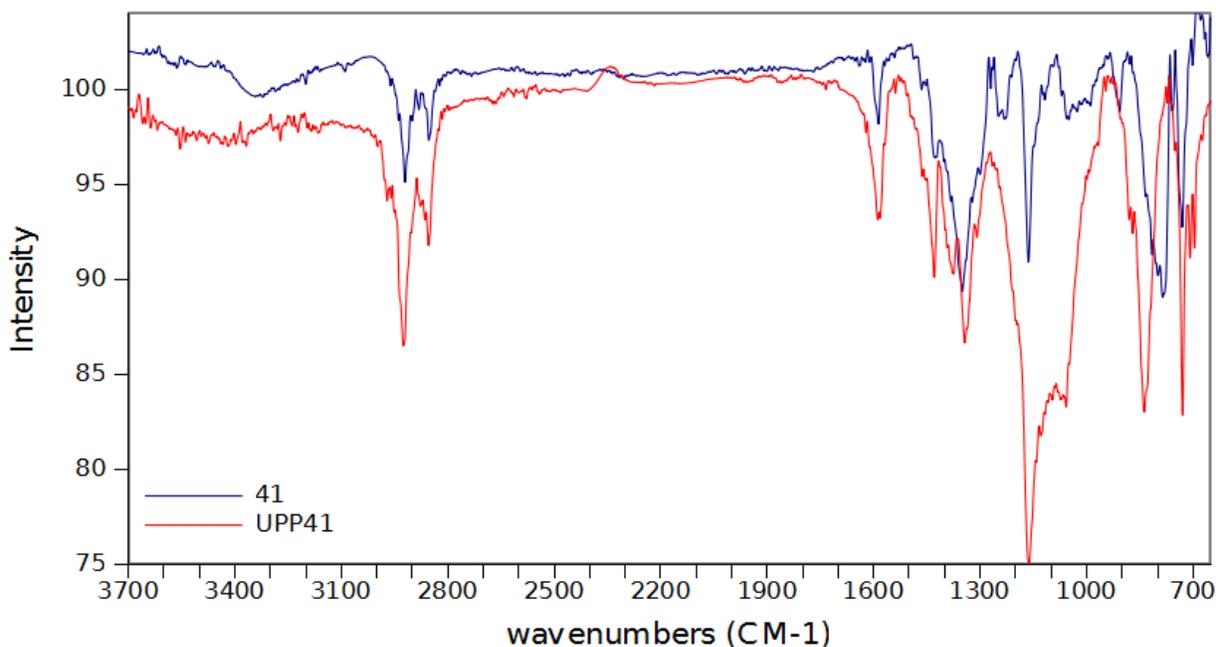


Figure 5- 12. IR of **41**(blue) and **UPP41** (red).

The IR of **UPP41** when compared to the monomer **41** displays many similarities, however, the differences between the monomer and polymer yield insights into nature of the polymer. The first difference is the intensity of the O-H peak at about 3450 CM^{-1} ; in the monomer this peak is fairly intense and well defined, however in the polymer this intensity and the definition of the peak is greatly reduced. This indicates that some of the boronic acids may have formed the boron anhydrides mentioned earlier. This effectively crosslinks the polymer, leading to the insolubility observed. The next difference in the polymer is the disappearance of the peak at about 800 CM^{-1} and the formation of the peaks at about 700 and 850 CM^{-1} . This change indicated the reduction in terminal olefin in the compound and increase in both the cis (700 CM^{-1}) and trans (850 CM^{-1}) internal olefins, indicative of polymerization. Similar results were obtained from **UPP39**.

