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INVESTIGATION INTO THE SYNTHESIS AND CHARACTERIZATION OF POLY(DIOXABOROLANE)S

by

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DEDICATION

In the memory of Dr. Marc S. Maynor

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First and foremost I have to thank God because without Him, this would have not been impossible. There are many people that have helped me reach this point and I am grateful to each and every one of you. Dr. Lavigne, I have learned so much from you: importance of paying attention to smallest of details when presenting to the importance of asking questions and questioning what you read, and how to “reason” through questions you may not know how to answers. I truly thank you for accepting and keeping me as a member of your group. Next, I would like to thank my parents, especially my mother Linder, who has always been there to encourage me and made sure that I stayed the course. To all of my friends and family, thank you for the encouragement, the ability to vent, and being available whenever I have needed you the most.

ABSTRACT

Boronate esters have evolved from being primarily used as sensors to being the integral linkage in complex materials such as macrocycles, covalent organic frameworks, and linear polymers. Poly(boronate)s, linear polymers that are linked via a boronate ester, have not been extensively researched. In 2005, the Lavigne group published the first manuscript on poly(dioxaborolane)s, i.e., six-membered, nonconjugated polyboronates. The behavior of the materials in solution was studied extensively, but little is known about the solid state properties of the material other than they form brittle films.

Poly(dioxaborolane)s are generated in high yield through a facile step-growth polymerization, but the reaction parameters, such as monomer choice, solvent choice, and the ratio of monomer to solvent, were never investigated. Herein, the optimization of experimental parameters will be discussed with respect to the role each factor plays and how optimizing these conditions increase the ductility of the film. Several different poly(boronate)s were also synthesized to show the robustness of the polymerization as well as attempting to control material properties. The viscoelastic properties of the polyboronates materials show that they possess toughness between polystyrene and PET.

It is well known that boronate esters are susceptible to hydrolysis, which is a point of concern for poly(boronate) materials. Therefore, we investigated the stability of three different types of materials: a homopolymer, random copolymer that contained monomers that are capable of pi-pi stacking, and a mesoporous polymer that contains a nonplanar tetraol. It was discovered the most ductile and stable film is the non-porous homopolymer.

Finally, to gain a better understanding of materials that have boronate esters incorporated into the main chain of the polymer, we synthesized diboronic acid and tetraol monomers that contain flexible alkyl groups. Focusing on simple substitution reactions, we were able to successfully synthesize several tetraols.

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CHAPTER 1: INTRODUCTION TO BORONATE LINKED MATERIALS

1.1 SCOPE

This chapter functions as an introduction to the boronic acid moiety and the boronic ester. To provide a better understanding of the interest in boronate ester linked materials, the chemistry behind the boron-diol interaction will be discussed. We will discuss the evolution of boronate esters as sensors to more complex materials such as macrocycles, covalent organic frameworks (COFs), and linear polymers.

1.2 BACKGROUND

A boronic acid is a compound that contains trivalent boron with one alkyl or aryl bond and two hydroxyl groups (**Figure 1.1**). Boronic acids have structures very similar to carboxylic acids in the regard that the boron center is sp^2-hybridized and has a trigonal planar geometry. However, unlike carboxylic acids, boronic acids do not naturally occur.[1] Frankland discovered the first alkyl boronic acid compound, ethylboronic acid, more than two centuries ago. About twenty years later, Michaelis and Beker reported the synthesis of phenyl boronic acid by hydrolyzing dichlorophenyl borane.[2] However, it was not until 1954 that the boronic ester was discovered. Kuivila and coworkers reported the formation of a cyclic boronic ester when phenyl boronic acid was added to a saturated solution of mannitol.[3] A boronic acid is converted into a boronic ester by undergoing a dehydration reaction with mono-, di- or multi-functional alcohols. Reacting boronic acids with either 1,2- or 1,3-diols results in the more stable cyclic diester (**Figure 1.1**).[4] Ester formation does occur in aqueous media at basic pH or if the boronic acid has an internal Lewis base to coordinate to boron.[5] Early applications exploited the ease of B-O covalent bond formation to design sensors for the detection of sugars. Boronic acid sensors have been designed for fluorescence, photoinduced electron transfer, and electrochemical detection. Further investigation led to the ability to incorporate selectivity into sensors by strategically placing diboronic acids in the sensor structure, opposed to the mono-functional boronic acid.[6]

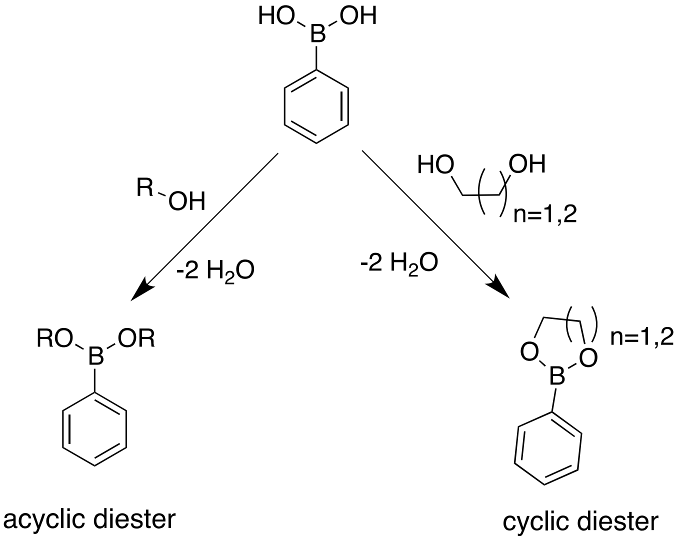


Figure 1.1: Boronic acid reacts with alcohols or diols to form boronate esters.

Boronate ester linkages are an excellent choice for a covalent linker due to the unique combination of their strength (~130 kcal/mol)[7], ease of formation, and inherent reversibility. The strength of the B-O bond is attributed to partial double bond character that results from the interaction of one of the lone pair electrons on oxygen and the empty *p*-orbital on the trigonal planar sp^2-hybridized boron.

A key facet of this strong, readily formed bond is its forgiving nature: under controlled conditions the reversibility of boronate ester formation favours production of the more thermodynamically stable species. This reversibility is a direct result of the Lewis-acidity of boron, which also makes it feasible to coordinate (either inter- or intra-molecular) weak nucleophiles to form sp^3-hybridized boron with tetrahedral geometry. The susceptibility to coordinate nucleophiles as weak as water, must be considered when designing aqueous applications for boronate ester-linked materials because structural integrity may be compromised in the presence of water. However, in recent work, synthetic strategies to provide hydrophobic protection from hydrolysis have been identified along with testing methods toward kinetic evaluation and comparisons of boronate ester hydrolysis.[8] These studies may provide additional control of the inherent reversibility, favouring the strong B-O bond.

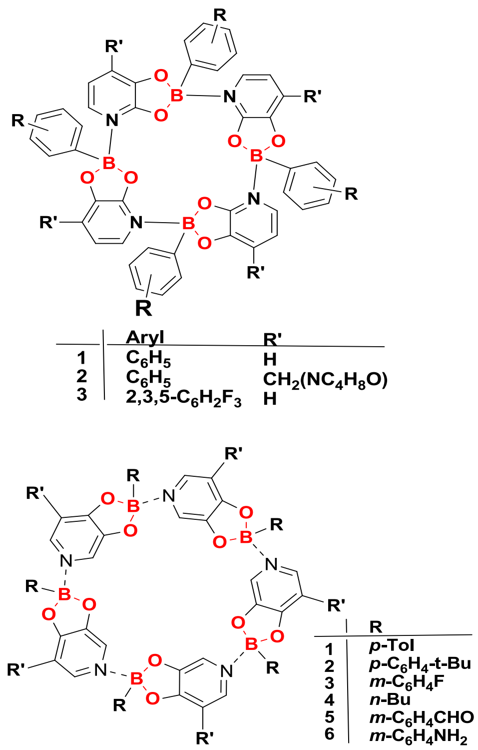
Molecular tectonics produced the engineering of porous boronic acid crystals. These materials self-assembled *via* hydrogen bonds and were robust enough to withstand removal and exchange of solvent guests. Inspired by the ease of self-assembly using non-covalent bonds, chemists were inspired to seek covalently self-assembled approaches.[9] The boronate ester has become a prototypical covalent linkage, which provides a stronger, yet reversible, bonding strategy in self-assembled molecular design.

In the past decade, a diverse collection of boronate ester-linked materials has been developed based on the condensation reaction of boronic acids with 1,2-diols. Undoubtedly, the increasing attention afforded to the B-O linkage is due, at least in part, to both the mild reaction conditions required for the formation of this covalent bond and the reversible nature of this linkage under specific conditions. These materials have found applications in many areas of materials science. Utilization of boronate ester bonds to connect carefully selected monomers has produced materials with interesting electronic properties, such as blue emissivity and semiconductivity; as well as porous materials with promising applications in gas storage, sequestration, separations, and semiconductivity.[10]

Today, the combined unique properties of boronic ester (Lewis acidity, reversible binding ability, and mild reaction conditions) have been advantageously used to assemble novel and more complex materials with applications beyond sensing. Some boronic ester-linked materials have been shown to self-assemble in the solid state,[11] form either macrocycles,[12-13] or network (two-dimensional, 2D and three-dimensional, 3D) solids[12c,14] called covalent organic frameworks (COFs), and linear polymers,[2b] some of which have been shown to be repairable.[11] The family of potential materials is continually growing as interest in the boronate ester expands. It should be noted that, although boronic acid side chains on polymers,[15] hydrogen bonding between boronic acids to form crystalline materials,[16] and boronate anhydrides[17] are all intriguing, they are not the focus of this dissertation. Herein, the focus will be on the structure-property relationships and applications of boronic ester-linked products. Considering the rapid development of these materials, it appears that the broad scope of design for future boronic ester materials is limited only by the chemist's imagination for defining structure and ingenuity in identifying applications.

1.3 Macrocycles

Soluble boronate ester linked macrocycles are formed by the reversibility of boron-oxygen ester bond formation in cooperation with boron-nitrogen dative bond (**Figure 1.2**). The first boronate ester macrocycles were formed from reacting substituted aryl boronic acids with 2,3-dihydroxypyridine.[13] Formation of the dative nitrogen-boron bond produces a macrocycle with an almost perfect square orientation and S_4 symmetry. The flexibility of the synthetic approach was tested and proven by producing macrocycles using substituted aryl groups (**Figure 1.2** top structure). Subsequently, the macrocyclic square made with four boronate ester-linked sides, was subsequently expanded to a pentagon center by changing the 2,3-dihydroxypyridine to 3,4-dihydroxy-pyridine.[14] These studies were followed by the design and production of more complex macrocycles, such as bicyclic cages, dendrimers and rotaxanes, and others with solvent-dependent structures.



	Aryl	R'
1	C_6H_5	H
2	C_6H_5	$CH_2(NC_4H_8O)$
3	2,3,5-$C_6H_2F_3$	H

	R
1	*p*-Tol
2	*p*-C_6H_4-t-Bu
3	*m*-C_6H_4F
4	*n*-Bu
5	*m*-C_6H_4CHO
6	*m*-$C_6H_4NH_2$

Figure 1.2: Examples of macrocycles that self-assemble via a combination of both covalent yet reversible boronate ester and dative B-N bonds.

Further functionalization of the exterior of a macrocycle was realized by incorporation of a *third* reversible reaction—imine formation—that produced dendritic nanostructures. Combination of 3,5-diformylphenylboronic acid, 2,3-dihydroxypyridine, and 3,5-bis(benzyloxy)-benzylamine promoted imine formation in a concerted reaction that produced the boronate ester sides of the cyclic core which were connected by boron-nitrogen dative bonds.[15] The six-hour, one-pot reaction produced dendritic macrocycles in over 50% yield. The resulting structures (**Figure 1.3**) have up to ten imine-connected R groups, and demonstrate the co-formation of all three reversible reactions without the need to pre-form the boronate ester, or the macrocycle, prior to imine formation.

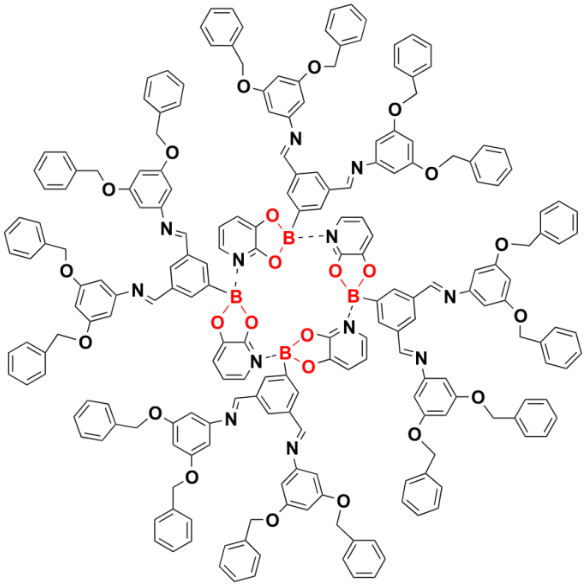
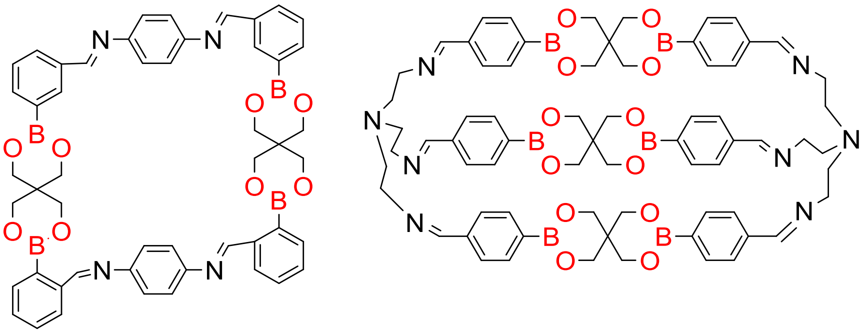


Figure 1.3: A dendritic macrocycle comprised of three reversible bonding motifs: boronate ester and dative B-N bonds connect the inner cycle, and imine linkages attach the outer branches.

Servin's group was able to form a macrocycle using a one pot, three-component synthesis, reacting 1,4-diaminobenzene with pentaerythritol and 3-formylphenylboronic acid.[18] The four-sided cage was held together by both boronate-ester and imine bonds. This strategy was employed to introduce even more structural complexity by replacing the 1,4-diaminobenzene with tris(2-aminoethyl)amine and changing from 3- to 4-formylphenylboronic acid to produce a chloroform macrobicyclic cage. Both structures are shown in **Figure 1.4**. Mass spectrometry and single-crystal X-ray analysis verified the macrobicyclic structure with a 20.5Å cavity. Remarkably, the cage (prepared in one-pot with 82% yield) is assembled *via* formation of 18 covalent bonds—12 of which were B-O bonds of boronate ester linkages. This complex structure undoubtedly owes its construction to these multiple forgiving and reversible boronate ester bonds. By taking advantage of this reversibility, nano-sized cages and macrocycles are designed.

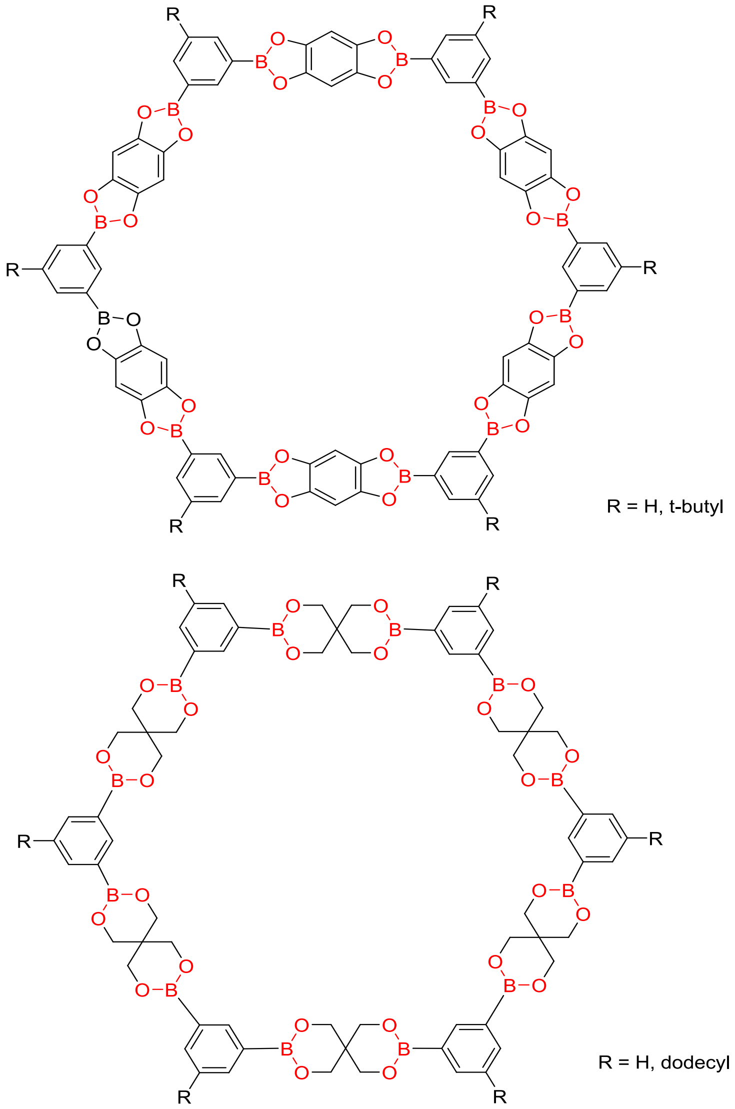


macrocycle

macrobicyclic cage

Figure 1.4: Examples of macrocycles linked by both boronate ester and imine bonds.

Planar macrocycles (**Figure 1.5**) that are connected solely by boronate ester bonds have been made based on 1,3-benzenediboronic acid with 1,2,4,5-tetrahydroxybenzene or pentaerythritol. [19] These macrocycles stack into supramolecular columns in an analogous manner to linear oligomers, and also form microporous channels as determined by nitrogen adsorption.[20] Proton NMR testing for end-group analysis and FTIR testing both showed no terminal hydroxyl groups, suggesting macrocycle formation. Molecular weight analysis was obtained by substituting the diboronic acid at the 5-position with t-butyl or dodecyl branches, which aided in solubilizing the products. Reasonable molecular weight for macrocycle formation with t-butyl was obtained, but suggested that the longer dodecyl substitution interfered with formation of a macrocycle and produced a polymer instead. Thus, there is an indication that varying substitutions on the diboronic acid may control polymeric or macrocyclic formation.



R = H, t-butyl

R = H, dodecyl

Figure 1.5: Examples of macrocycles linked by only boronic ester bonds.

Other boronic ester-linked macrocycles of Takahagi's group also do not require any dative B-N bonds for cyclization (**Figure 1.6**).[21] Takahagi used 1,4-diboronic acid and an enantiomeric mixture of bis-diol to form boronate ester linkages. Changing reaction time, solvent, and guest molecules formed either insoluble polymers or soluble macrocycles of various sizes. The [2+2] macrocycle was formed from adding two equivalents of diboronic acid with a racemic mixture of the bis-diol. Interestingly, when optically pure bis-diol was used the macrocyclic ring did not form and polymerization occurred instead. It was shown that toluene promoted the [2+2] macrocycle, but benzene promoted the [3+3] product in which the enantiomer ratio of the bis-diol was 2:1. The slight difference in guest solvent promoted formation of one macrocycle over the other. Also, interconversion between the [2+2] to [3+3] macrocycles was demonstrated by changing the toluene or benzene guest. Again, this interconversion would not be possible without the inherent reversibility of the boronate ester formation.

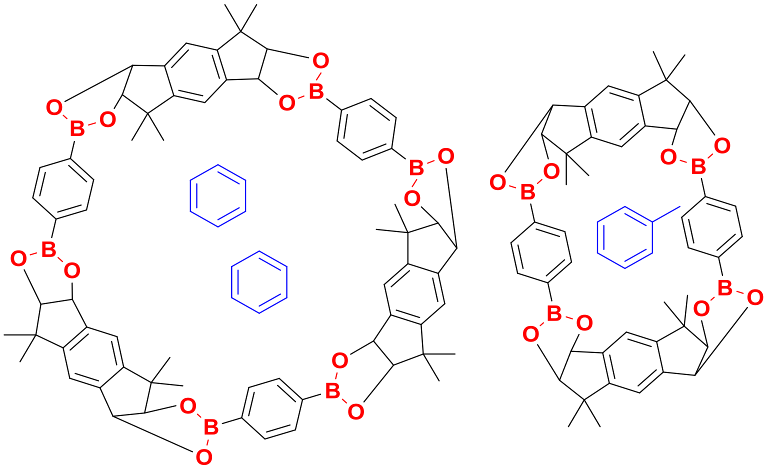


Figure 1.6: A unique boronate ester-linked macrocyclic system—interconversion from [3+3] to [2+2] cycles is solvent-dependent.

Yet more molecular complexity was achieved *via* boronate ester and B-N dative bond formation when a rotaxane was produced.[24] The combination of catechol with phenyl boronic acid formed the stoppers, which were linked through dative bonds with a 1,2-di(4-pyridyl)ethylene linker, to form the axle. The axle was encircled by a crown ether as shown by **Figure 1.7**. The crown ether was capable of slipping onto the dipyridyl axle due to the reversibilities of both the dative B-N bond and the boronate ester formation. These macrocycles, dendrimers, and rotaxanes represent the trend in increasing structural complexity characteristic of recent boronate ester research.

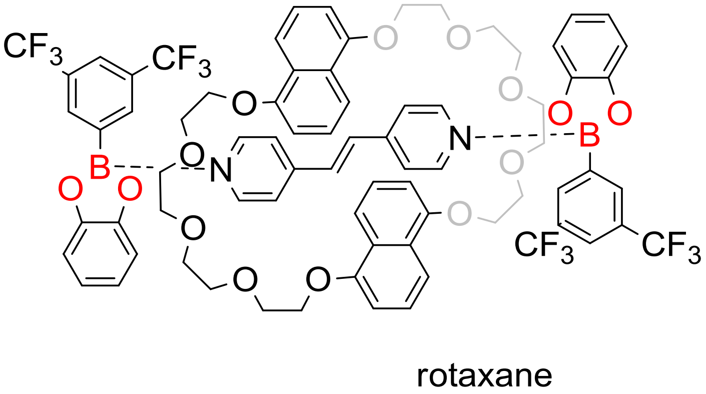


Figure 1.7: The boronate ester stoppers of this rotaxane cooperate with B-N coordination to allow the crown ether to slip onto the dipyridyl axle.

1.4 Covalent Organic Frameworks

Here, the reversibility of the boronate ester formation is vital in the production of the highly ordered micro- and mesoporous crystalline frameworks. Condensation reactions between carefully designed and synthesized (or purchased) difunctional aromatic boronic acids with difunctional aromatic 1,2-diols have resulted in both 2- and 3-dimensional covalent organic frameworks (COFs).

1.4.1 Two-dimensional COFs

In a 2-dimensional COF, planar, aromatic monomers are linked by boronate ester bonds, forming polymeric sheets. These sheets stack face-to-face through π-interactions and result in the formation of void-space or channels (see **Figure 1.8a**).

The first two reported COFs (COF-1 and COF-5) were designed by Yaghi and colleagues.[10c] COF-1 was a boroxine-linked framework made from self-condensation of 1,4-benzenediboronic acid (BDBA). The 27Å mesoporous channels of COF-5 (**Figure 1.8b**) were formed by a three-day sealed tube reaction of commercially available BDBA with 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) in 73% yield.

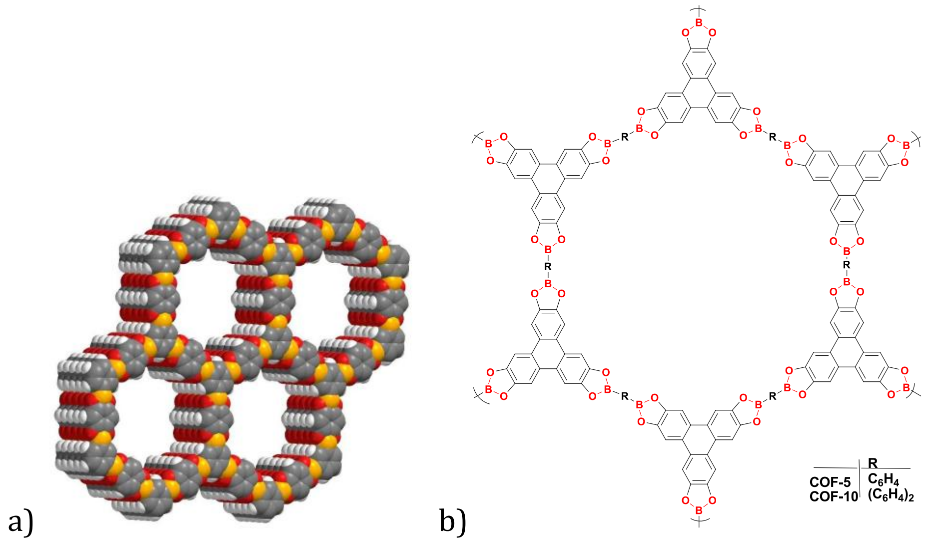


Figure 1.8: a) A representation of 2-dimensional stacked sheets in a COF with hexagonal pores. b) COF-5, formed from BDBA and HHTP, was the first boronate ester-linked 2D COF reported.

on a ten milligram scale. BET surface area for COF-5, calculated from nitrogen isotherms at 77 K, was 1590 m^2 g^{-1}.

Concurrent research in the Lavigne lab resulted in the development of COF-18Å (**Figure 1.9**) with 18Å channels resulting from the condensation reaction of 1,3,5-benzene triboronic acid (TBA) with 1,2,4,5-tetrahydroxybenzene (THB).[22] The framework was achieved in an open refluxing system under nitrogen on a gram-scale with greater than 95% yield *via* a three-day reaction. Like COF-5, COF-18Å exhibited a very high BET surface area of 1260 m^2g^{-1}.

The monomers for the COF-18Å were synthesized in the Lavigne lab, which made them readily modifiable. By increasing the length of alkylation on the bis-diol monomer, pore size was tailored to produce gradually smaller microporous channels.[23] Incorporation of methyl, ethyl, and propyl groups reduced the 18Å pore to 16, 14, and 11Å, respectively. The resulting frameworks, COF-16Å, COF-14Å, and COF-11Å, were made in the same manner as COF-18Å in >90% yield on the gram scale. Although the BET surface areas of the alkylated pores were lower than COF-18 Å, the hydrogen uptake per pore was actually enhanced by the incorporation of the non-polar groups. Additionally, the hydrolytic stability of these alkylated 2D COFs is better than the bare-pore frameworks.[8] Similar protection of the boronate ester linkage from degradation in aqueous applications may be beneficial for linear polymers and macrocycles as well, and this alkylation approach could provide crucial stability.

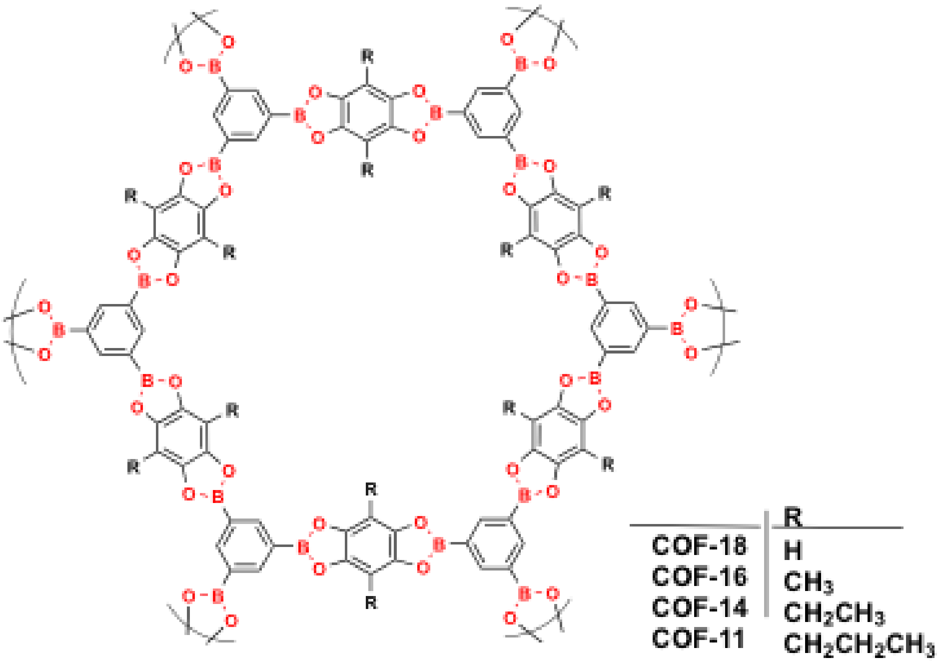


Figure 1.9: Tailored pore size was achieved in the design of this family of 2D COFs. COF-18 Å is synthesized from TBA and THB. Alkylated THB monomers replaced THB to make COF-16Å (methyl), COF-14Å (ethyl), and COF-11Å (propyl). Increasing alkyl length in the COF pores was shown to improve hydrolytic stability of the framework.

Demonstrating an alternative method to tailor pore size, more 2D COFs were produced which included COF-6, COF-8, (**Figure 1.10**) and COF-10 (shown in **Figure 1.10b** analogous to COF-5).[21] These boronate-ester linked frameworks were made by reaction of HHTP each with a different boronic acid. COF-6, like COF-18Å, was made with TBA. The use of this tris-diol (HHTP) with TBA resulted in 8.7Å hexagonal pores. For COF-8, the larger triboronic acid, 1,3,5-benzenetris(4-phenylboronic acid) (BTPA) produced larger pores (16.4Å). And, finally, COF-10's largest pores of 31.7Å were made when 4,4-biphenyldiboronic acid (BPDA) was used. The Langmuir surface areas for these materials were found by nitrogen isotherm to be 980, 1400, and 2080 m^2g^{-1} for COF-6, -8, and -10, respectively. (The BET surface areas were not reported.)

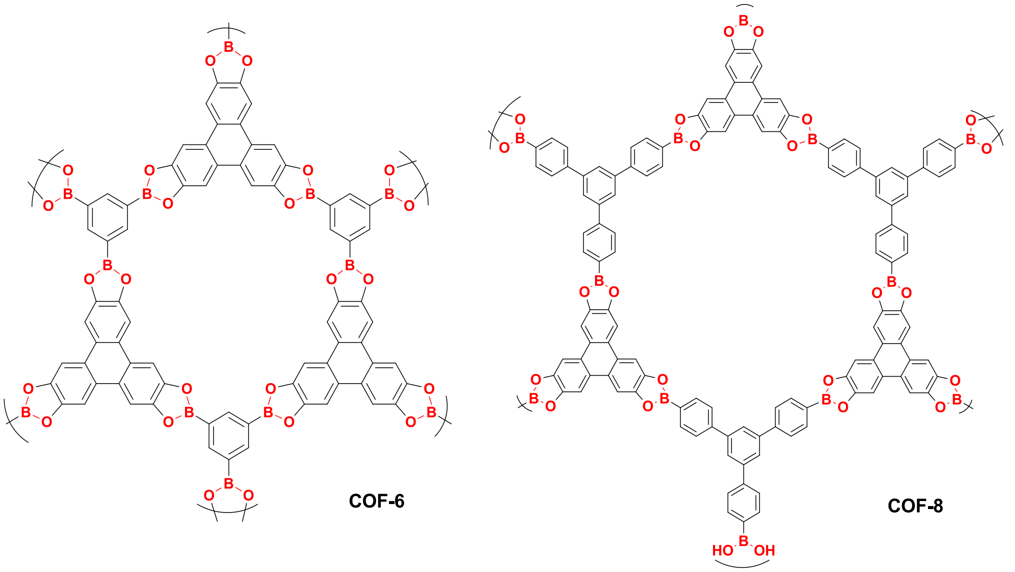


Figure 1.10: Pore size modifications by careful selection of monomers give three more 2D COFs: COF-6 and COF-8 and COF-10 (shown with COF-5 in Figure 1.8b)

Designing and synthesizing new materials is a challenge enjoyed by many pure research chemists, but the ultimate goal of finding practical applications will promote the use of boronate ester linked materials in the real world. In a boronate ester, when the empty *p*-orbital of the *sp*^{2}-hybridized boron is coplanar with aromatic monomers, the intriguing capacity to extend conjugation of planar systems exist; thus, incorporating more than mere porosity and crystallinity to the resulting boronate ester linked materials. As an outstanding example, Jiang and coworkers have not only developed a new COF, they have also extensively analyzed its properties and found TP-COF (**Figure 1.11,** left structure) to be semi-conducting and blue luminescent.[12a] By combining HHTP with pyrene diboronic acid (PDBA), these researchers have engineered a mesoporous, blue-luminescent, semiconducting TP-COF with a pore diameter of 32Å across the hexagonal channels. BET surface area by nitrogen adsorption was found to be 868 m^{2}g^{-1}. The stacking of the planar boronate ester-linked sheets was shown to have triphenylene and pyrene units each superimposed on themselves. For this COF, intramolecular singlet energy transfer from triphenylene to pyrene was proposed as the mechanism for its blue luminescence. Additionally, this material demonstrated p-type semiconducting character from I-V profile experiments.

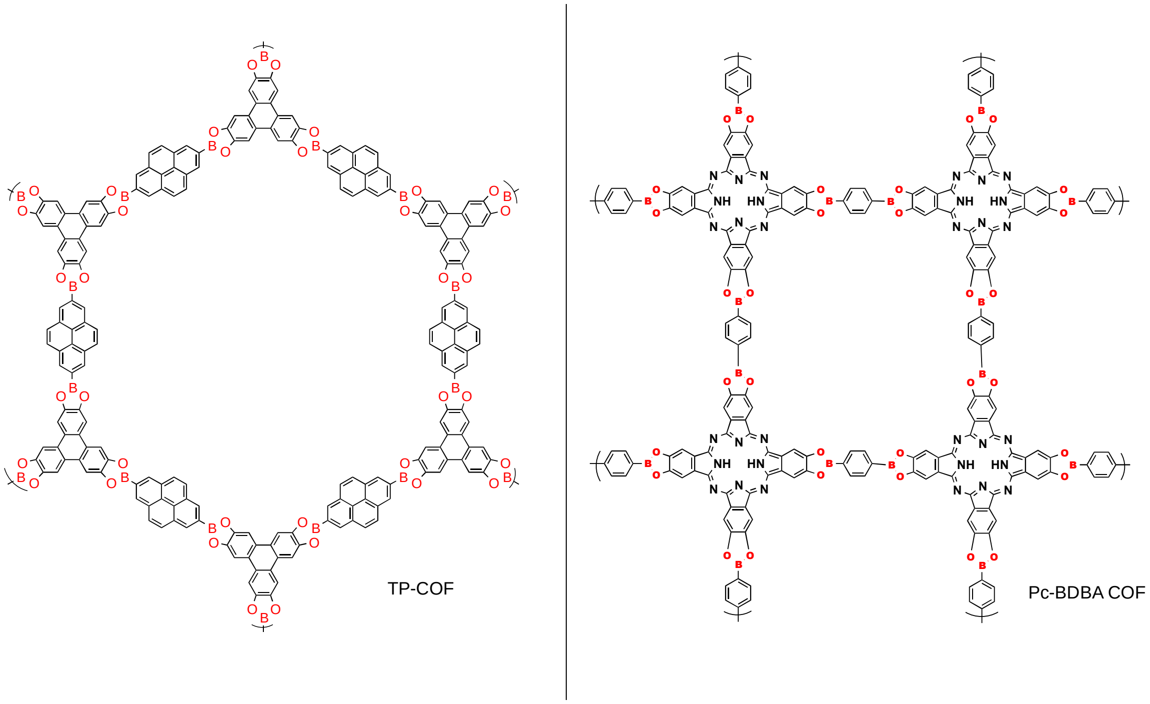


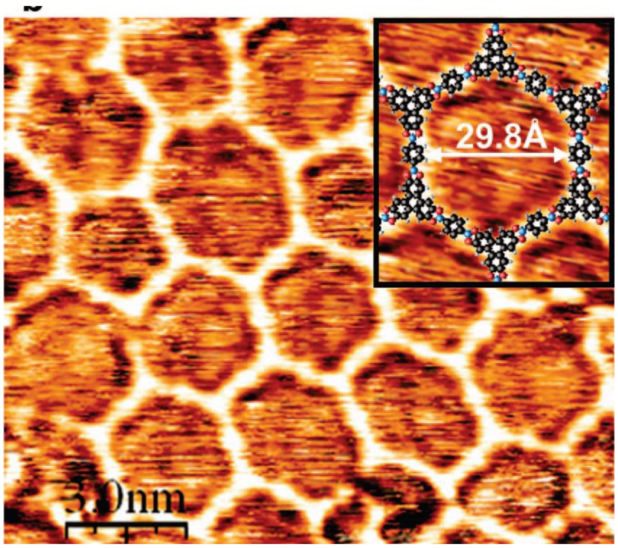
Figure 1.11: TP-COF uses HHTP and PDBA to make a blue-luminescent COF in the first report of an application beyond gas storage for a 2D COF.

Dichtel's group has synthesized a square latticed COF that may be used to build organic photovaltic devices.[24] Phthalocyanine terta(acetonide) (Pc) was reacted with 1,4-benzene diboronic acid (BDBA) in the presence of the Lewis Acid

BF_3•OET_2 to produce a two-dimensional square lattice COF, Pc-PBBA COF (**Figure 1.11,** structure on right). During the solvotherm condensation, BF_3•OET_2 has the dual role of deprotector and catalyst. The resulting Pc-BDBA COF has thermal stability near 500 °C. Nitrogen gas adsorption was used to determine that the material is mesoporous with a Langmuir surface area of 506 m^2g^{-1}. Pore size and volume distributions were determined using the Barrett-Joyner-Halenda model for mesoporous materials. The pore size was determined to be ~2 nm with a maximum pore area of 469 m^2g^{-1} and a maximum pore volume of 0.258 cm^3g^{-1}. The material absorbs light ranging from the visible to near-infrared and the newly modified synthetic method makes it possible to incorporate a wider variety of catechols into COFs.

Analyses of other 2-dimensional COFs for these types of properties will likely result in new electronic use for these insoluble self-assembling solids. Previous studies of boronate COFs focused on their high surface areas and subsequent ability to adsorb and store gases. The electronic properties of TP-COF and Pc-BDBA COF demonstrate, once again, the utility of boronate linkages in the formation of versatile materials.

Pristine face-to-face π-stacking of aromatic molecules is the principal obstacle of small molecule semiconductor design for organic field effect transistors[25] and photovoltaic devices.[26] 2D COFs assembled *via* the reversible boronate ester linkage promote this desired stacking arrangement of the planar electron-rich boronic acid and diol monomers. The next step is fabrication of single and thin-layer films of COFs containing semiconducting small molecules covalently locked in place. The first report of a surface covalent organic framework (SCOF) formed in layers on a metal surface was achieved by Porte and coworkers.[27] SCOF-2 is boronate ester-linked (**Figure 1.12**) produced by sublimation and subsequent co-condensation of BDBA with HHTP (the same monomers used in COF-5) under ultrahigh vacuum, forming a thin film with almost 30Å pores on a silver surface. The use of planar molecules, along with the reversibility in formation of boronate esters combine to allow self-assembly of a uniform film for this surface COF.



SCOF-2

Figure 1.12: SCOF-2 is a boronate ester linked 2D COF formed in a thin layer on a silver surface. This STM image confirms the expected hexagonal pores in the film which corresponds to stacking of the aromatic monomers—a desired feature for thin film electronics applications. Reprinted with permission from *J. AM. CHEM. SOC.* **2008**, *130*, 6678–6679. Copyright 2008 American Chemical Society.

An alternative method of casting COF thin films is by condensing the monomers in the presence of a single-layer graphene (SLG) substrate, resulting in vertically aligned films that have long range order.[28] Synchrotron X-ray diffraction showed that the thin films of COF-5, TP-COF, and a Ni Pc-BDBA COF were all vertically aligned and have long-range ordering, which differ from the randomly oriented powder versions of the COFs.[12a,12c,27] Scanning electron microscopy (SEM) confirmed that substrates are completely covered by the COF films and also provided a measure of the thickness of the films. Growing COF-5 on SLG-Cu for 30 minutes results in 195±20 nm thickness. Focused ion beam milling showed the films grown on SLG-Cu substrate contain several bulk COF-5 crystallites and notable roughness. Films grown on SLG/SiO_2 for 2 hours have a thickness of 95±5 nm, less bulk crystallites and no observable cracks. Even when equivalent reaction times were used for both substrates, the SLG/Cu substrate consistently had a higher thickness. The most uniform films were obtained when grown on SLG/SiC for 8 hours resulting in 73±3 nm thickness.

The transmission and absorbance of the semiconducting TP-COF and Ni Pc-BDBA COF were analyzed on the transparent SLG/SiO_2 substrate. The ultraviolet/visible/near infrared spectrum of TP-COF film shows a more defined peak than the powder version due to improved vibrational resolution. Both TP-COF film and powder are photolumiencent because efficient energy transfer from the HHTP moiety to the pyrene moeity still occurs. The Ni Pc-BDBA COF film proves that crystalline COF films can be made from COFs with lattices other than hexagonal symmetry. As expected, these films (as well as the powders) are nonemissive due to H-aggregation of the phthalocyanine, however, they do strongly absorb in the visible region. The vertical alignment and porosity make these films promising precursors for ordered heterojunction films to be incorporated into organic photovoltaic devices.