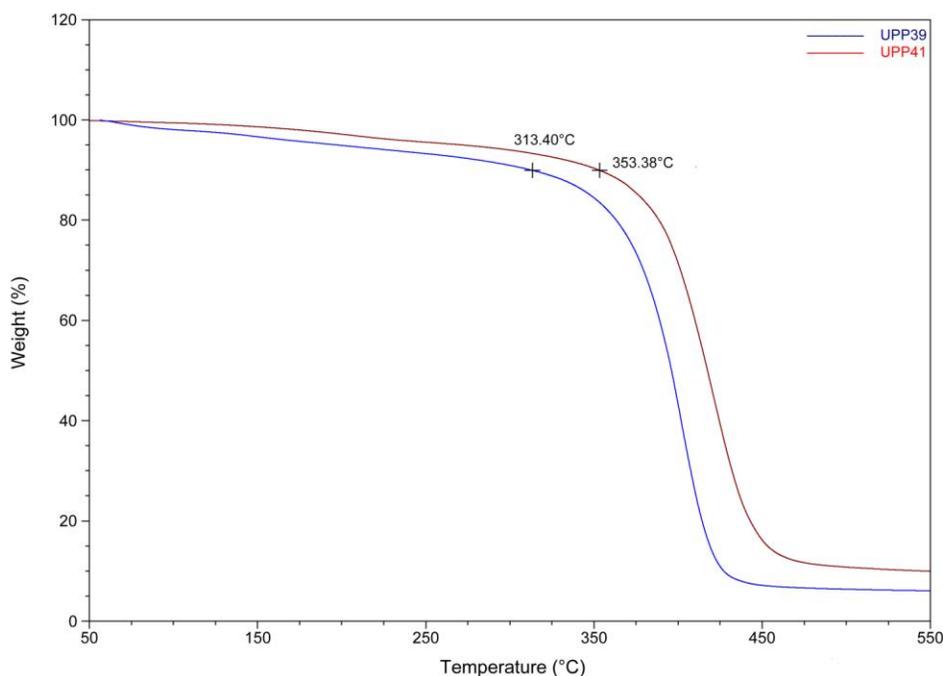


Figure 5- 13. Thermal stability of **UPP39** (blue) and **UPP41** (red)

The thermal stability of **UPP39** and **UPP41** was then examined using thermal gravimetric analysis (TGA). Both polymers demonstrate good thermal stability, maintaining 90 weight% until over 313°C and 353°C respectively. These decomposition temperatures are consistent with many unsaturated ADMET polymers, especially polymers containing acid and ester functionality.

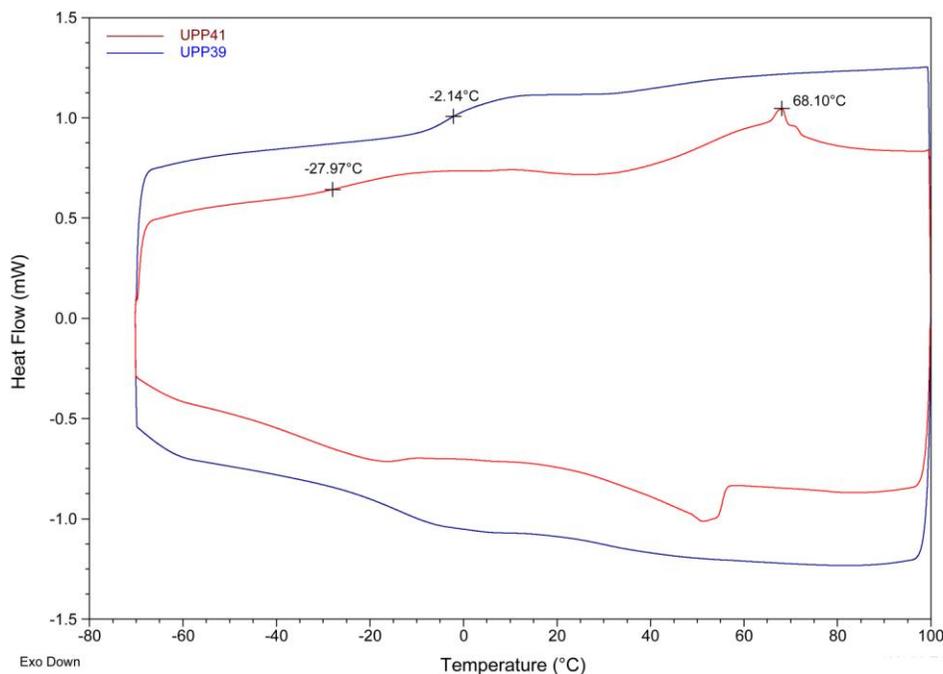


Figure 5- 14. Thermal transitions of **UPP39** (blue) and **UPP41** (red)

Finally, the two polymers were characterized via differential scanning calorimetry (DSC). **UPP39** displayed no T_m which is consistent with shorter ethylene spacers between functional groups and unsaturation in the backbone. The T_g of the polymer was -2°C. The glass transition temperature was fairly high when compared to other ADMET polymers; however a fairly high percentage of the polymer backbone was the ridged phenyl ring which can increase the T_g . **UPP41** displayed a significantly lower T_g than **UPP39**, around -28°C, this was expected since the relative concentration of phenyl ring in the back bone is much lower. In contrast to the DSC of **UPP39**; **UPP41** did display a

T_m at approximately 68°C. The peak is fairly broad indicating a variety of crystalline species that melt at slightly different temperatures. Interestingly, the first heating cycle of **UPP41** displayed a much sharper melting exotherm. This could be the result of the polymer annealing for long periods of time above the T_g , causing rearrangement into a more thermodynamically stable conformation. The presence of a melting temperature was unusual in an ADMET polymer with unsaturation in the backbone. The crystallinity in this case was presumably due to presence of free boronic acid.