1.4.2 Three-dimensional COFs

The design of frameworks based on boronic acid monomers with diols was expanded from 2D to 3D COFs by researchers in Yaghi's group.[16] The same tris-diol, HHTP, that was used in many of the 2D COFs described above, was used with 3-dimensional tetrahedral tetraboronic acids *tetra(*4-dihydroxyborylphenyl)methane (TBPM) or *tetra(*4-dihydroxyborylphenyl)silane (TBPS) to produce COF-105 and 108 (**Figure 1.13**), respectively, in about 50% yield. Rather than channels, which are found in 2D COFs due to stacking of planar sheets, 3D COFs have cavities, which can accommodate up to 29.6Å spheres. These materials are exceedingly low in density (COF-105, 0.18 gcm^{-1}, and COF-108, 0.17 gcm^{-1}) and are ideally suited for storage of gases and small molecules, due to the pore accessibility from all surfaces of the crystal structure.

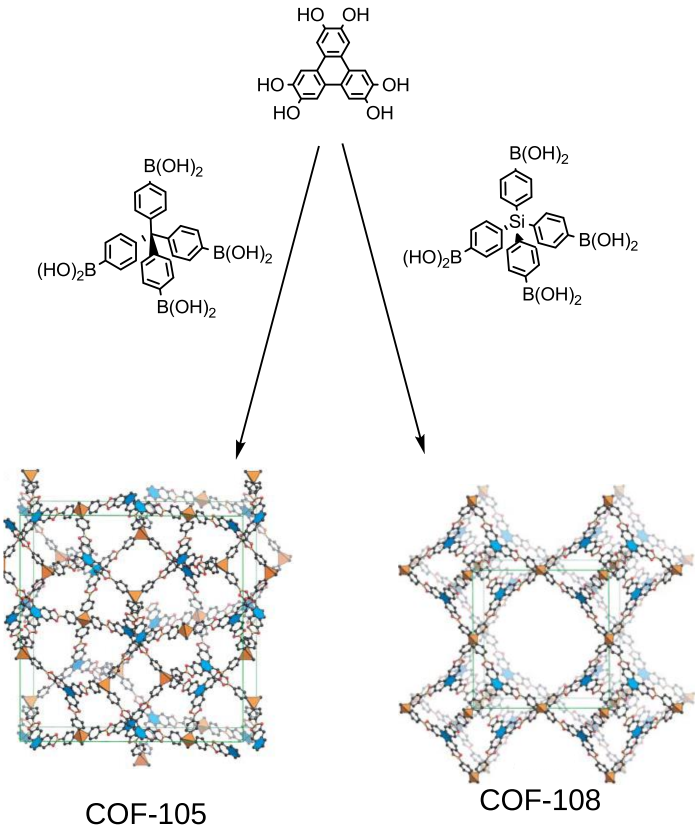


Figure 1.13: 3D boronate ester linked COFs made from HHTP with TBPM (COF-105) and TBPS (COF-108). These frameworks have very low densities and high surface areas making them well-suited for gas storage applications. Need to get permission from Science to use this from *Science,* **2007**, *316*, 268-272.

Projections and simulations have predicted excellent gas storage properties for 3D COFs.[29] There is increasing interest in optimizing porous materials for hydrogen storage to be used in conjunction with proton exchange membrane fuel cells. Computational studies by Smit and colleagues have predicted that lithium doping of 3D COFs should increase (and possibly double) the weight percent hydrogen at both 77 K and at 298 K.[30] The potential use of boronate ester-linked 3D covalent organic frameworks as gas storage hosts has been shown as a feasible approach for gases such as nitrogen, carbon dioxide and methane by numerous synthetic and materials research groups.[12a,25-26,31-32] COF enthusiasts eagerly anticipate the experimental confirmation of the remarkable gas storage predictions for these most elegant boronate ester linked frameworks. Additional future 3D COF studies may be aimed at separations, size-dependent sequestration, catch-and-release, and molecular sieving.

1.5 Tetrahedral boron *via* coordination

Via either inter- or intramolecular coordination between nitrogen and the empty *p*-orbital on boron, tetrahedral boronate ester polymers are realized. Using an intramolecular approach, Shinkai and colleagues synthesized sugar-linked diboronic acid polymers from boronic acids linked with chiral saccharides (**Figure 1.14**).[33] These polymers contain trigonal planar boron *ortho* to tertiary benzyl amine and exhibit predictable CD spectra based on D- or L- sugar incorporation.

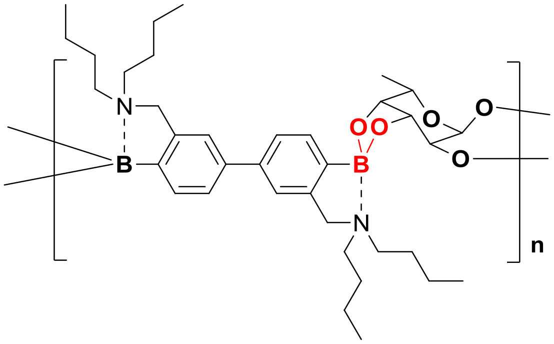


Figure 1.14: Boronate ester-linked polymer with intramolecular B-N coordination

Tetrahedral boronate esters have also been prepared *via* intermolecular B-N coordination with bipyridyl linkers. These boronate ester polymers (**Figure 1.15**) utilized the lone pair electrons on pyridyl nitrogen to form dative B-N bonds, thus rehybridizing the sp^2-boron to sp^3.[34] Using 4,4-bipyridine or 1,2-bis(4-pyridyl) ethylene linkers, diboronate ester units (formed from 2:1 aryl boronic acid : bisdiol) were joined by B-N bonds to form unique tetrahedral crystalline boron polymers. These polymers dissociate to bis(dioxaborole) and bipyridyl linker in chloroform, emphasizing the ephemeral nature of the B-N dative bond. However, the diester and linker units can recombine to regenerate the polymer upon solvent removal.

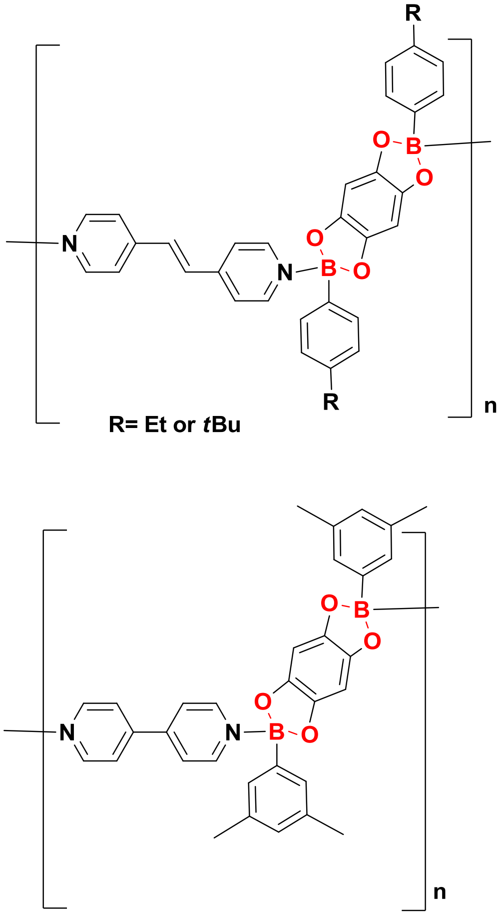


Figure 1.15: Diboronate ester units linked by intermolecular B-N coordination form polymers, which dissociate and recrystallize in selected solvents.

1.6 Oligomers and Linear Polymers

The first reported boronate ester linked linear polymer material occurred in 1960. The design of boronate ester-linked oligomers and polymers, in which the boron center may be either trigonal planar sp^2 or tetrahedral sp^3, has produced materials with novel structures, interesting electronic properties, and unique repairability. In this section we present representative small molecules and polymers.

1.7 Trigonal planar boron

In the area of small molecule synthesis, bis(dioxaboroles) based on 1,2,4,5-tetrahydroxybenzene and a monoboronic acid, or a diboronic acid with a 1,2-diol (**Figure 1.16**), were produced in good yield (70-90%) in a straightforward dehydration reaction in toluene. These bis(dioxaborole)s are planar molecules that stack due to π-π interactions and hydrogen bonding resulting in a phenyl-boron-phenyl pattern.[35] Solid-state ^{11}B NMR confirmed sp^2 hybridized boron, while X-ray analysis confirmed both the planarity and the off-set π-stacking arrangement of the assembled molecules. In this offset arrangement, the electron-deficient boron is found between adjacent layers of high electron density from phenyl π-clouds.

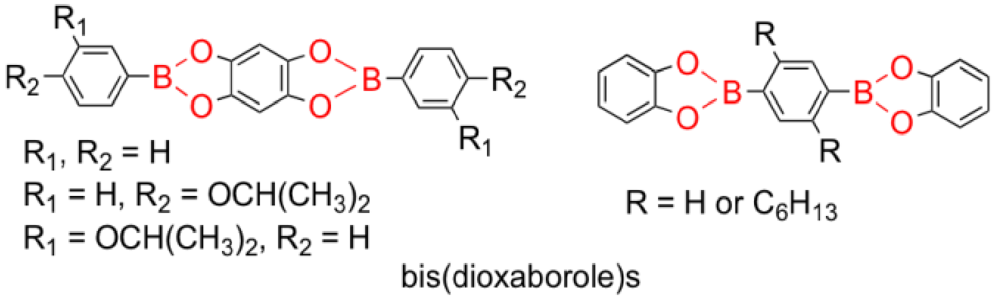


Figure 1.16: Examples of boronate esters self-assemble into ordered π-stacked arrangements with electron deficient boron sandwiched between phenyl layers.

Efforts to investigate the extended conjugation afforded by the empty *p*-orbital on the boron of the boronate ester have revealed the blue-emissive properties of such materials.[12b] Use of 9,9-dihexylfluorene-2,7-diboronic acid with 1,2,4,5-tetrahydroxybenzene produced poly(boronate ester)s (**Figure 1.17**) which were soluble in organic solvent and exhibited red-shifted absorbance compared to a control diester made from 9,9-dihexylfluorene-2,7-diboronic acid capped with catechol. Although higher molecular weight polymers can be produced from longer reaction times, they are less soluble in organic solvents and do not significantly shift the maximum absorbance wavelength. Here, extended conjugation was demonstrated *via* this boronate ester-linked polymer and the study demonstrates the potential use of similar polymers as semiconducting materials.

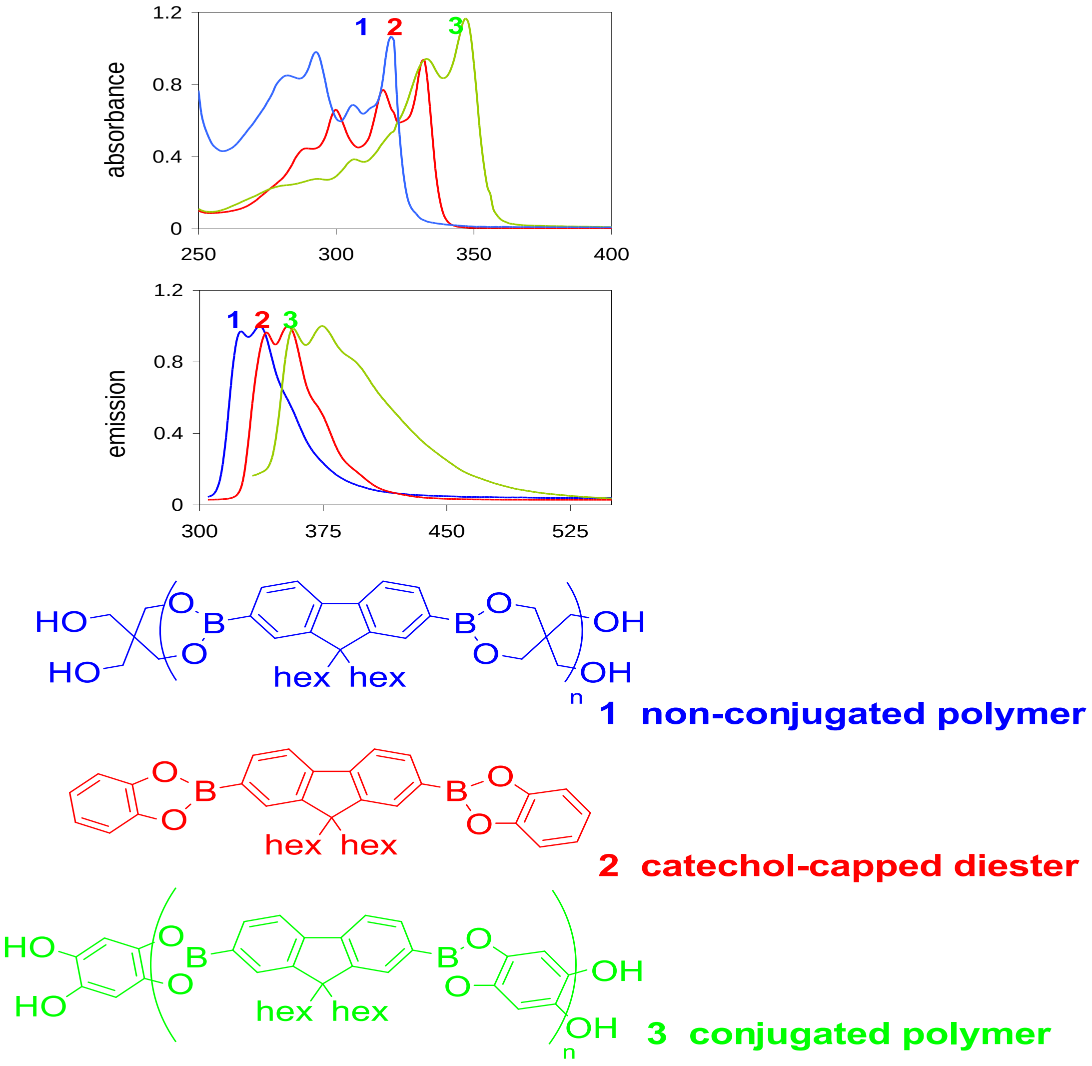


Figure 1.17: Absorbance and emission spectra of blue emissive conjugated boronate ester polymer 3 (green) compared to conjugated diester 2 (red) and non-conjugated polymer 1 (blue).

The non-conjugated bis(dioxaborolane) polymers based on boronate ester linkages formed from 9,9-dihexylfluorene-2,7-diboronic acid and pentaerythitol were found to be self-repairing.[11] When stored in wet chloroform (~1 % water v/v) the boronate ester linkages were broken, resulting in a reduction in molecular weight. Following hydrolysis of the ester, dehydration restored the high molecular weight thus producing a repaired polymer. This repairing process, depicted in **Figure 1.18**, was reproduced over multiple cycles and is significant because of the rarity for a repair without re-introduction of monomers or catalyst. Once again, this repairability may be attributed to the reversibility and facile formation of the boronate ester linkage.

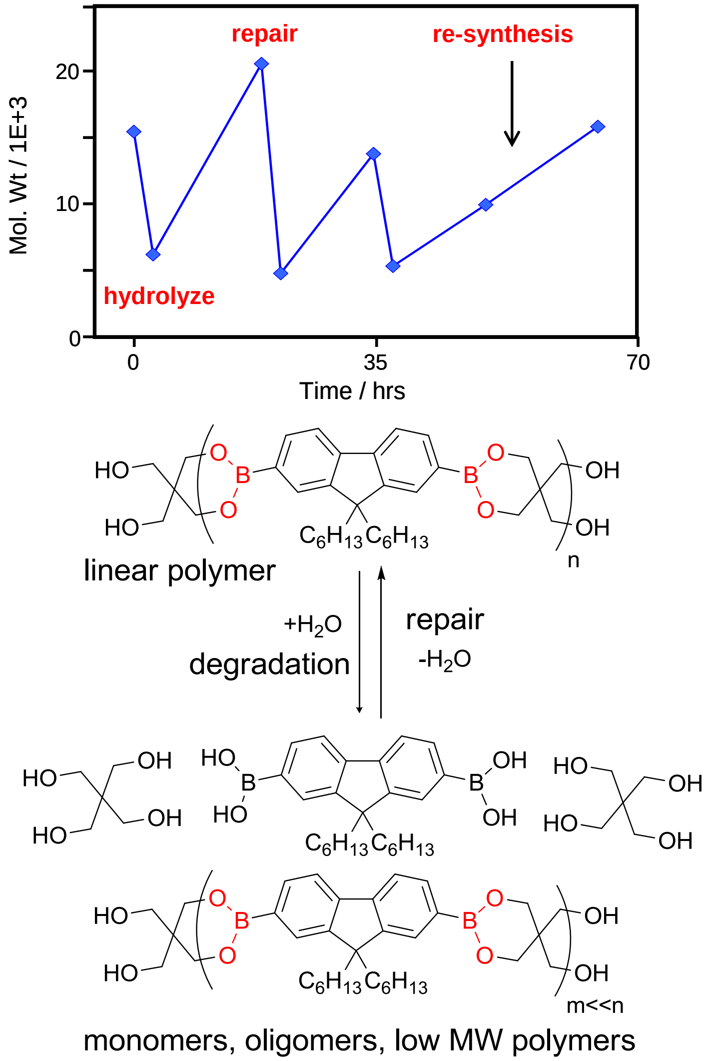


Figure 1.18: Repairable boronate ester-linked polymer: molecular weight decreases with hydrolysis and increases with dehydration (repair).

1.8 Summary and Outlook

In small molecules, macrocycles, linear polymers, and covalent organic frameworks, the boronate ester linkage has proven to be the keystone in this family of self-assembled materials due, in part, to the mild reaction conditions and intrinsic reversibility of B-O covalent bond. Central to this ester is the intriguing boron atom. Boron's ability to extend π-conjugation or coordinate to Lewis bases, both due to its *sp*^{2}-hybridization and consequent empty *p*-orbital, provides the synthetic chemists with a design tool, which is unavailable with other atoms. The ability to incorporate intriguing electronic properties or the capability for small molecule storage makes boronate ester materials viable for applications beyond sensing. The future application of boronate esters may include single layer 2D semiconductors, self-repairing polymers, and low-density materials for hydrogen storage. Alternatively, controlled hydrolysis and repair of boronate ester microporous COFs could prove useful for catch-and-release of small molecules. Currently, a wide range of monomers are available (either for purchase or through synthesis), the reaction conditions and proof-of-concept are well established. Linear poly(boronate)s have not been thoroughly investigated. Herewithin, we will discuss the physical, thermal, and mechanical properties of these novel boronic ester-linked polymers. Due to the fact that the polymer backbone is held together via a covalent, but dynamic bond, the stability of these materials will be investigated in the presence of weak, moderate, and strong nucleophiles. We have also investigated the synthesis of more flexible monomers to study the influence on polymer proprieties.

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CHAPTER 2: SYNTHESIS AND CHARACTERIZATION OF POLY(DIOXABORLANE)S

2.1 INTRODUCTION

Until the late 1920s, many scientists believed that covalently bonded compounds could not exceed a molar mass of 5000 Da, and what appeared to be large molecules were only colloidal substances. Staudinger slowly convinced fellow scientists that these colloidal substances were actually macromolecules made from covalently linked small molecules, leading to what is now known to be polymer chemistry.[1] Classical polymer theory categorizes macromolecules based upon the polymerization mechanism. If the polymer is made by a sequential addition of monomer units to the active end of a polymer chain it is considered an addition polymer or a chain growth polymer (**Figure 2.1**).[2] Chain growth polymers normally require an initiator to create an active monomer species, which continue to add onto the growing polymer chain end until the active species is terminated. Chain growth polymers (i.e. polystyrene, poly(methyl methacrylate) and poly(vinyl chloride)) were the first synthetic polymers to be produced on an industrial scale. Over the past 15 years, great progress has been made in understanding the mechanism of chain growth polymerizations leading to the discovery of “living polymerizations” and controlled/living radical polymerizations. These techniques, offer the ability to precisely control molecular weight (MW), the ability to obtain monodispersed materials (polydispersity index is close to 1), and design complex architectures.[3-4] Because of the nature of the research within this

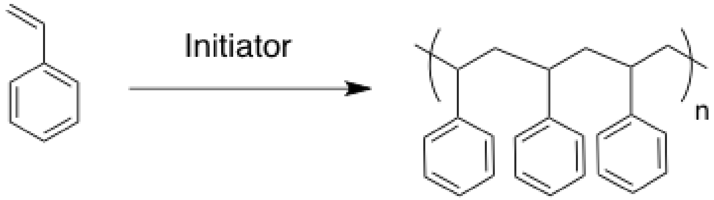


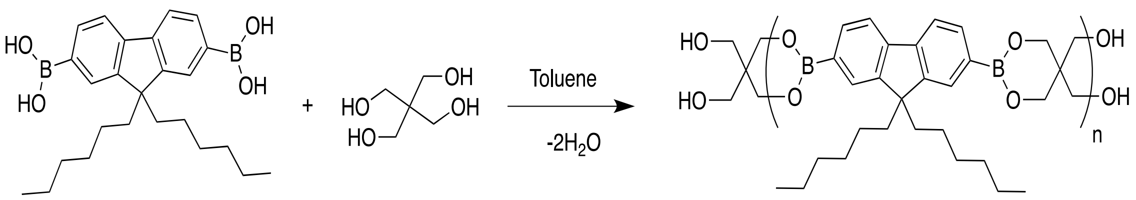
Figure 2.1: Example of addition polymerization. A radical initiator activates styrene and sequential addition of monomer results in the formation of polystyrene. An initiator is required to start the polymerization process.

dissertation, addition polymers will not be discussed in further detail.

The second classical polymer category is step-growth polymerization. Polymers are considered step-growth polymers if during the propagation step, a small molecule (such as H_2O or HCl) is released and monomer units can be added from both ends of a growing polymer chain. Difunctional or multifunctional monomers react to first form dimers, trimers, etc.; then, longer oligomers are formed as the reaction proceeds, eventually producing longer polymer chains. Because of the mechanism of step growth polymerizations, high molecular weight polymers (related to long polymer chains) are achieved only with high percent conversion of monomers. It should be noted that there are some polymers that produce small byproducts during propagation, but are not considered step-growth because monomer units can only add to one end of the polymer chain.[3-4]

Being that monomers are adding from both ends of the polymer chain and monomers and oligomers are assumed to have equal reactivities, the minimum polydispersity index for these materials are 2.0; inferring that it is impossible to produce monodispersed material via a step-growth polymerization.[1-4] It is also predicated that step-growth polymers should have molecular weights that easily exceed 50,000 Da at high conversion, but because of monomer imbalance, the presence of impurities, or the decomposition of end groups, these molecular weights are not always attainable.[2b] The interest in step-growth polymers remains because of the ease of which it allows one to incorporate functional groups into the backbone of polymeric materials.

In 2005, the Lavigne group discovered a novel polymeric material, known as poly(dioxaborolane) by performing a step-growth polymerization using the monomers 9,9-dihexylfluorene-2,7-diboronic acid with pentaerythritol in toluene without the addition of a catalyst (**Figure 2.2**).[5] Unlike traditional step-growth polymers, poly(dioxaborolane)s are produced in high yield without the presence of a catalyst or stringent reaction conditions. This material was shown to undergo solid-state polymerization and possess the ability to self-repair if hydrolyzed. Unfortunately, much is not understood about poly(dioxaborolane)s because their mechanical properties and the characteristics of the film have not been investigated. What is known is that these materials have high dispersity (especially at higher molecular weights) and very low ductility. Within this chapter, we will discuss changes made to the polymerization conditions in order to obtain a self-supporting poly(dioxaborolane) film. We will also discuss the synthesis of two novel poly(boronate)s and the effects of incorporating a labile boronate ester or a tetraol that contains a kink into the polymer main chain.



monomer **1** monomer **2** Polymer 1

Figure 2.2: Synthesis of poly(dioxaborolane) (**Polymer 1**) through a step growth polymerization in toluene using 9,9-dihexylfluorene-2,7-diboronic acid (monomer 1) and pentaerythritol (monomer 2).

2.2 BACKGROUND ON POLY(DIOXABOROLANE)S

Starting around the 1990s, a new class of polymers emerged: supramolecuar polymers, which are polymers that are held together by non-covalent, highly directional interactions. Being held together by secondary interactions results in the formation of a dynamic material with properties that range from reversibility to stimuli responsive.[6,7,8] Unfortunately, the dynamic nature of these polymers also make them very difficult to characterize using tradition polymer characterization techniques, such as gel permeation chromatography (GPC), viscometry, or light scattering. The reason being is that the molecular organization of supramolecular polymers is significantly influenced by changes in solvent, concentration and temperature. Therefore, several combinations of classical polymer characterization techniques have to be used to elucidate structural information of these types of materials.[7] This large disadvantage has created the need for a more stable class of polymers that still possess the dynamic nature of supramolecular polymers.

Poly(dioxaborolane)s are held together via a covalent, yet dynamic six-membered, non-conjugated boronate ester. Boronate esters are made from the reversible interaction between a boronic acid and diol (see **Chapter 1** for further detail). The Lavigne group is interested in poly(dioxaborolane)s because the linkage creates a dynamic material with an inherent reversibility. Additional benefits of incorporating this linkage into the backbone of the polymer chain are simplification of the synthetic process, elimination of a stringent reaction environment, and no need for the addition of catalyst. By having an integral main chain covalent boronate ester linkage, poly(dioxaborolone)s are stable in dry organic solvents, making it possible for these polymers to be characterize by traditional polymer characterization techniques such as NMR, GPC, and viscosity.[5]

As stated earlier, step-growth polymerizations require high percent conversion and equimolar amounts of monomer to produce high molecular weight material. We found that increasing the extent of reaction (p) from 0.98 to 0.99 by increasing the polymerization time from 1.25 hours to 10 hours was the difference between obtaining material with molecular weights of 28,300 Da (n=58) and 46,100 Da (n=94) (**Table 2.1**).[9] These results are aligned with the expectations of a step-growth polymerization: high molecular weight material is not achieved until the majority of the monomer has reacted to form polymer. Our system, however, deviates from classical step growth polymerizations upon using an imbalance of monomer amounts. For traditional step growth polymers, having even the slightest monomer imbalance will impede polymer growth and the presence of a large excess of either monomer will produce only short oligiomers.[1-2] Contrary to the nature of step growth polymerizations, we obtain a polymer with MW of 11,500 Da (n=22) in the presence of using a ten-fold excess of the tetraol, pentaerythritol. Normally, having such a large excess of one monomer would result in the formation of dimers and trimers (n= 2 or 3). Poly(dioxaborolane)s with molecular weights greater than expected can be obtained using a large excess of tetraol because of the limited solubility of pentaerythritol in toluene. Despite having as much as a ten-fold excess of one monomer added to the reaction vessel, the amount of pentaerythritol dissolved in solution is significantly less. As polymer starts to form, more of the tetraol is pulled into solution, creating what is known in the literature as a spoon-feeding mechanism.[10]

Table 2.1: Monomer ratio, reaction time, vacuum processing all are methods used to control the MW of poly(dixoborolane)s.

Diol equiv.	Reflux time (hour)	Vacuum processing time	M_n (end group analysis)	Repeat unit (n)	M_w (GPC)	PDI
1	1.3	0	28,300	58	27,800	2.6
10	1.3	0	11,400	22	9,700	3.8
1	10	0	46,100	94	45,000	5.4
10	10	0	43,500	88	42,000	3.3
1	1.3	7 days	76,900	157	--	--
10	1.3	3 days	15,000	30	15,900	3.8
10	1.3	7 days	13,800	27	18,000	4.9

An additional benefit of incorporating the boronate ester linkage into the main chain of a polymer is the ability to perform solid-state polymerization. Storing the polymer under vacuum results in transesterification of the boronate esters, increasing the molecular weight of the material without having to add a catalyst or additional monomer. After being stored under vacuum for one week, the molecular weight of poly(dioxaborolane) increased from 28,300 Da to producing an insoluble material. As a result of this study, we decided to increase the length of the alkyl portion of the diboronic acid monomer to prevent solubility issues. A portion of the material was partially dissolved and determined to have a molecular weight of 76,900 Da. Even with having higher molecular weight material, the films of the material were still extremely brittle and difficult to handle.

2.3 OPTIMIZATION OF THE SYNTHESIS OF POLY(DIOXABOROLANE)s

To increase the ductility of poly(dioxaborolane) films, we investigated the effects of increasing monomer solubility and concentration during the polymerization process. In step-growth polymerizations, polymer chain growth is directly related to the collisions (or reaction) of endgroups. However, the concentration range has to be optimized for each polymer system: to little monomer decreases the probability of collision, but too much monomer results in gelation both situations are detrimental to polymer growth.[11] By determining the working range of monomer concentration, we will be able to optimize the molecular weight of our polymer system resulting in increased amount of chain entanglement, which will result in more ductile or flexible material. Traditionally poly(dioxaborolane)s are synthesized at a monomer to solvent ratio of 1.6 %w/v because of the limited solubility of pentaerythritol in nonpolar toluene. We found that increasing monomer concentration to 2.1 %w/v in toluene only produced 60% soluble material that has a weighted average molecular weight of 12,000 Da. The remaining material was a mixture of a gel and the unreacted pentaerythritol. Because the solubility of both monomers is critical in order to increase the initial monomer concentration, it was necessary to found a solvent system that dissolves both monomers. Results of a solubility study showed that the more polar solvent 1,4-dioxane dissolves both monomers **1** and **2** (shown in **Figure 2.3**) when heated above 45 °C. To circumvent the issue of forming insoluble material at higher molecular weights, we exchanged monomer 1 from 9,9-dihexylfluorene-2,7-diboronic acid to 9,9-didodecylfluorene-2,7-diboronic acid.

Polymer batches were synthesized using initial monomer concentrations of 2.0, 2.7, 4.2, 10.3, 15.0, 15.4, 15.7, 18.5, 20.0 and 22.0 %w/v in 1,4-dioxane for a period of 5 hours. GPC analysis was used to determine the average weighted molecular weight, as well as the average number molecular weight and PDI. As a method of control over the PDI, we used an equimolar ratio of monomer because previous studies (**Table 2.1**) has shown that the PDI of poly(dioxaborolane) increases when using pentaerythritol in excess. Using equivalent amounts of monomers during the polymerization prevented us from knowing whether the polymer was capped with diols or boronic acid, thus preventing the use of ^{1}H end group analysis to determine the average number molecular weight of the polymer. We found that using a monomer concentration of 15.7 %w/v resulted in the growth of polymer chains with our highest obtainable molecular weight of 40,000 Da via solution polymerization. Decreasing the concentration to 15.0 %w/v decreases M_w to 27,000 Da and for polymers synthesized at 2.0 %w/v produces polymers with M_w of 13,000 Da, which indicates a decrease in the ability of end groups to react to increase the length of polymer chain. The same decrease in M_w was measured when the monomer concentration was higher than 15.7 %w/v. At 18.5 %w/v, the M_w is closer to 30,000 Da and at 22.0 %w/v the molecular weight further decreases to 5,000 Da, showing that having too high of a monomer concentration is also detrimental to polymer growth. We determined that using concentrations lower than 15.7 %w/v or higher than 16.1 %w/v results in obtaining lower molecular weight materials by making it more difficult for end group collisions by having too few molecules present, which makes it harder for the end groups to find each other, or preventing adequate reactions by having too many molecules present, which makes the solution too viscous, hindering movement of molecules.

Despite having the longer dodecyl side chains, we are able to cast self-supporting (ductile) films of polymers synthesized at a monomer concentration of 15.7 %w/v. In the polymer field, it is well known that having longer side chains can actually decrease chain entanglement; however, with poly(dioxaborolane)s we have shown otherwise. One probable explanation is the dodecyl side chains are not within the same plane as the polymer backbone; therefore, possibly allowing or even contributing to increased chain entanglement. Poly(dioxaborolane)s synthesized that contain the hexyl side chains, always produce brittle films, even when using a 15.7% w/v monomer concentration.

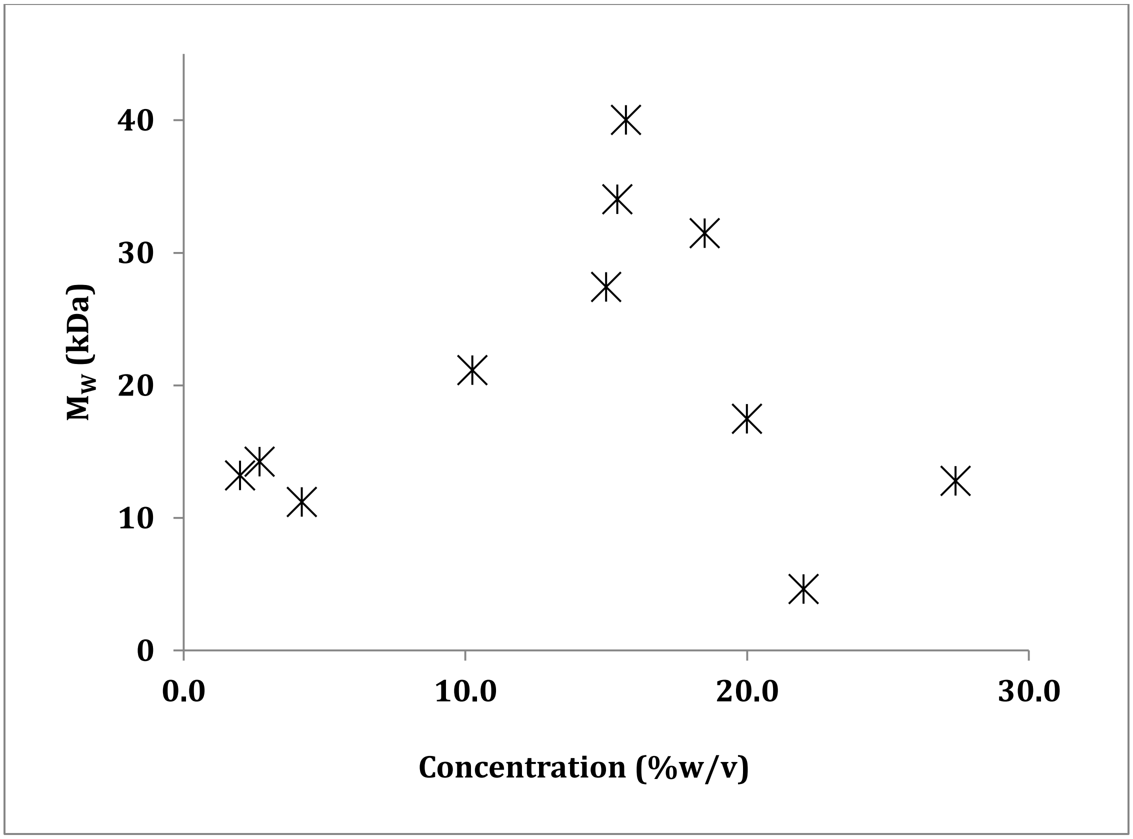


Figure 2.3: After performing a performing several polymerizations with monomer concentrations ranging from 2.0-27.4 %w/v, it was shown that the highest molecular weight material, M_w = 40 kda, is obtained using an initial monomer concentration of 15.7 %w/v.

In an attempt to further optimize the synthetic process, an *in situ* NMR study of the polymerization was performed to see if polymer chain growth could be quantified. To ensure that the end group of the polymer would be the diol moiety, a two-fold excess of monomer **2** was used. Monomer **1** was used to ensure the accuracy of end group analysis because having the longer dodecyl side chains suppressed the terminal methylene peaks more than the hexyl side chains.[5] Both monomers were dissolved in deuterated dioxane before being combined in a NMR tube with activated molecular sieves. Within 2-minutes of initiating polymerization, growth of the polymer main chain methylene peak was detected at 4.06 ppm as opposed to 4.16 ppm as seen in deuterated chloroform (**Figure 2.5**). Unfortunately, after 30 minutes into the experiment, there was no formation of upfield resonances (expected around 3.90 ppm) to indicate the formation of polymer endgroups. We concluded that only formation of dimers and trimers were occurring being due to saturation of the molecular sieves, allowing water molecules to be present in solution and impeding polymer growth. From this experiment, we decided a better way to investigate polymerization kinetics was to remove small aliquots from polymerization and use NMR analysis to monitor polymer growth.

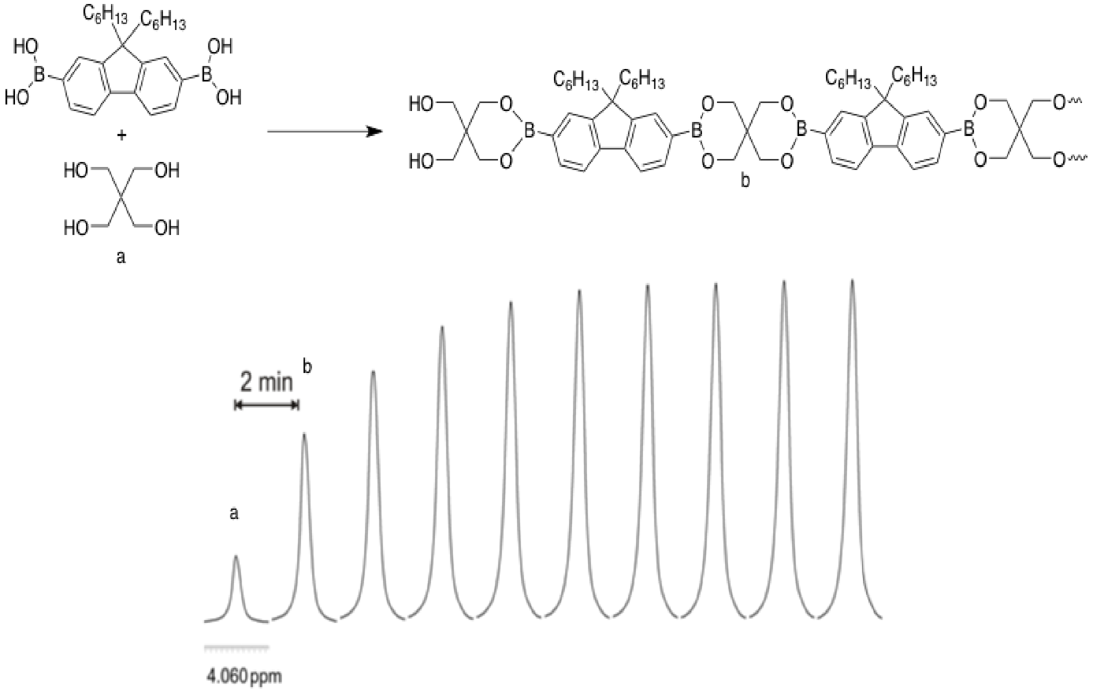
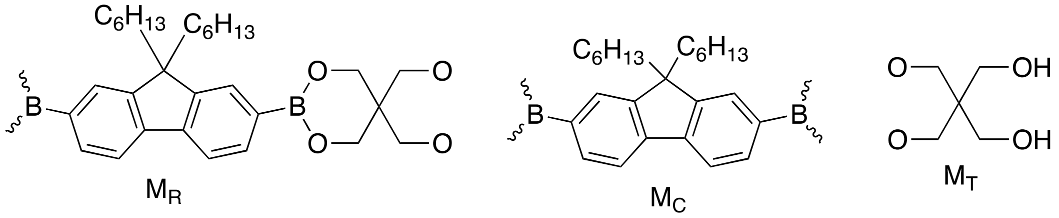


Figure 2.4: NMR spectrum of an *in situ* study of the formation of polydioxaborolanes in deuterated dioxane. Boronate ester is formed within 2 minutes as indicated by the time difference between peaks *a* and *b*, but plateaus off quickly due to water formation saturating the molecular sieves added to the NMR tube.

By using equation in **Figure 2.5** (where M_r is the mass of the repeat unit, M_c is the mass of the polymer core, and M_t is the mass of the end groups), average M_n of the polymer is found.[5] The zero time point (T_0) was taken immediately after monomers were combined. The reaction was continued for 15 hours with small increments being removed periodically for NMR analysis. Through end-group analysis, it was determined that n=9 at the first point of sample removal, T_0. However, it was also determined that n=9 at the end of the 15 hour reaction. This could be the result of increasing the solubility of both monomers eliminates the ability to produce polymers in the presence of a large excess of one monomer. Because of this, only oligomers formed and drying the samples under reduced pressure, the M_n was increased due to transesterification in the solid state.[5]



$$Mn = n(Mr) + Mc + 2(Mt)$$

Figure 2.5: Structures of the repeat unit (M_R), main chain core (M_c) and the end groups (M_T) that are used to calculate M_n after ^1H NMR end group analysis.

From here, we concluded that the best way to gain a more in-depth understanding of the polymerization kinetics was by *in situ* monitoring the polymerization using FTIR reaction analysis otherwise known as a ReactIR. We attempted to monitor conversion from boronic acid to boronate ester because it is well known that boronic anhydrides, acids, and esters have a distinctive pattern of peaks in the fingerprint region of IR spectroscopy that can be used to identify a specific boronic moiety.[12] However, due to the instrument not being able to accurately detect peaks below 600 cm^{-1}, we were not able to focus on the fingerprint region, which resulted in not being able to monitor the conversion from boronic acid to boronate ester.

To further optimize our polymerization parameters, we measured the effect of time on the molecular weight of poly(dioxaborolane). We have shown that increasing the polymerization time from 1.25 hours to 10 hours results in a 1.5 fold increase in the average weighted molecular weight as well as a significant increase in PDI (**Table 2.1**). However, we were not confident if the same held true in a solvent were both monomers are completely soluble. Poly(dioxaborolane)s were synthesize in dioxane using a monomer concentration of 15.7% w/v and GPC analysis was used to monitor average MWs as the polymerization proceeded. The reaction was ran for 10 hours and within 15 minutes of initiating polymerization, average M_w of 12,000 Da was measured; and after 1 hour, the average M_w reached 30,000 Da, which is where it remained for the remainder of the polymerization (**Figure 2.6**). The extent of polymerization for the material is 0.98, indicating the dynamic nature of these materials allows for quick conversion from monomer to polymer.