5.3 Conclusions

By using the monomers synthesized in chapter 4, both boronic acid and boronic ester polymers have been formed via ADMET. The boronic ester polymer was polymerized using both bulk and ionic liquid polymerization techniques. Bulk conditions resulted in very low molecular weights, however using ionic liquids; high molecular weight polymers were formed. Upon saturation of the residual double bonds in backbone of the polymer, unique thermal behavior has been demonstrated.

Boronic acid polymers with 20 and 8 carbons between each functional group have also been made. These polymers have proven to be intractable, probably due to chemical crosslinking formed by formation boron anhydrides under vacuum conditions. These polymers were characterized via FT-IR. These IR spectra indicate that the repeat unit remained intact and the terminal olefin of the monomer disappeared and internal olefins were observed. These polymers demonstrate good thermal stability and unique thermal properties, presumably due to the boronic acid functionality. Due to the insolubility of these polymers, further characterization was not possible.

5.4 Experimental

5.4.1 Materials and Instrumentation

1-Butyl-3-methylimidazolium hexafluorophosphate was purchased from AK Scientific and purified via a neutral alumina plug followed by degassing via freeze-pump thaw in triplicate. All other materials were purchased from Aldrich and used without further purification unless noted. Grubbs 1st and 2nd generation catalyst (G1 and G2) as well as Hoveyda-Grubbs 1st and 2nd generation catalyst (HG1 and HG2) were kindly provided by Materia, Inc. Anhydrous solvents were obtained from an anhydrous solvent system. All ¹H NMR, and ¹³C NMR were obtained on a Varian Mercury 300MHz spectrometer and recorded in CDCl₃. ¹H and ¹³C chemical shifts were referenced to signals from CDCl₃. Mass spectrograms were carried out on a Thermo Scientific DSQ MS. Elemental analyses were carried out by Atlantic Microlab, Inc. Thermogravimetric analysis (TGA) was performed on TA Instruments TGA Q1000 Series using dynamic scans under nitrogen. Differential scanning calorimetry (DSC) analysis was performed using a TA Instruments Q1000 series equipped with a controlled cooling accessory (refrigerated cooling system) at 10 °C/min. Differential scanning calorimetry (DSC) analysis was performed using a TA Instruments Q1000 series equipped with a controlled cooling accessory (liquid nitrogen cooling system) at 10 °C/min. Gel permeation chromatography (GPC) was performed at 40 °C using a Waters Associates GPCV2000 liquid chromatography system with an internal differential refractive index detector and two Waters Styragel HR-5E columns (10 μm PD, 7.8 mm i.d., 300 mm length) using HPLC grade THF as the mobile phase at a flow rate of 1.0 mL/min.

5.4.2 Procedures

General procedure for ADMET polymerization in ionic liquids. Under constant argon flow, 1 equiv. of boron-containing monomer was added to flame-dried Schlenk flask equipped with a magnetic stir bar. Also under constant argon flow 1.5mL of 1-butyl-3-methylimidazolium hexafluorophosphate was added. .5-1 mol% of Grubbs 1st generation catalyst was then added to the reaction mixture. The reaction was then placed under high vacuum and polymerized for 48 hours at 50°C. At this time another .5-1 mol% of **G1** was added to the reaction and polymerized for another 24-48 hours at 50°C. After the requisite time the reaction was quenched with a solution of 2mL of ethyl vinyl ether in 10mL of toluene. The ionic liquid was extracted twice more with toluene. The organic layer was separated from the ionic liquid via pipette and the solvent removed under vacuum. The polymer was then dissolved in a minimal amount of toluene and precipitated into 250mL of cold ethanol or methanol. The polymer was filtered out and thoroughly characterized via NMR, DSC, TGA, and GPC.