We also decided to see if we are able to produce polymer in a completely soluble system using a ten-fold excess of the tetraol monomer, pentaerythritol. We synthesized two polymers: one using equimolar ratios of tetraol to diboronic acids as well as a polymer incorporating a ten-fold excess of tetraol to diboronic acid. The MW of each was monitored using GPC analysis. For the polymer synthesized with stoichiometric amounts of monomer, the highest M_w was reached within 30 minutes of starting the polymerization. The polymer synthesized with a ten-fold excess of pentaerythritol, had average M_w of 5,500 Da within the first ten minutes of the reaction but quickly decreases to 2,500 Da and plateaus. This could be the result of having a boronic anhydride instead of the diboronic acid, and as the polymerization proceeds, anhydride is converted to ester.

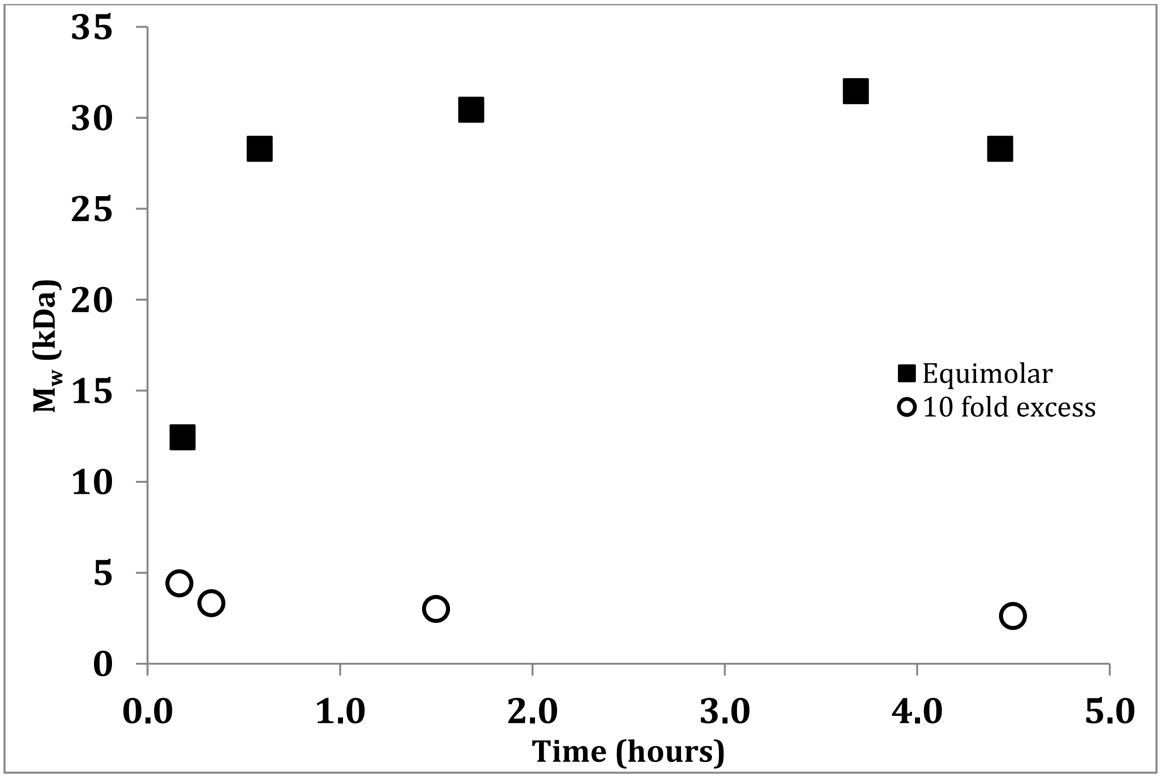


Figure 2.6: Polymers synthesized in dioxane using 1:1 (black squares) and 10:1 (open circles) equivalents of pentaerythritol to fluorene diboronic acid. Black squares a show that after 1 hour MW does not increase any further. Using a solvent that completely solubilizes both monomers eliminates “spoon feeding” preventing the ability to synthesize higher molecular weight material.

2.3.1. SYNTHESIS OF POLY(DIOXABOROLANE)S INCLUDING 1,4-PHENYLENE DIBORONIC ACID

A second poly(dioxaborolane) was synthesized to evaluate what contribution, if any, the dodecyl side chains have on the mechanical and physical properties of the polymer. We synthesized **Polymer 2.1** (shown in **Figure 2.7**), a random copolymer, by incorporating 1,4-phenylene diboronic acid (PDBA) into the polymer backbone. The polymerization was carried out using the same reaction conditions for the original poly(dioxaborolane)s: 5 hour polymerization time and using a 15.7 %w/v monomer concentration. Various random copolymers were synthesized by using a stoichiometric ratio of tetraol to diboronic acids, with different equivalents of fluorene diboronic acid (FDBA) to 1,4-phenylene diboronic acid (PDBA). Polymers were made with 5, 10, and 17% of PDBA (**Table 2.2**).

Table 2.2: GPC Analysis was used to measure the weighted and number average molecular weight of polymers synthesized using different amounts of PDBA. Increasing the amount of PDBA resulted in a change in clarity of the films, suggesting more ordering of the polymer chains than in the original poly(dioxaborolane)s.

Amt. 1,4-PDBA (mol%)	M_w (Da)	M_n (Da)	Film Appearance
0	32, 650	19,195	Clear/colorless
5	11,924	3743	Flaky/ clear
10	161,678	49,148	Cloudy
17	52,545	13,212	Cloudy

We hypothesized that as the mol% of PDBA incorporated into the random copolymer increases, the elasticity and processability of the film would decrease because PDBA based polymers are largely insoluble materials.

Poly(dioxaborolane)s synthesized at a monomer concentration of 15.7 %w/v produced an elastic, clear and colorless film when drop casted from benzene. We did not observe any trend between the amounts of PDBA incorporated into **Polymer 2.1** and the elasticity of the film; however, we did see an effect on the mechanical properties of original poly(dioxaborolane) in comparison to **Polymer 2.1**, which is discussed in further detail in **Section 2.4**. We expected the addition of 5 mol% of PDBA would not greatly effect the quality of the film, but instead we were only able to produce brittle and flaky polymer films. Incorporating 10 mol% PDBA produced a polymer with an average weighted molecular weight around 162,000 Da and the casted film was cloudy, yet self-supporting suggesting more ordering of the polymer chains (see **Section 2.4**). Polymers synthesized with 17 mol% PDBA had weighted average molecular weights around 53,000 Da and also produce cloudy films. These films were not as flexible as the polymers that contain 10 mol% of PDBA. NMR analysis produced spectra identical to that of the original poly(dioxaborolane)s, preventing the ability to elucidate whether the structure of the copolymer is random or block.

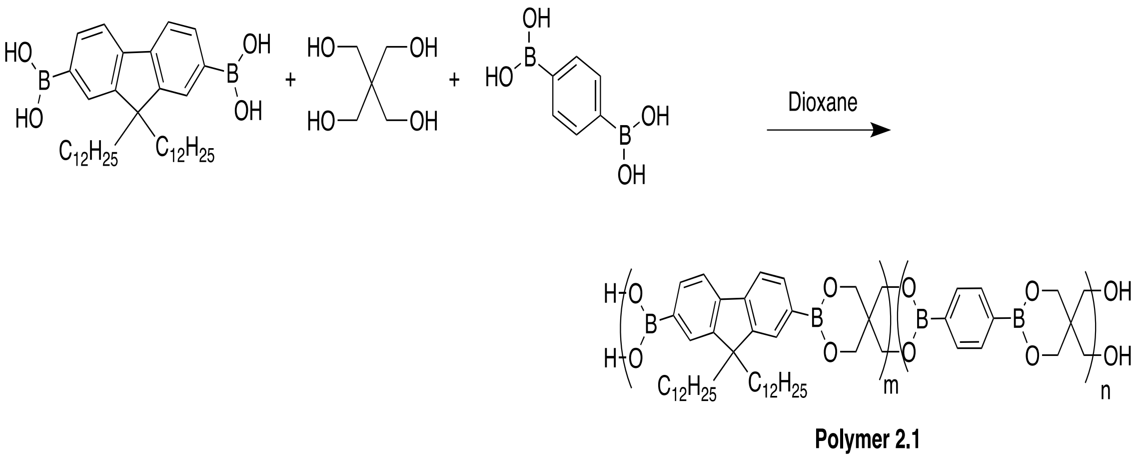
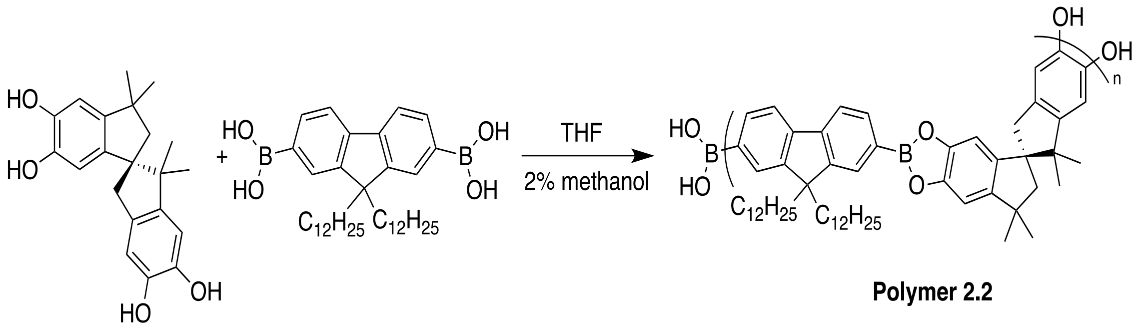


Figure 2.7: Synthesis of random copolymer from pentaerythritol, 9,9-didodecylfluorene-2,7-diboronic acid and 1,4-phenylene diboronic acid in dioxane.

2.3.2. SYNTHESIS OF MESOPOROUS POLY(BORONATE) FILMS

Polymers of intrinsic microporosity (PIMs) are a class of recently developed amorphous, porous material that contains a kink, which is normally a spirocenter.[13] To our knowledge, our research group is one of the first to synthesize boronate-ester linked PIMs. We have shown that these amorphous materials are microporous with BET surface areas ranging between 200-300 m^2/g.[14] These promising results probed investigation of synthesizing a solution-processable, porous thin films.

Step-growth polymerization between 9,9-didodecylfluorene-2,7-diboronic acid and commercially available 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane was carried out using a tetrahydrofuran/methanol solvent mixture (**Figure 2.8**). After polymerization, a film was dropcast from benzene and analyzed using FT-IR, GPC, and ^1H NMR.



Polymer 2.2

Compound 2.1

Figure 2.8: Synthesis of a mesoporous boronate-linked polymer. Porosity is the result of incorporating a spirocenter from the tetraol shown, **Compound 2.1**.

The most notable change between the polymer spectrum and monomer spectra is the attenuation of the broad hydroxyl stretches (**Figure 2.9**). The presence of peaks corresponding to B-O bending at ~1330, 1068, and 695 cm^{-1} in the fingerprint region further indicate that polymerization occurred.

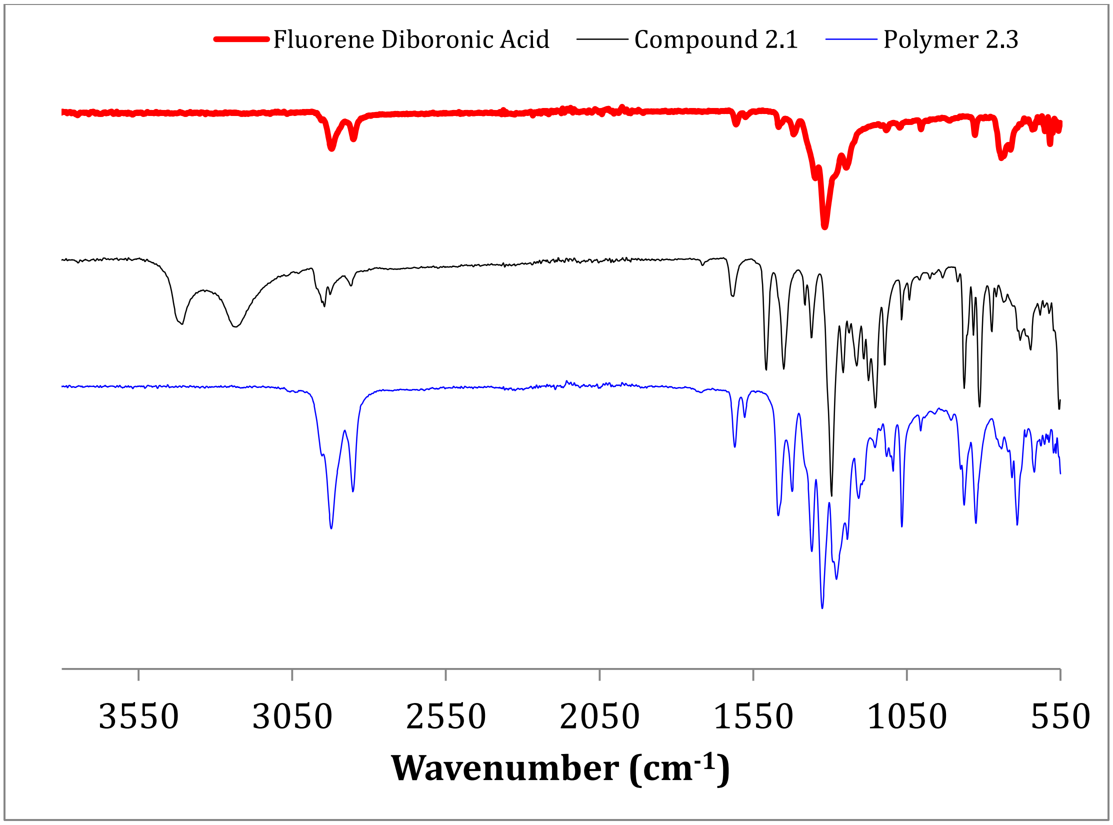


Figure 2.9: FT-IR spectra showing the differences between **Polymer 2.3** and its monomers. Upon formation of polymer, the intensity of the hydroxyl peaks from **Compound 2.1** is attenuated.

Further confirmation of the formation of boronate ester moiety is the ability of the material to dissolve in chloroform. The polar monomers are insoluble in chloroform, and no peaks were seen in the respective NMR spectra. End group analysis for this material was not performed because the endgroups are random due to the fact we used equimolar monomer ratios. The molecular weight was evaluated using GPC analysis and determined to be 21.3 kDa. To determine the porosity of the material, carbon dioxide (CO_2) uptake was measured at 77 K and revealed a Type III isotherm (**Figure 2.10**), indicating a weak interaction between CO_2 and that the adsorbent stacks in a multilayer, possibly forming mesopores.[15]

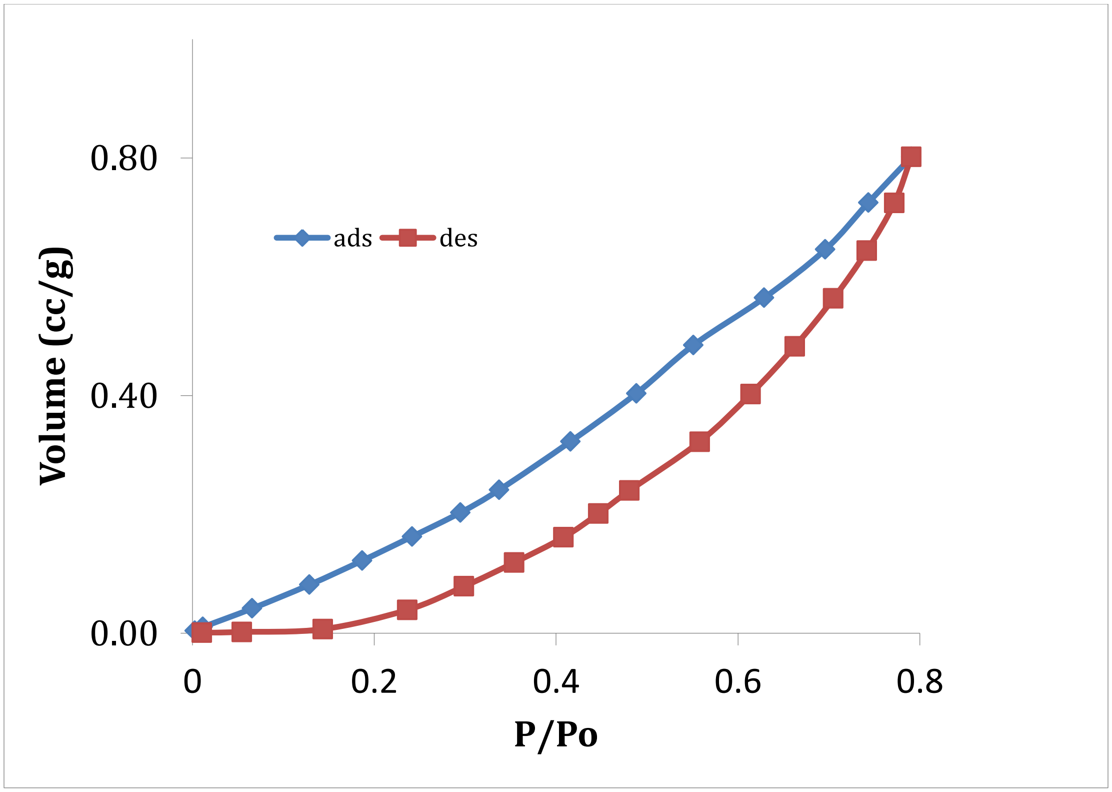


Figure 2.10: Isotherm showing the adsorption and desorption of **Polymer 2.3**. Desorption of CO_2 does not align with the adsorption of the gas showing hysteresis. The shape of the hysteresis indicates that the PIM is mesoporous and stacks in multiple layers.

2.4 SELF-SUPPORTING FILMS VIA CROSSLINKING AND COORDINATION

Polymers 2.1 and **2.2** lacked the ductility of the original poly(dioxaborolane)s; therefore we sought to increase the elasticity by cross-linking the material to increase cha. Triboronic acid (TBA) was the first cross-linker that we incorporated into the material. All three monomers: 9,9-didodecylfluorene-2,7-diboronic acid, pentaerythritol, and 5 mol% of TBA were added to a round bottom flask with 1,4-dioxane and a Dean-Stark trap was assembled. The mixture was heated to reflux for 1.5 hours before being removed from heat. The reaction mixture was then concentrated by placing under reduced pressure and we were left with an insoluble gel-like material. At this point, we are only interested in thin films of poly(dioxaborolane)s; therefore, we decided to focus on another method of cross-liking: using amines (**Figure 2.11**).

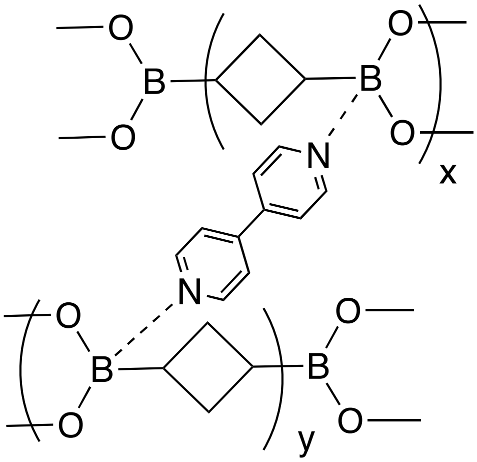


Figure 2.11: Schematic showing the coordination of a cross-linker such as 4,4'-bipyridine. The lone pair of electrons on nitrogen can coordinate with the empty *p*-orbital on boron, which will result in an increase in chain entanglement.

As discussed in **Section 1.5**, boronate esters can coordinate with nucleophiles because of the empty *p-orbital* on boron. This coordination has been used to form macrocycles,[16] rotaxanes,[17] and coordination polymers.[18] We decided to use the coordination to our advantage by using it to cross-link the polymer chains in poly(dioxaborolane)s. Based upon the molecular weight of the polymer, the amount of boron species present was calculated to determine how much of the amine should be added. Different amine compounds: 4,4'-bipyridine, 1,2-(dipyridin-4-yl) ethene were added to pre-formed polymer material by dissolving and stirring the mixture overnight. The next day, the films were drop casted from benzene. Unfortunately, the films remained brittle and failed to pass the crease test, which consists of folding the film three times and creasing along the folding point.

2.5 THERMAL AND MECHANICAL PROPERTIES OF POLY(DIOXABOROLANE)s

Common polymerization characterization techniques such as differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), measure the response of materials, as they are place under a controlled temperature program. Thermal analysis is commonly used in research and development to prevent material failure. It also gives information that can lead to process optimization and can be used as a method of determining the quality of a material.

DSC measures phase transitions within a polymeric material by monitoring heat flow as a function of time and temperature. For our purposes, we used DSC to measure the glass transition temperature (T_g), and to see if we could detect any melts or crystallization of our materials. Previous work revealed that the polymers are stable up to temperatures of 400 °C in air; therefore, we were able to safely test our films up to 250 °C without risking degradation.

The temperature at which a polymer goes from a glassy state to a softer, rubbery state is called its glass transition temperature.[1] It shows as a defined step transition in the heating cycle of a DSC scan. When running a DSC scan, it is common to do a heat-cool-heat cycle instead of a single heating run to remove thermal history placed on the sample during film processing. Analysis of the second heat gives more accurate information about the sample.

A heat-cool-heat DSC scan was collected for both poly(dioxaborolane)s containing only the 9,9-didodecylfluorene-2,7-diboronic acid and pentaerythritol, which will be referred to as the homopolymer, as well as for **Polymer 2.1** (**Figure**

2.12). Because the first heat is used to remove the samples thermal history, it is not shown. The cooling scan (not shown) for both polymers showed no signs of crystallization, which supports the material being highly amorphous. Both polymers have what appears to be a broad T_g in the second heat. Poly(dioxaborolane) that does not contain PDBA, which will be referred to as the homopolymer, has a T_g onset at 63 °C. **Polymer 2.1** with the 2:1 ratio of FDBA:PDBA has a T_g onset at 70 °C. The increase in T_g is most likely due to a decrease in the amount of alkyl side chains present. The homopolymer has an endotherm in the temperature range of 154-160 °C, which could be due to a melting of the side chains or the release of pentaerythritol, which melts around 180 °C. **Polymer 2.1**, however, did not have any similar transitions. Neither polymers contained a melting peak (T_m), which is as expected because the material is not semi-crystalline.

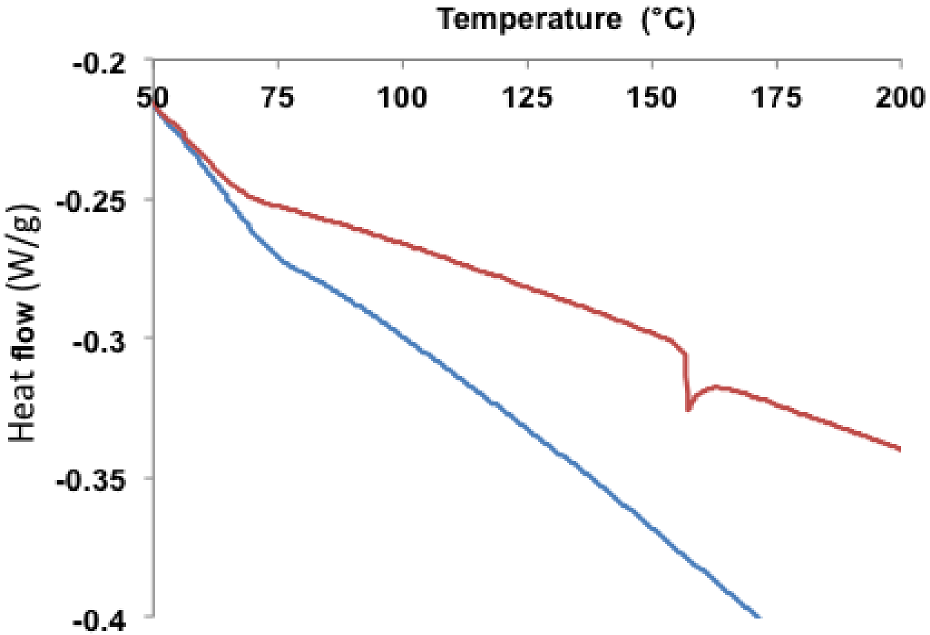


Figure 2.12: DSC scan (2nd Heat) of homopolymer (red) and the **Polymer 2.1** with 2:1 ratio of FDBA:BDBA(blue). Both samples display T_g's however, the homopolymer contains an endotherm above 150 °C that is not seen in **Polymer 2.1**.

Glass transition temperature is a kinetic phenomenon, meaning that it is reversible and dependent upon cooling rate. By cooling a sample at different rates, it is possible to determine if the endotherm is a T_g. An experiment was performed to see if increasing the cooling rate from 5 °C/min to 20 °C/min would result in a change in the glass transition temperature or the detected endotherm for the homopolymer (**Figure 2.13**). The spectrum collected using the faster cooling rate of 20 °C/min resulted in a shift of the T_g to a higher temperature range and a shift of the endothermic peak to a higher temperature range of 169-173 °C. Based on this analysis, it is reasonable to conclude that the transition is due to a T_g masked by enthalpic relaxation.

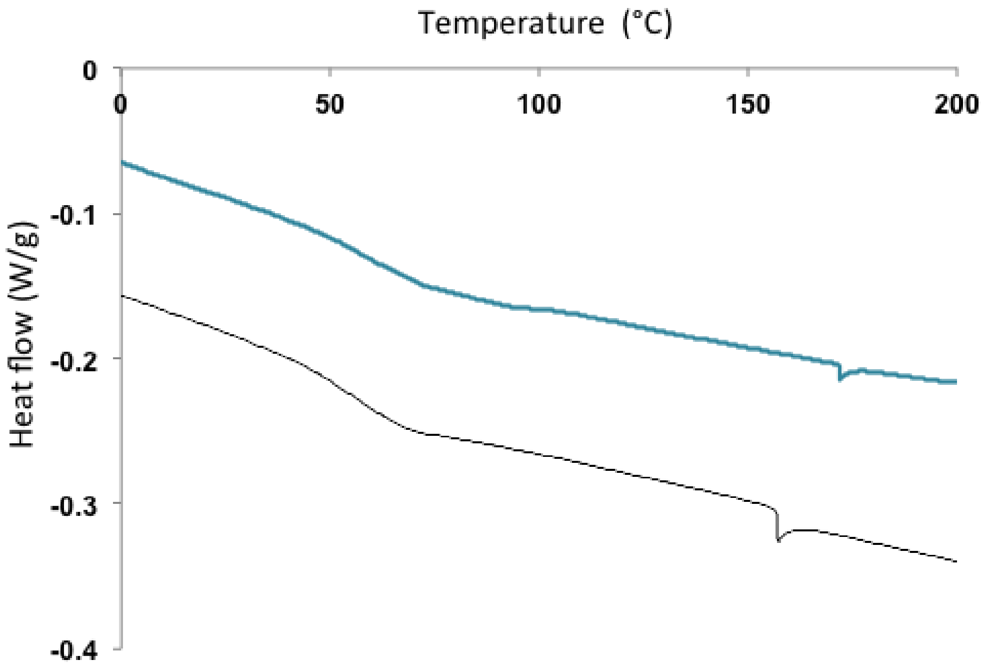


Figure 2.13: Increasing the cooling rate resulted in broadening the temperature range for the step transition. The grey graph has a cooling rate of 5 °C/min and the blue graph has a cooling rate of 20 °C/min.

The data analysis from the DSC was not completely conclusive; therefore, DMA was used as a method to gain further information about the thermal properties as well as the mechanical properties of poly(dioxaborolane)s because it is a more sensitive technique. DMA is applying a cyclic force to a film while performing a temperature or frequency scan to measure the material's viscoelastic properties. DMA gives information on the storage modulus (E'), loss modulus (E"), and the loss tangent. The storage modulus gives information about the stiffness of the material and measures the elasticity of a material. The loss modulus (E") measures the ability of the material to dissipate heat during deformation and gives insight into the viscous properties of the polymer. The loss tangent, tan delta, is the ratio of E"/E' is known as the dampening coefficient.[19]

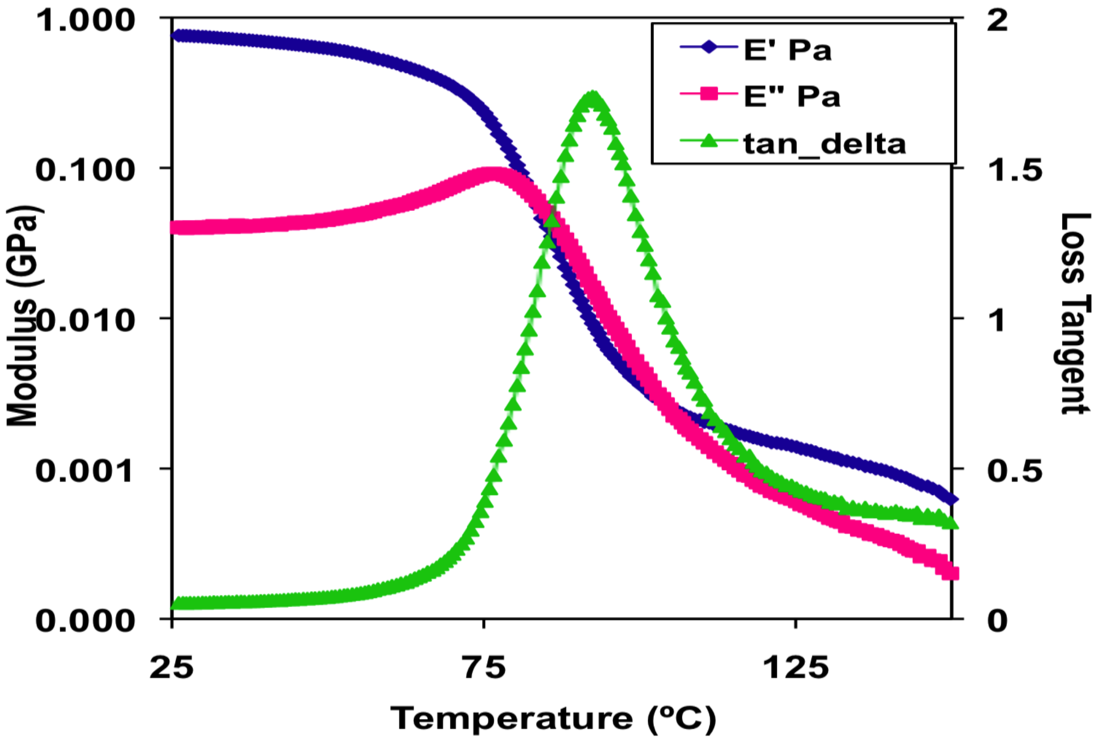


Figure 2.14: DMA analysis of the poly(dioxaborolane). Both E' and E'' are independent of temperature in the glassy region. In the rubbery region, both values decrease drastically.

At 30 °C, E' is 0.722 GPa giving the homopolymer poly(dioxaborolane)s a stiffness somewhere between PET and polystyrene.[20] In the glassy region (**Figure 2.15**), the storage modulus is independent of temperature; however, upon approaching the T_g, E' starts to drastically decrease. According to DMA, the T_g onset is 60 °C, which correlates with the DSC data.

Next, the effects of decreasing the amount of alkyl side chains and increasing the molecular weight of the homopolymer were investigated. A **Polymer 2.1** containing 18% of 1,4-benzene diboronic acid was synthesized and the homopolymer was stored under vacuum for 1 week to increase the molecular weight of the material.[5] The storage modulus of the homopolymer stored under vacuum increased to 0.950 GPa at 30 °C. The storage modulus of **Polymer 2.1** at the same temperature decreased to 0.381 GPa. All three films have different glass transition temperatures. **Polymer 2.1** has the highest T_g and the homopolymer stored under vacuum has a slight increase in T_g. Interestingly, the random copolymer has the highest E' value in the rubbery region.

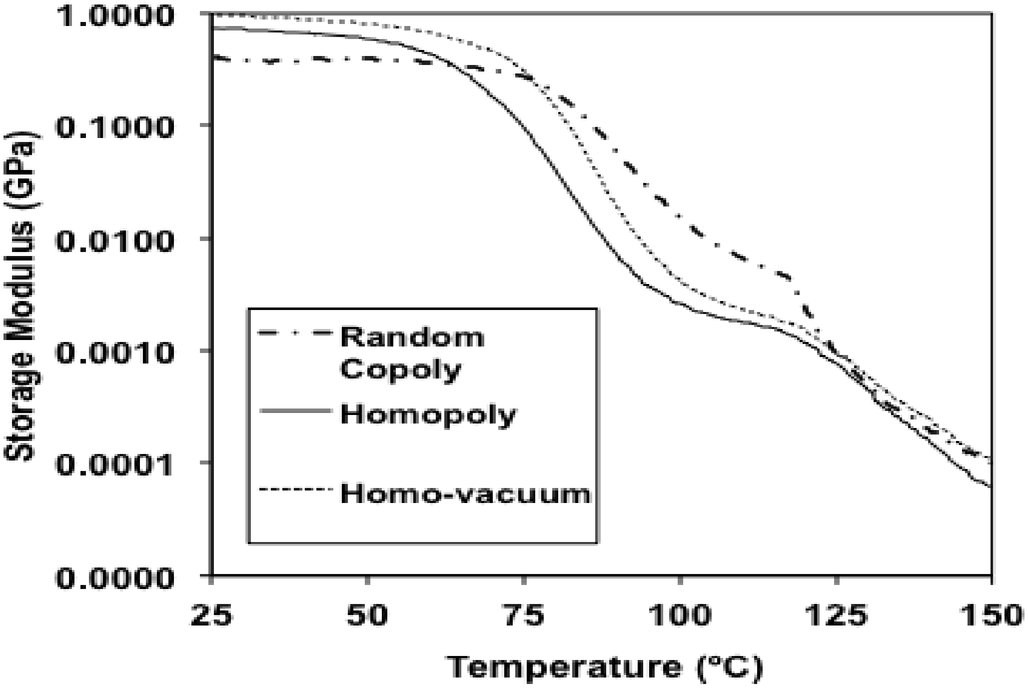


Figure 2.15: The storage modulus of poly(dioxaborolane)s increase when stored under vacuum. The storage modulus for the copolymer decreases significantly.

The ability of materials to dissipate engergy is shown by the peak value of the loss tangent (**Figure 2.16**). At each sample's T_g, we see that the loss tangent peak value is less for the **Polymer 2.1** than for the two homopolymers. This could be the result of a decrease in chain entanglement or segmental stacking due to the reduce number of alkly side chains present in the copolymer.

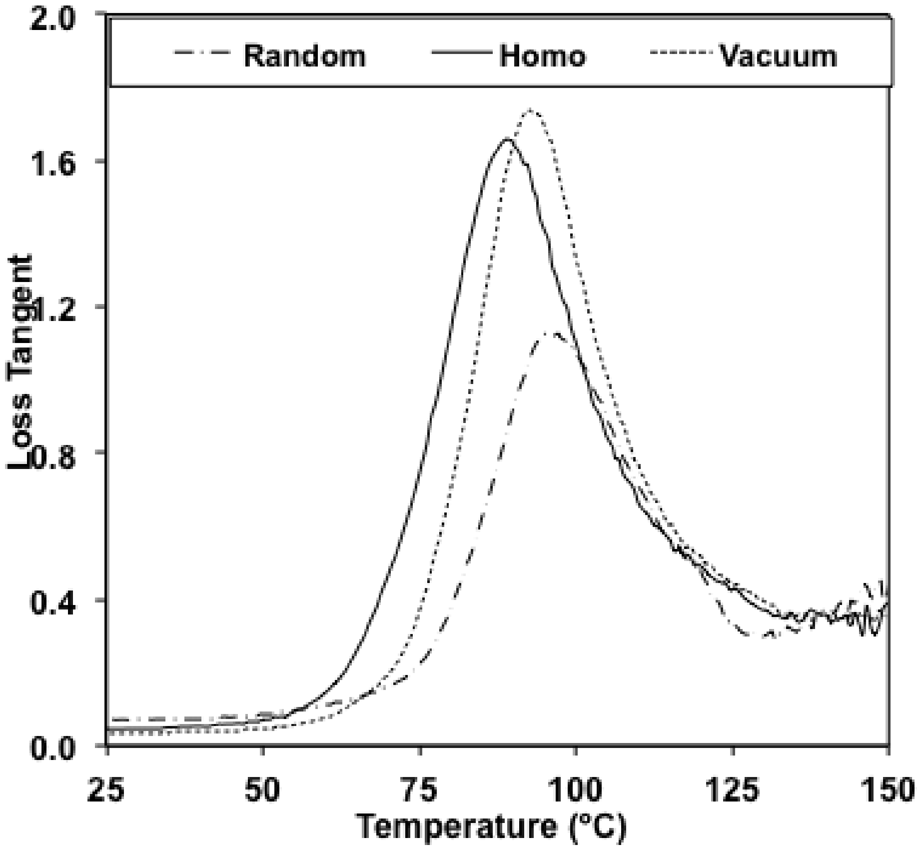


Figure 2.16: Loss tangent spectra for the polymers.

2.5 SUMMARY AND OUTLOOK

Significant progress has been made in the area of polymer chemistry since the days of Staudinger, who was one of the first scientists to prove the existence of macromolecules. The area of chain growth polymerizations has resulted in the ability to produce polymers with narrow polydispersities and the ability to control molecular weight. Unfortunately, the same amount of progress has not been seen in the area of step-growth polymerization.

Step-growth polymerizations offer the ability to incorporate functional groups into the polymer backbone. Due to the polymerization mechanism, it is nearly impossible to produce monodispersed materials. We are able to obtained lower dispersed materials by switching to a more polar solvent and increasing the initial monomer concentration. By optimizing monomer solubility and concentration, self-supporting poly(dioxaborolane) films are synthesized. Increasing the solubility of the monomers prevents the ability to synthesize high molecular weight polymers in the presence of large excess of tetrol; however, materials with molecular weights higher than expected are formed. This could be the result of formation of boronic anhydrides preceding the formation of the ester. The polymerization kinetics was investigated, but the formation of the boronate ester happens so quickly that we were unable to quantify it as it occurred.

Next, DSC and DMA were used to determine the thermal and mechanical properties of poly(dioxaborolane)s. Both analytical techniques gave similar values for the onset of the glass transition temperature. Based on DMA, it was determined that poly(dioxaborolane)s have a stiffness that is between that of PET and polystyrene. Storing the polymer under vacuum increases this stiffness and the stiffness is decreased when 1,4-benzene diboronic acid is incorporated into the polymer main chain.

By optimizing the polymerization of this subclass of polyboronates, we have made it one step closer to learning more about these novel polymers. Having a basic idea on the behavior of these materials could lead to the development of a real-world application for these polymers.

2.6 EXPERIMENTAL SECTION

Materials. Monomers were purchased from Sigma Aldrich and used without further purification. Solvents benzene and 1,4-dioxane were from Acros Organics. Toluene was obtained from Innovative Technologies solvent purification system.

Instrumentation. The *in situ* NMR study was preformed on the 500 MHz NMR. The kinetic study and polymer analysis was performed on either the 400 MHz NMR in $DCCl_3$. GPC analysis was performed using a Shimadzu LC-10AT system calibrated with PS standards ranging from 580-299,400 Da, with tetrahydrofuran as the mobile phase. DMA analysis was performed using a TA Q800 DMA.

Synthesis of Homopolymer: To a 15 mL round bottom flask 9,9-didodecylfluorene-2,7-diboronic acid (0.3105 g, 0.562 mmol) and pentaerythritol (0.0716 g, 0.562 mmol) were added with a stir bar. For the concentration studies, the appropriate amount of dry dioxane was added to obtain the concentrations of 2.0 %w/v, 2.7 %w/v, 4.2 %w/v, 10.3 %w/v, 15.0 %w/v, 15.4 %w/v, 15.7 %w/v, 15.9 %w/v, 18.5 %w/v, 20.0 %w/v, 22.0 %w/v, and 27.4 %w/v for each polymerization. A Dean Stark apparatus was attached and the reaction was heated to reflux for 5 hours. Solvent was removed by rotary evaporation, producing a colorless, brittle film. The film was stored under reduced pressure (1mm/in Hg) for 5 hours to remove residual solvent. GPC analysis determined that storing the film under vacuum for 5 hours does not significantly increase the molecular weight. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.90-7.58 (m, 6H, Ar H), 4.16 (s, 8H, O-CH_2-C), two terminal methylene groups as shoulders at 4.06 and 3.99, 2.01 (br t, 4H, α-CH2-), 1.19-0.93 (m, 12H, -CH2-), 0.77 (t, 6H, -CH3), 0.60 (br s, 4H, β-CH2-).

***Insitu* NMR analysis**: Using 1,4-dioxane-d8, a 7 mmol solution of diboronic acid and pentaerythritol were made. Approximately 2 activated 3 Å molecular sieves were added to the NMR tube. Experimental temperature was 80 °C, collecting scans every 2 minutes, monitoring the growth of the main chain methylene peak.

Synthesis of Polymer 2.1: Random copolymers were synthesized using a equivalent amounts of pentaerythritol and diboronic acids. The ratios for the 9,9-didodecylfluorene-2,7-diboronic acid to 1,4-phenylene diboronic acid monomers were approximately 2:1, 4:1, and 10:1. For random copolymer containing the 2:1 ration of fluorene diboronic acid to phenylene diboronic acid, 0.1753 g (1.29 mmol) of pentaerythritol, 0.5007 g (0.85 mmols) of 9,9-didodecylfluorene-2,7-diboronic acid and 0.0735 g (0.44 mmol) were added to a 15 mL round bottom flask along with 5 mL of distilled dioxane. Solution was stirred and purged with nitrogen gas for 15 minutes before heating was started. Reaction mixture was allowed to reflux for 3 hours and formed a cloudy, colorless solution.. Reaction mixture was filtered and dried. GPC analysis determined that the weighted molecular weight average of 16, 457 Da with a PDI = 3.3. Films were dropcast from benzene. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.90-7.58 (m, 6H, Ar H), 4.16 (s, 8H, O-CH_2-C), two terminal methylene groups as shoulders at 4.06 and 3.99, 2.01 (br t, 4H, α-CH2-), 1.19-0.93 (m, 12H, -CH2-), 0.77 (t, 6H, -CH3), 0.60 (br s, 4H, β-CH2-).