Polymerization of 29 in ionic liquids. .5g of **29**, 1 mol% of **G1**, 1.5 mL of 1-butyl-3-methylimidazolium hexafluorophosphate, reacted at 50°C for 48 under vacuum. Another 1 mol% of **G1** was added and reacted under vacuum for another 48 hours. Mn: 58000 g/mol ¹H NMR (300MHz, CDCl₃, ppm): δ= 7.80 (d, 2H); 7.40 (d, 2H); 5.40 (m, 2H); 4.55 (s, 2H); 3.4 (m, 1H); 2.10-2.00 (q, 4H); 1.75-1.10 (m, 44H) ¹³C NMR (75 MHz, CDCl₃, ppm): δ= 142.67, 134.97, 130.14, 127.01, 83.84, 79.22, 70.70, 34.02, 33.99, 30.04, 29.81, 29.76, 29.69, 29.34, 29.14, 25.17, 25.04.

Hydrogenation of 29 via TSH and TPA. 1 equiv. of **UPP29** was dissolved in dry o-xylene in a flame dried 3-neck flask. 3 equiv. of p-toluenesulfonyl hydrozine (TSH) and tripropyl amine (TPA) was then added and the reaction vessel was equipped with a

reflux condenser and an oil bubble. The reaction was refluxed until no nitrogen was observed being released from the bubbler, about 3 hours. Another 3 equiv. of TPA and TSH was added and refluxed. This was repeated twice more. The reaction was then cooled, and the solvent removed. The resulting residue was then dissolved in a small amount of toluene and precipitated into cold ethanol. The polymer was collected via filtration and dried under vacuum yielding **SPP29**.

^1H NMR (300MHz, CDCl_3 , ppm): δ = 7.80 (d, 2H); 7.40 (d, 2H); 4.55 (s, 2H); 3.4 (m, 1H); 1.75-1.10 (m, 50H) ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ = 142.67, 134.97, 127.01, 83.84, 79.22, 70.70, 30.04, 29.81, 29.76, 29.69, 29.34, 29.14, 25.17, 25.04.

Polymerization of 39 in ionic liquids. .25g of **39**, 1mol% of **G1**, 1.5 mL of 1-butyl-3-methylimidazoiium hexaflourophosphate, reacted at 50°C for 48 under vacuum. Another 1mol% of **G1** was added and reacted under vacuum for another 24 hours. The insoluble polymer was filtered from the reaction.

FT-IR (ATR, CM^{-1}): 2910, 2840, 1600, 1375, 1175, 840, 710

Polymerization of 41 in ionic liquids. .25g of **41**, 1mol% of **G1**, 1.5 mL of 1-butyl-3-methylimidazoiium hexaflourophosphate, reacted at 50°C for 48 under vacuum. Another 1mol% of **G1** was added and reacted under vacuum for another 24 hours. The insoluble polymer was filtered from the reaction.

FT-IR (ATR, CM^{-1}): 3450, 2920, 2800, 1600, 1325, 1140, 840, 710

CHAPTER 6 Summary and Future Work

6.1 Summary

The work herein displays the use of boron-containing Lewis acids in various olefin metathesis applications. Ionic liquids were also studied as new reaction medium for acyclic diene metathesis polymerization.

Boron-containing Lewis acids were first studied for their effect on the various Grubbs and Hoveyda-Grubbs catalysts. Grubbs catalysts have displayed increase yields in the presence of the appropriate concentration of pinacol phenyl borate. The Hoveyda-Grubbs catalysts, which do not contain phosphine ligands, predictably do not display any increase in yields. Surprisingly, Hoveyda-Grubbs 2nd generation catalyst displays a decrease in conversion. Since this effect is not seen with Hoveyda-Grubbs 1st generation catalyst, it is proposed that Lewis acid interacts with N-heterocyclic carbene, destabilizing the catalyst. The products were also analyzed for isomerization. The reactions run with catalysts prone to isomerization, Grubbs and Hoveyda-Grubbs 2nd generation catalysts, displayed a dramatic decrease in isomerization. This study demonstrates the utility of boron-containing Lewis acids in olefin metathesis.

Next the use of 1-butyl-3-methylimidazolium hexafluorophosphate was studied for application as a new reaction medium for ADMET polymerization. A concentration study found that .5 mol% catalyst loading was ideal for reaching high molecular weight polymers. By keeping the reaction in solution, maximum molecular weights were reached in 48 hrs. Purity of the ionic liquid was found to be very important; any residual imidazole will prevent the formation of polymer. Addition of phosphoric acid, however, allowed the polymerization to proceed. Addition of a boron-containing Lewis acid did not

prevent imidazole from shutting down the polymerization, but did increase molecular weights when added to the polymerization under other conditions. Solubility of the monomer in the ionic liquids plays an important role, when the monomer is only minimally soluble low molecular weights are obtained. However, at higher temperatures, above the monomers melting point, high molecular weights are obtained.

Syntheses of boronic acid monomers have proven to be a challenge. First alkyl boronic acid monomers were attempted, however, due to instability of the monomer, this approach was abandoned. Next a variety of aryl boronic acid monomer syntheses were attempted. Using this approach a variety of boronic acid and ester monomers have been synthesized. Deprotection of boronic acid was also studied. The pinacol protecting group has proven difficult to remove, however, benzylic protecting groups were observed to cleave under hydrogenation conditions using Pd/C.

Using the precise monomers synthesized above, precision polymers were then made. The pendant phenyl boronic ester polymer was polymerized using Grubbs 1st generation catalyst and molecular weights of 58000 were obtained. Upon hydrogenation, the glass transition temperature was increased, also an endotherm associated with the pendant phenyl ring was observed.

6.2 Future Work

6.2.1 Analysis of Boronic Acid Polymers via X-ray Scattering

Now that the precise boronic acid polymers have been synthesized, they can be studied to determine their morphology. As mentioned previously, both the precision carboxylic acid and phosphonic acid polymers have shown unique morphologies only seen in the precision polymers. Carboxylic acid polymers, pK_a of about 4.75, demonstrated a hydrogen bonded layered morphology, while the phosphonic acid

polymer, pK_a of about 1, demonstrated more ionic character. Since boronic acid polymers are the least acidic, their morphology should be different still. This work will be carried out by our collaborators in Karen Winey's group at University of Pennsylvania.

6.2.2 Synthesis of other Boron-Containing Lewis Acid Monomers

A variety of other precision boron-containing Lewis acid monomers can be synthesized (Figure 6 - 1). These polymers display a wide range of Lewis acidities, boronic acid being the lowest, pinacol boronic ester in the middle, and triphenyl borane being the most acidic. The morphology of precise acid polymers demonstrates a dependence on the acid pK_a , ranging from ionic aggregates to hydrogen bonded dimers. Is this true for aprotic Lewis acids? The purpose of this study is to determine how the morphology of a polymer is affected by the Lewis acidity of the pendant group.

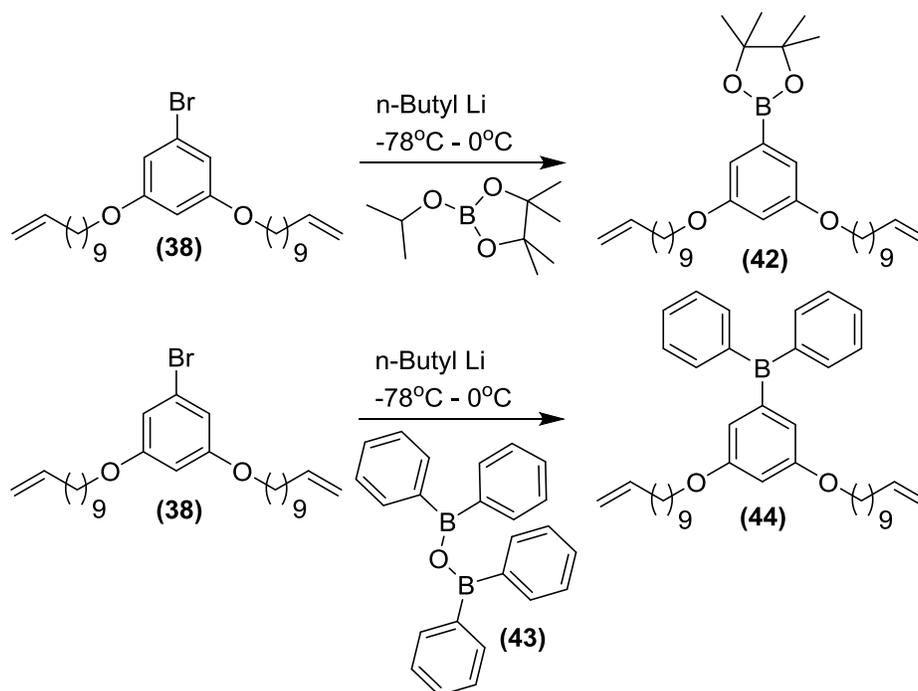


Figure 6 – 1. Synthesis of boron-containing Lewis acid monomers (42, 44)

Two other monomers are proposed to be synthesized, the boronic ester and diphenyl borate monomers. The synthesis of these monomers would be largely the

same as the synthesis for the boronic acid monomers (**39-41**). Lithiation could then be conducted using the isopropoxyboronic acid pinacol ester instead of the tripropyl borate for the boronic ester monomer. The diphenyl borate monomer could be synthesized by conducting the lithiation with diphenylboronic anhydride (**43**) as the boronating agent.