Synthesis of Mesoporous Polymer (Polymer 2.2): To a reaction vessel, 0.2532 g (0.430 mmols) of 9,9-didodecylfluorene-2,7-diboronic acid and 0.1471 g (0.430 mmols) with 4.9 mL of distilled THF and 0.1 mL of methanol. The reaction mixture was stirred and purged with N_2 gas for 15 minutes, allowing everything to solubilize. Reaction was heated until solvent began to reflux and continued for 16 hours. Sample was dried on under reduced pressure overnight. Film was dropcast from benzene. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.52 (s, 4H), 7.90-7.58 (m, 6H, Ar H), 6.61 (s, 4H), 6.01 (s, 4H), 4.16 (s, 8H, O-CH_2-C), 2.01 (br t, 4H, α-CH2-), 2.27-2.06 (m, 1.19-0.93 (m, 12H, -CH2-), 0.77 (t, 6H, -CH3), 0.60 (br s, 4H, β-CH2-).

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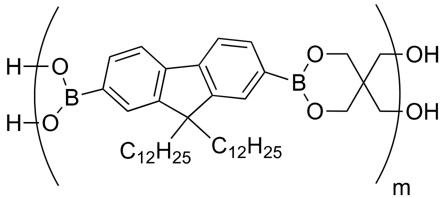
CHAPTER 3: STABILITY OF BORONATE LINKED FILMS

3.1 INTRODUCTION

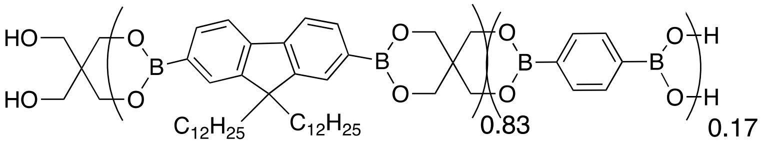
Because of the growing awareness of sustainability, focus has been shifted away from conventional polymers to more environmentally friendly materials.[1-2] It is well known that boronate esters are susceptible to hydrolytic cleavage in solution.[3] **Chapter 1** discusses how having as little as 0.1% w/v of water present in a poly(dioxaborolane) solution results in degradation down to monomers within a 24 hour time-frame. More interestingly, the molecular weight (MW) of the polymer is recovered by storing the polymer under vacuum, and this process is repeatable over several cycles, each time being able to fully recover the polymers original MW.[4] The ability to hydrolyze and repair the polymeric system without having to add any type of catalyst demonstrates the inherent reversibility of this system. The use of polymers in solution is not common; thus, research interests were directed towards evaluating the stability of poly(dioxaborolane) films and other poly(boronate)s.

3.2 POLYMER STABILITY

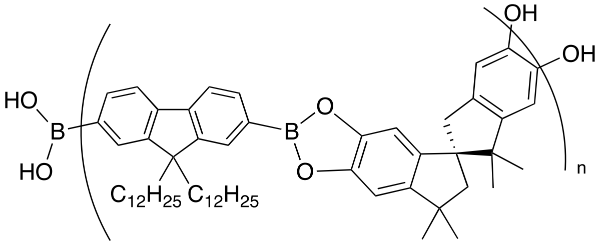
Bowie *et. al.* reported that in the presence water vapor, 6-membered-ring phenyl boronates are more stable than 5-membered-ring phenyl boronates because latter has significantly more ring strain, coordination is preferred. It was also reported that adding alkyl substituents to the ring enhances the stability.[5] Poly(dixaborolane)s are connected via a 6-membered cyclic structure, meaning that the stability of the polymer film should be greater than that of the polymer in solution. To evaluate of the dodecyl side chains contribute to the stability of the polymer, 1,4-phenylene diboronic acid (PDBA) was incorporated into the polymer backbone. By having PDBA in the polymer, we are decreasing the presence of the alkyl side chains. A poly(boronate) connected via a 5-membered boronic ester was synthesized as well to compare the stability of the different sized rings. Using the same reaction times, monomer concentration, and film casting procedure, three different poly(boronate) films were synthesized (**Figure 3.1**): the homopolymer (**Polymer 3.1**), the random copolymer containing 17.5% PDBA (**Polymer 3.2**), and a mesoporous polyboronate (**Polymer 3.3**). The initial molecular weight of the homopolymer was 20 kDa and despite of having equal reaction times, the weight average molecular weight (M_w) of the copolymer was closer to 53 kDa and the M_w of **Polymer 3.3** was 14.5 kDa. Drop cast films of **Polymers 3.1**, **3.2**, and **3.3** were placed in a humidity chamber that was controlled to 100% relative humidity by exposing to 23% sulfuric acid/water mixture. Over a period of one week, the mass of each of the films was checked daily to see if swelling was occurring. Based on film mass, there was no uptake of water. To determine if any degradation occurred, the molecular weight of each film was analyzed using GPC (**Figure 3.2**). GPC analysis for **Polymer 3.1** shows no change in molecular weight; however, **Polymers 3.2** and **3.3** had significant decreases in their respective molecular weights.



Polymer 3.1



Polymer 3.2



Polymer 3.3

Figure 3.1: Polyboronate structures: Polymer 3.1 (homopolymer), Polymer 3.2 (random copolymer synthesized with 2:1 fluorene diboronic acid to benzene diboronic acid), and Polymer 3.3 polyboronate connected using a five-membered cyclic ester.

Polymer 3.2 contains the less bulky and labile 1,4-benzene diboronic acid, which explains the ability of the water to coordinate to the film and cause degradation. **Polymer 3.3** degradation can be attributed the incorporation of 5,5’-6,6’-tetrahydroxy-3,3,3’,3’-tetramethyl-1-spirobisindane into the polymer backbone creating pores, making the boronate more susceptible to nucleophilic attack.

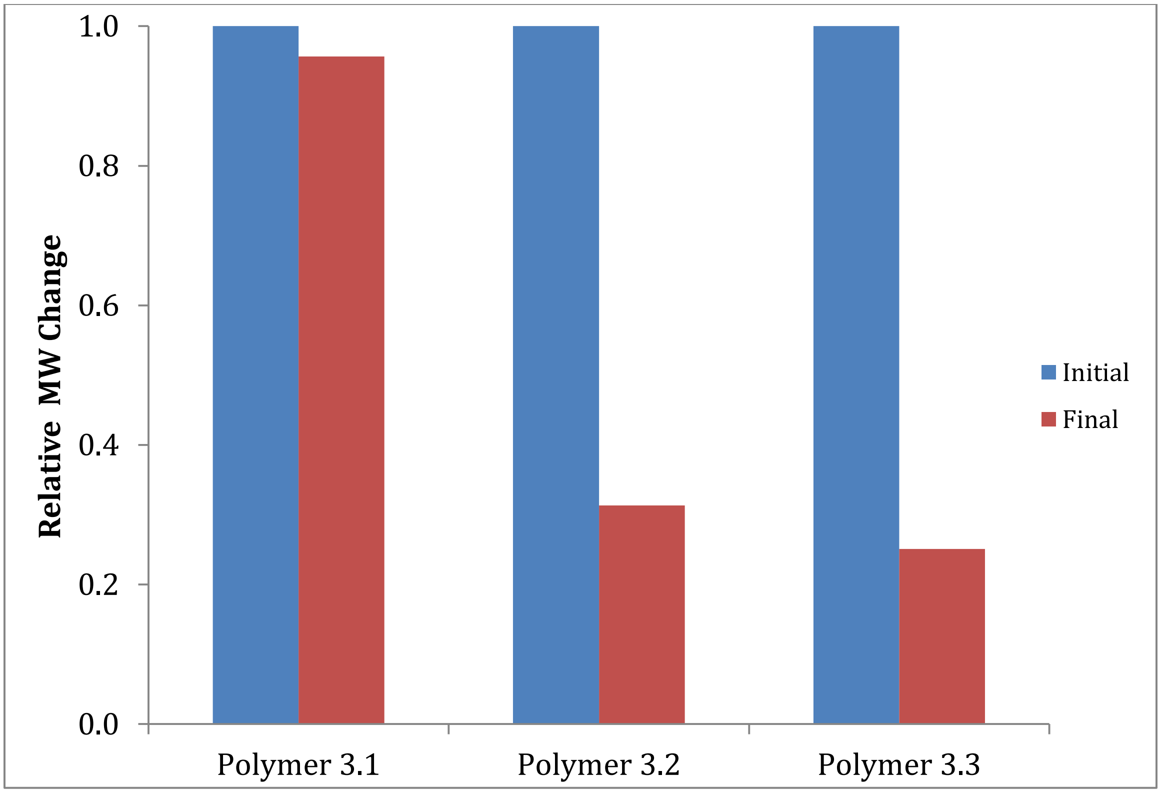


Figure 3.2: Plot of relative MW for the polymers before and after exposure to 100% humidity for one week. Polymer 3.1 is stable when exposed to water vapor but Polymers 3.2 and 3.3 have a significant decrease in MW.

Knowing that **Polymer 3.1** is stable in the presence of water vapor, the stability of the polymer in different aqueous environments (neutral, acidic, and basic) was investigated (**Figure 3.3**). Within a 24 hour time period, **Polymer 3.1** does not degrade even when submerged into aqueous solutions regardless of pH.

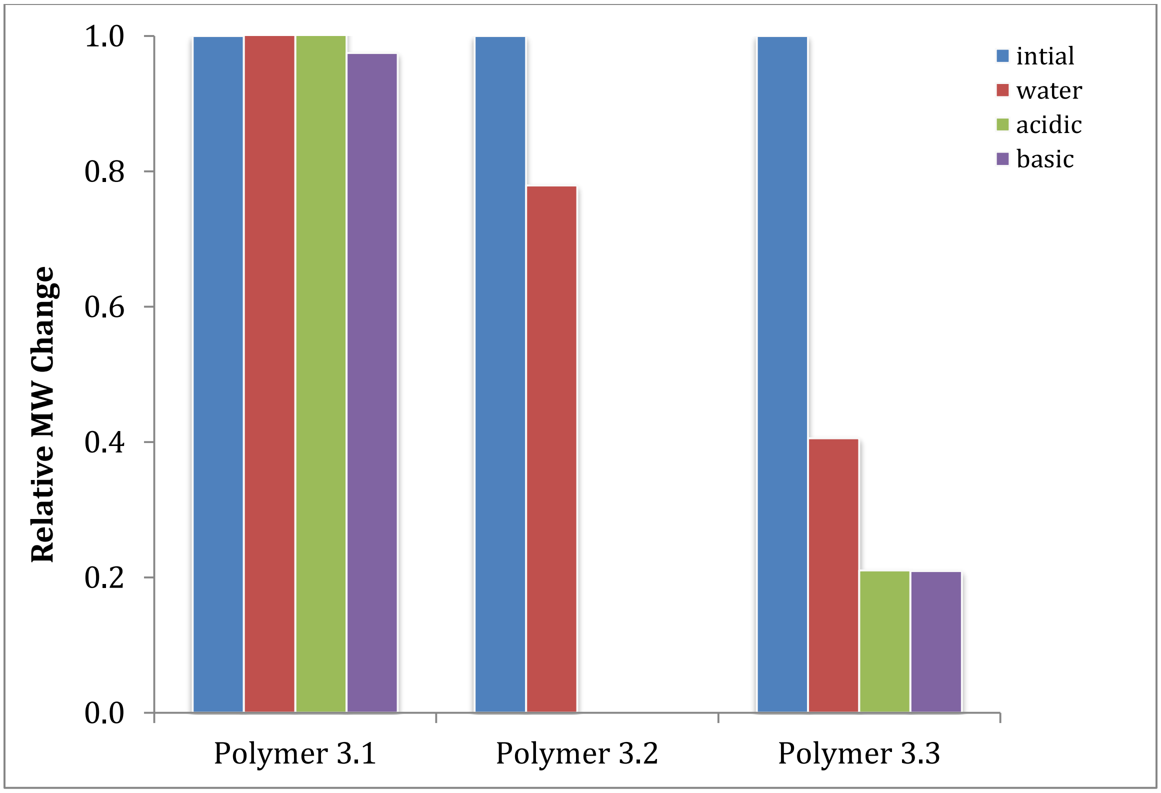
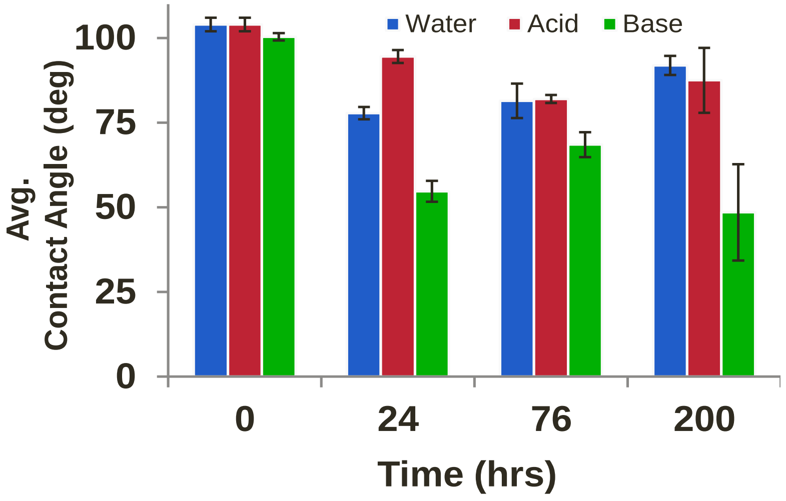


Figure 3.3: Plot shows polymers' initial MW (blue) and MW after immersion into water (red), acid (green), and base (purple). The MW for Polymer 3.2 after immersion is not shown because material was insoluble after exposure to basic conditions for 24 hours.

From this data a closer look into the polymers stability was investigated. **Polymer 3.3** was not studied further due to its lack of stability and **Polymer 3.2** was modified to contain a 12.5% 1,4-phenylene diboronic acid (PDBA) to see if the stability of the random copolymer polymer would increase. We also evaluated the effect of film thickness on polymer stability by spin casting polymer films onto a glass substrate. The dropcast films have a uniform thickness of 0.25 mm. We were able to decrease the film thickness to 0.10mm by spin coating the polymer solution onto a glass substrate. Spin coated **Polymer 3.1** and modified **Polymer 3.2** were exposed to different solutions: neutral (distilled water), acidic solutions of both 2 M

HCl and 0.2M HCl, and basic solutions of both 2 M NaOH and O.2 M NaOH. Films were exposed to conditions for as long as one week by immersing the film into its respective solution. Contact angle, molecular weight, and mass monitoring were used to detect changes within the polymer films.

Spun cast **Polymer 3.1** is initially hydrophobic, has a contact angle of 100° (Top graph in **Figure 3.4**) and has an initial weighted molecular weight average (M_w) of 35 kDa. Upon exposure to water and a 2 M HCl solution, the contact angle decreased slightly, but still remained largely hydrophobic indicating the film is stable. The M_w of the films exposed to these same solutions saw no change, just as there was no change in the film mass. However, exposure of the polymer to a 2.0 M basic solution resulted in film degradation in as little as 24 hours. After 24 hours, we measured a significant decrease in the contact angle of the film, indicating that the film is no longer hydrophobic. The decrease in contact angle correlates with the decrease in M_w that was determined by GPC analysis: the initial film M_w decreased to ~10 kDa after only 24 hours. Interestingly, the M_w did not decrease further, even after leaving the film in basic solution for 15 days.



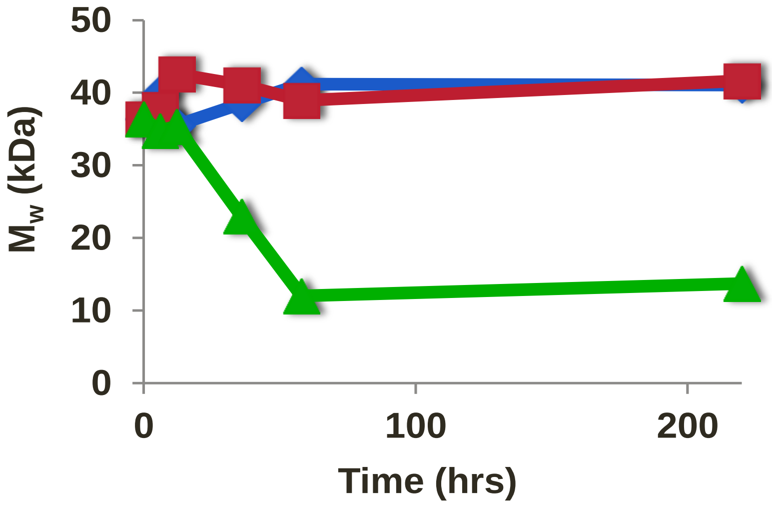


Figure 3.4: Exposure of a spun cast film to neutral (blue) and acidic (red) solutions has a small effect on contact angle (top graph) and no effect on the molecular weight of the polymer (bottom) suggesting only a surface interaction between **Polymer 3.1** and neutral or acidic solutions. Basic (green) solutions, however, causes significant decrease in contact angle (top) and M_w (bottom) of spun cast **Polymer 3.1**, showing degradation of the film.

However, **Polymer 3.2** containing only 10% of 1,4-benzene diboronic acid was completely degraded according to GPC analysis after only being exposed to the 2M basic solution for 24 hours (**Figure 3.5**). The contact angle measurements show that after 8 days the film is so degraded that it is not possible to obtain a contact angle for the film. The film appearance changed from cloudy and colorless to dark green.

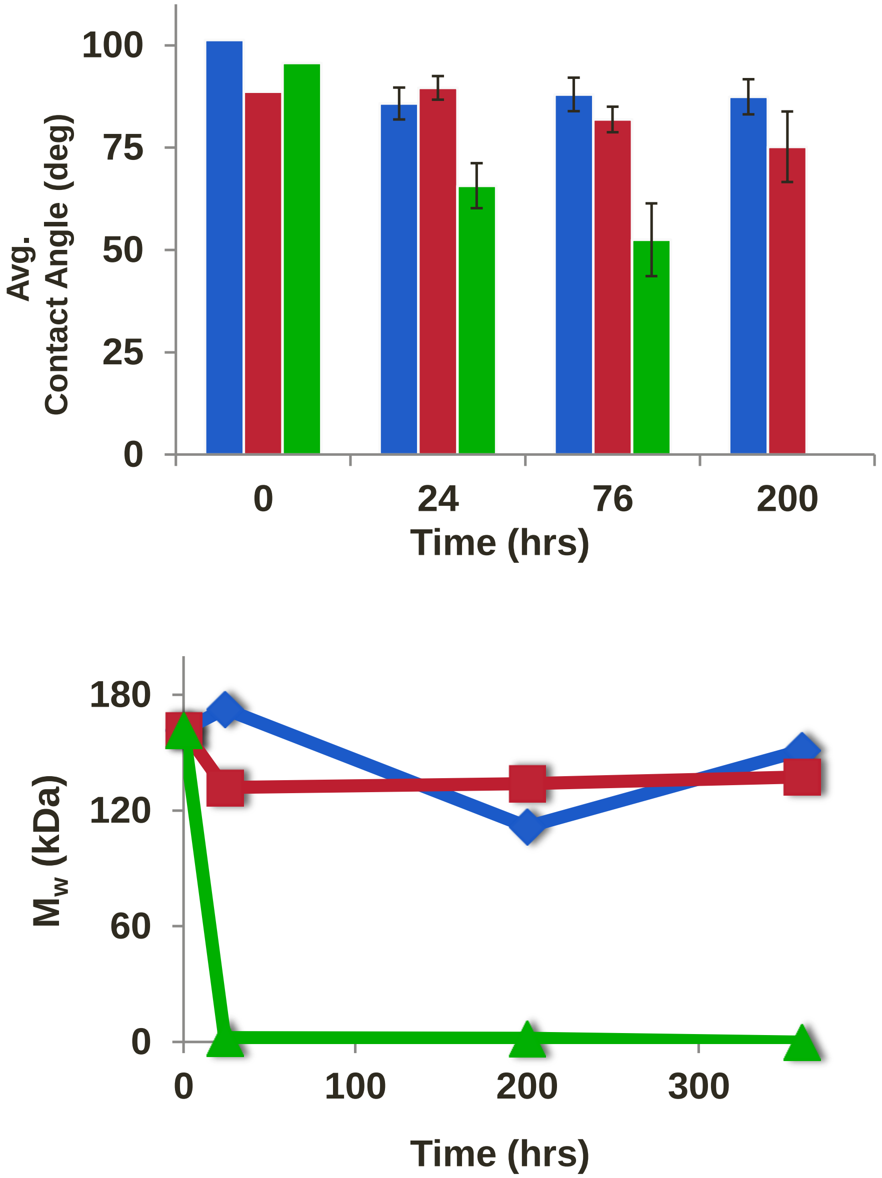


Figure 3.5: Plot of contact angle (top) and M_w (bottom) of the random copolymer containing 10% 1,4-benzene diboronic acid. Incorporating PDBA into the polymer does not change the stability of the film in neutral or acidic solutions, but it increases the rate of degradation in basic solutions.