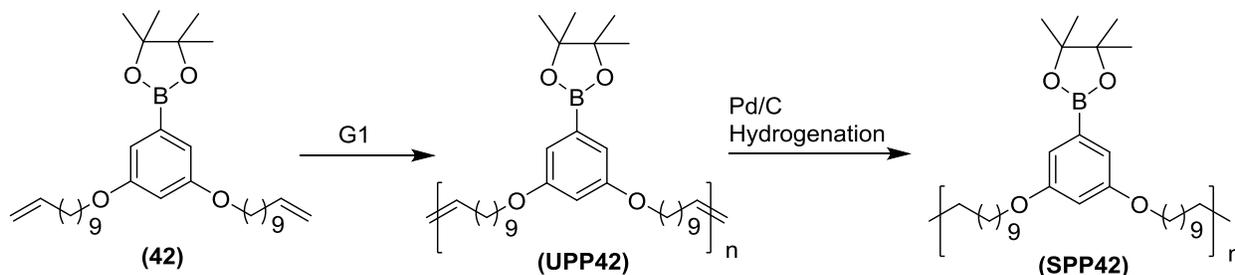


Figure 6 - 2. Precise polymerization and hydrogenation of 2-(3,5-bis(undec-10-en-1-yloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**42**)

Once these monomers are synthesized they can be polymerized using ADMET polymerization, followed by hydrogenation of the double bonds (Figure 6 – 2 and 6 – 3). The morphology can be studied using X-ray diffraction and the thermal properties can be analyzed.

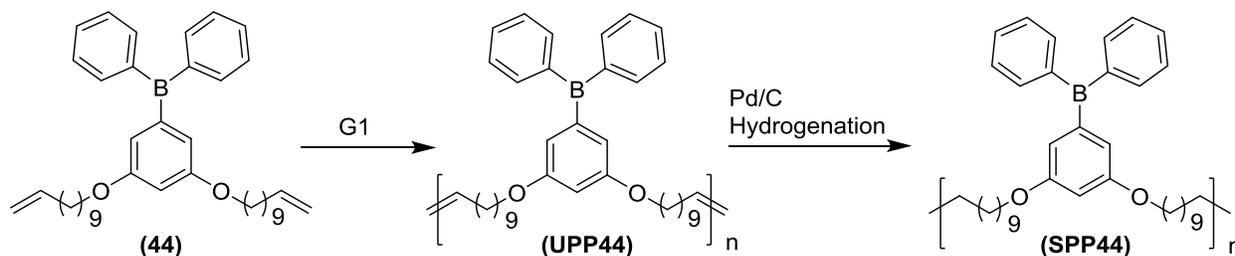


Figure 6 - 3. Precise polymerization and hydrogenation of (3,5-bis(undec-10-en-1-yloxy)phenyl)diphenylborane (**44**)

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BIOGRAPHICAL SKETCH

Chester (Chet) Kent Simocko was born in Bar Mills, Maine in 1986. He is the son of Gertrude Kent and Robert Chris Simocko. After graduating from Bonny Eagle High School, he began studying chemistry at Rensselaer Polytechnic Institute (RPI) in Troy, New York. He studied the use of waste cellulose for new green polymers under Prof. James Moore for 2.5 years and synthesized fluorescent displacer for use in displacement chromatography under Prof. Steven Cramer for 1 year. In 2008, he graduated from RPI with a Bachelors of Science. in chemistry and move to the University of Florida (UF) to pursue a PhD in chemistry. He decided to join the Wagener group and pick up work with the acid project, synthesizing precision boronic acid polymers. This project is done in collaboration with Dr. Karen Winey at University of Pennsylvania. During his time at UF, he developed a collaboration with Dr. Timothy Swager at the Massachusetts Institute of Technology (MIT) studying the use of ionic liquids on olefin metathesis. He enjoys cycling, having twice completed the Horse Farm Hundred Century ride, as well as home brewing and is a member of the Hogtown Brewers. He has won numerous awards in homebrew competitions from all over the state of Florida.