The concentration of the acidic and basic solutions were decreased to 0.2 M to see if a relationship exists between the amount of nucleophile that is present and the rate or degree of degradation. Both the drop cast and spun cast films for **Polymer 3.1** were tested. The contact angle for the drop cast polymer is not as reliable due to the curvature of the film. However, the trend seems to hold true for neutral and acidic conditions: the contact angle has a slight decrease initially but plateaus off. Exposure to 0.2 M NaOH solution causes a significant decrease after 76 hours, but when tested at the 120 hour mark, it seems as if the contact angle increases (**Figure 3.6**).

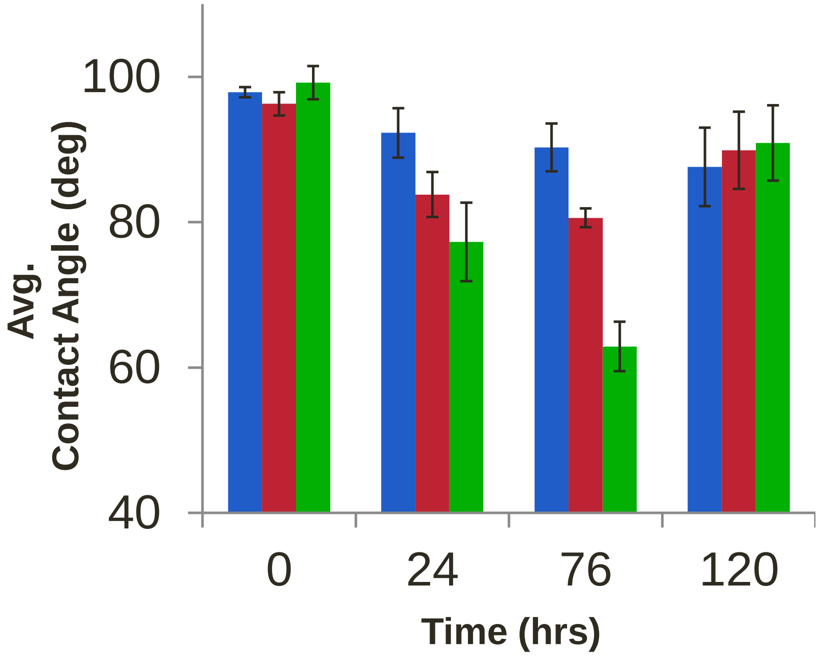


Figure 3.6: Plot of contact angle for the drop cast Polymer 3.1. Variability between measurements is large, making it difficult to see if the film follows the stability trend.

One explanation is the large standard deviation associated with the measurements. GPC analysis and UV-Vis absorption were used to obtain a better idea of what was occurring within the film. The initial M_w of the film was 38.3 kDa and the final M_w after exposure for 200 hours the M_w decreased to 28.8 kDa, showing some but not complete degradation of the film. A UV-Vis scan shows that the film absorbance does not change after being exposed to basic conditions for 200 hours (**Figure 3.7**), supporting the claim of very little hydrolysis.

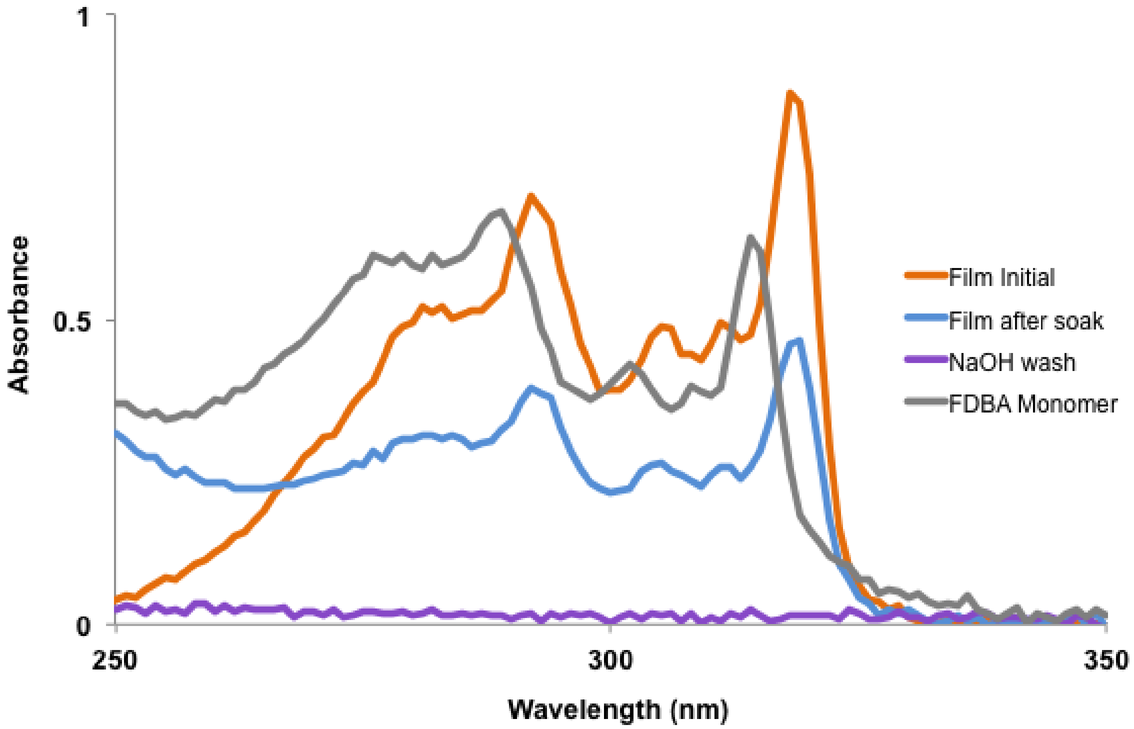


Figure 3.7: UV-Vis absorbance spectra supporting that exposure of dropcast **Polymer 3.1** results in very little hydrolysis.

The spun cast version of the same film showed a decrease in the average contact angle from 83.3° to 60.3° when exposed to 0.2M of NaOH (**Figure 3.8**). The M_w decreased from 39.5 kDa to 22.0 kDa showing some degradation of the film.

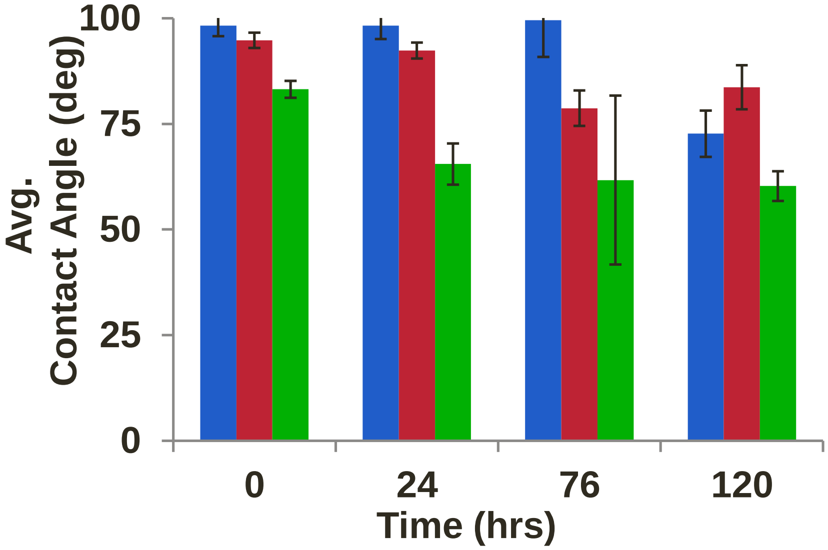


Figure 3.8: Plot showing how contact angle of spun cast **Polymer 3.1** is affected when left in water (blue); 0.2M HCl (red) and 0.2M NaOH (green).

For **Polymer 3.2**, we only looked at the spun cast films because of the brittleness of the dropcast films. It is here that the first deviation from the observed trend is seen. The film exposed to 0.2M HCl has very little change in the contact angle, but the film exposed to water decreases from an initial contact angle of 100° to 73.8°. The film exposed to basic conditions has a decrease in contact angle to 60.8° (**Figure 3.9**). GPC analysis of the film exposed to basic conditions for about two weeks show that the M_w remains practically the same as it did initially, going only from 25.6 kDa to

23.4 kDa, indicating a slower rate of degradation in the less concentrated NaOH solution.

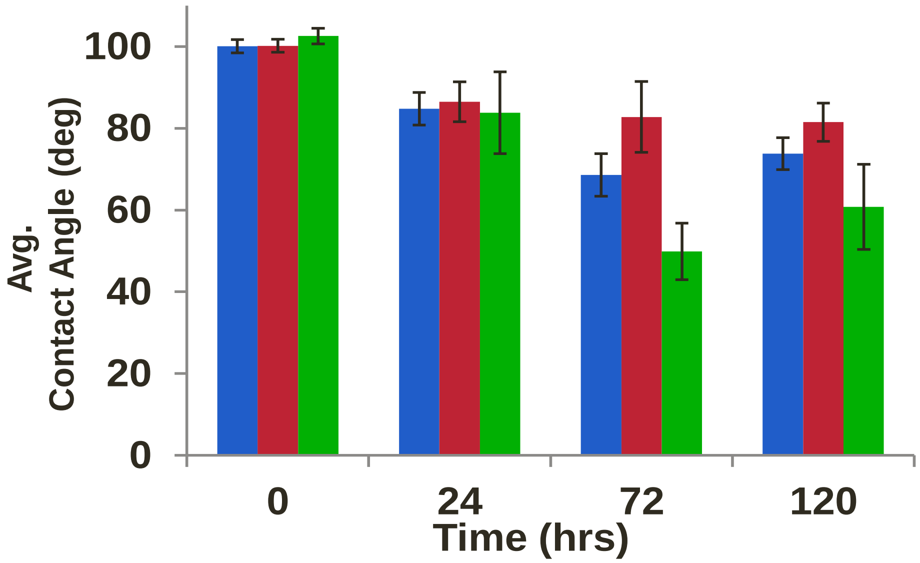


Figure 3.9: Contact angle measurement for the random copolymer exposed to water, 0.2 M HCl, and 0.2 M NaOH solutions.

3.3 SUMMARY AND OUTLOOK

Our first generation poly(dioxaborolane)s have drawn our interest because they are generated through a facile synthesis, capable of solid-state polymerization, and are able to self-repair after being hydrolytically damaged while in solution. Never before has the stability of poly(boronate) films been investigated. This chapter examined the stability of first generation poly(dioxaborolane)s along with various modified poly(boronate) films. We have explored the stability of the homopolymer (synthesized using 9,9-didodecylfluorene-2,7-diboronic acid and pentaerythritol), a random copolymer (synthesized using 9,9-didodecylfluorene-

2,7-diboronic acid, 1,4-phenylene diboronic acid and pentaerythritol) and a mesoporous polymer. When exposed to water vapor, the homopolymer does not undergo hydrolytic damage or exhibit polymer swelling. This could be the result of the dodecyl alkyl groups being fully extended and providing a barrier around the boronate ester linkage, thus preventing the water from being able to coordinate with boron's empty p-orbital.

Next, we investigated the homopolymer's and the copolymer's stability after being immersed in neutral, acidic, and basic solutions. We found that we could increase the stability of the random copolymer by including less of the liable 1,4-phenylene diboronic acid. Both the homopolymer film and the copolymer containing 10% of benzene diboronic acid film were stable in the presence of water, 0.2M and 2M HCl, Based on the contact angle measurements, the interaction between the film with water and the film with the acidic HCl solution is purely surface interactions. There were not any changes in the bulk properties of the film. However, upon exposure to strongly basic solutions we detected some degradation. The amount of degradation seen is dependent upon on solution concentration and film thickness. We saw that the drop cast homopolymer films have very little degradation when exposed to a 0.2M NaOH solution. The spun cast homopolymer film degrades more but does not degrade back to its monomers. These results suggest that it is possible to tailor the stability of poly(dioxaborolane)s. By doing so, we may be able to create an easily recyclable polymer.

3.4 Experimental Procedure

Materials. Monomers were purchased from Sigma Aldrich and used without further purification. Solvents benzene and 1,4-dioxane were from Acros Organics. Dioxane was distilled over calcium hydride and benzophenone. Toluene was obtained from Innovative Technologies solvent purification system.

Instrumentation. NMR analysis was preformed on the either the Varian 300 MHz or the Varian 400 MHz NMR. GPC analysis was performed using a Shimadzu LC-10AT system calibrated with PS standards ranging from 580-299,400 Da, with tetrahydrofuran as the mobile phase.

Synthesis of Polymer 3.1: To a 15 mL round bottom flask 9,9-didodecylfluorene-2,7-diboronic acid (0.3105 g, 0.562 mmol) and pentaerythritol (0.0716 g, 0.562 mmol) were added with a stir bar. A Dean Stark apparatus was attached and the reaction was heated to reflux for 5 hours. Solvent was removed by rotary evaporation, producing a colorless, brittle film. Film was dissolved and benzene and drop casted. The film was stored under reduced pressure (1mm/in Hg) for 5 hours to remove residual solvent. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.90-7.58 (m, 6H, Ar H), 4.16 (s, 8H, O-CH_2-C), two terminal methylene groups as shoulders at 4.06 and 3.99, 2.01 (br t, 4H, α-CH2-), 1.19-0.93 (m, 12H, -CH2-), 0.77 (t, 6H, -CH3), 0.60 (br s, 4H, β-CH2-).

Synthesis of Polymer 3.2: For random copolymer containing the 2:1 ration of fluorene diboronic acid to phenylene diboronic acid, 0.1753 g (1.29 mmol) of pentaerythritol, 0.5007 g (0.85 mmols) of 9,9-didodecylfluorene-2,7-diboronic acid and 0.0735 g (0.44 mmol) were added to a 15 mL round bottom flask along with 5 mL of distilled dioxane. Solution was stirred and purged with nitrogen gas for 15 minutes before heating was started. Reaction mixture was allowed to reflux for 3 hours and formed a cloudy, colorless solution.. Reaction mixture was filtered and dried. GPC analysis determined that the Mw= 16, 457 with a PDI = 3.3. Films were dropcast from benzene.

Synthesis of Polymer 3.3: Into a 10 mL round bottom flask, 0.200g (0.34 mmols) of 9,9-didodecylfluorene-2,7-diboronic acid was mixed with 0.1153 g (0.34 mmols) of 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1-spirobiindane in 4.9 ml of toluene and 0.1 ml of methanol. Solution was stirred and purged with nitrogen gas for 15 minutes before heating began. Allowed reaction to reflux for 3 hours before removing from heat. Solution is clear with a light brownish color. Concentrated material under reduced vacuum. Film was dropcast from benzene.

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CHAPTER 4: SYNTHESIS OF FLEXIBLE DIBORONIC ACIDS AND TETROLS

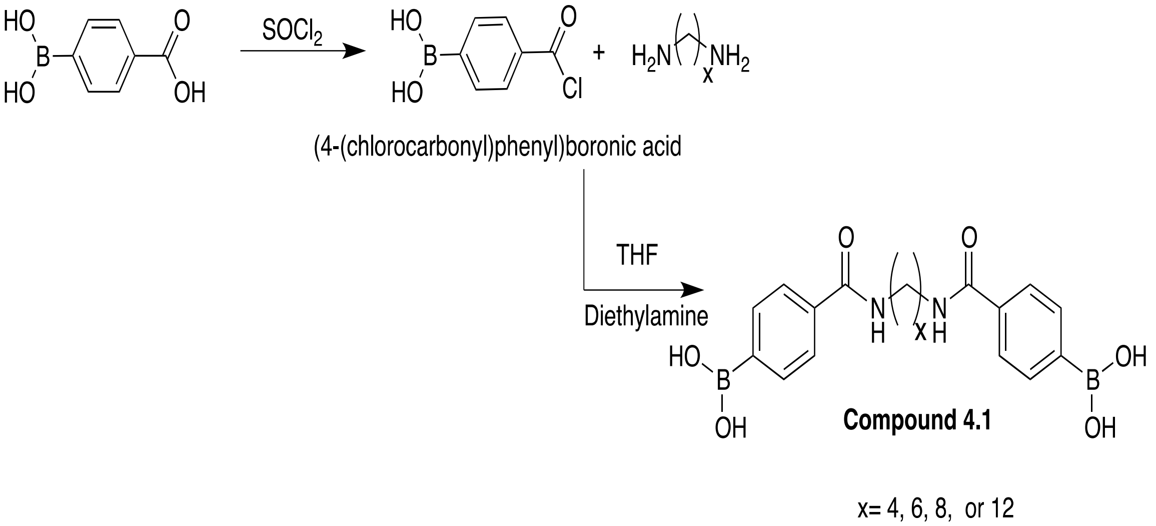
4.1 INTRODUCTION

The main chain of poly(dioxaborolane) consists of a fluorene moiety bonded to a tetraol via a six-membered cycle, creating a rigid polymer structure. The 9,9-dihexylfluorene-2,7-diboronic acid was chosen to increase the solubility of the material[1] and the tetraol was chosen to minimize the ability of the material to cross link.[2] After learning more about the mechanical properties and the stability of the materials in the solid state, we decided to investigate to see if any significant changes would occur in the properties of the material if the flexibility of the monomers were increased.

Polymers that are connected through collinear bonds, such as polyparaphenylene, normally have a rigid structure. Polyethylene, on the other hand, is a flexible polymer because non-planar bonds hold the main chain of the polymer together, requiring very little energy to rotate one part of the material with respect to another part.[3] Knowing this information, we decided to synthesize a series of flexible diboronic acid monomers and tetraol monomers.

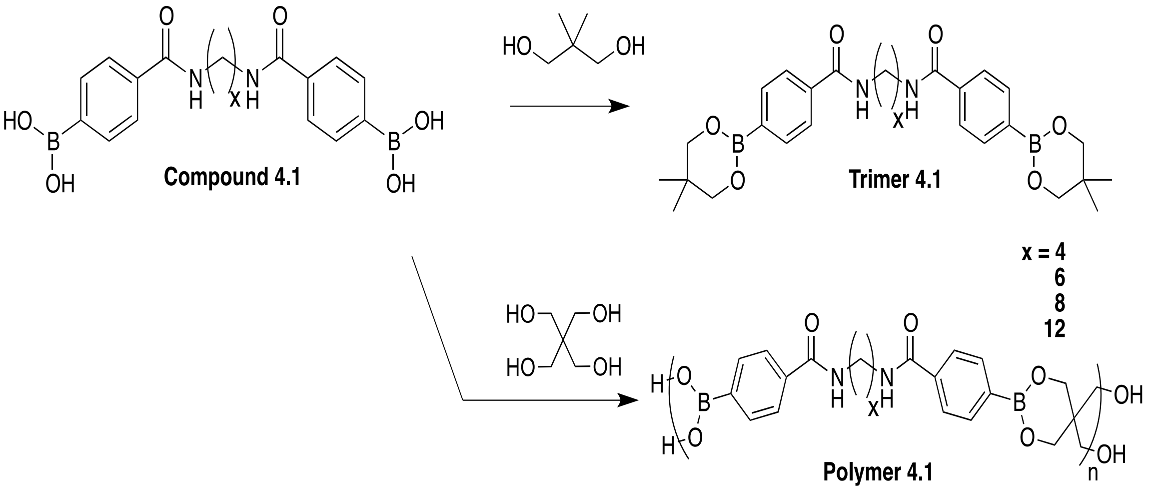
4.2 SYNTHESIS OF DIBORONIC ACIDS MONOMERS

We targeted the synthesis of flexible aromatic diboronic acids because they are more stable than aliphatic diboronic acids.[4] **Scheme 4.1** shows the synthetic route used to obtain **Compound 4.1,** which is a diboronic acid monomer that contains two amide functional groups.[5] This reaction scheme was chosen because the carboxylic acid of the 4-carboxybenzoic acid is easily transformed to the acyl chloride by treating with thionyl chloride ($SOCl_2$). Once the 4-(chlorocarbonyl)phenyl boronic acid was obtained, monomers with different alkyl linkers were synthesized by reacting with diamines of various lengths. To test the correlation between flexibility and viscoelastic properties, four different amines were chosen to react with 4-(chlorocarbonyl)phenyl boronic acid: 1,4-butane diamine; 1,6-hexane diamine; 1,8-octane diamine; and 1,12-dodecane diamine in the presence of diethylamine. The resulting compounds are soluble in dimethyl sulfoxide and the structure was confirmed through NMR analysis and was consistent with the literature.



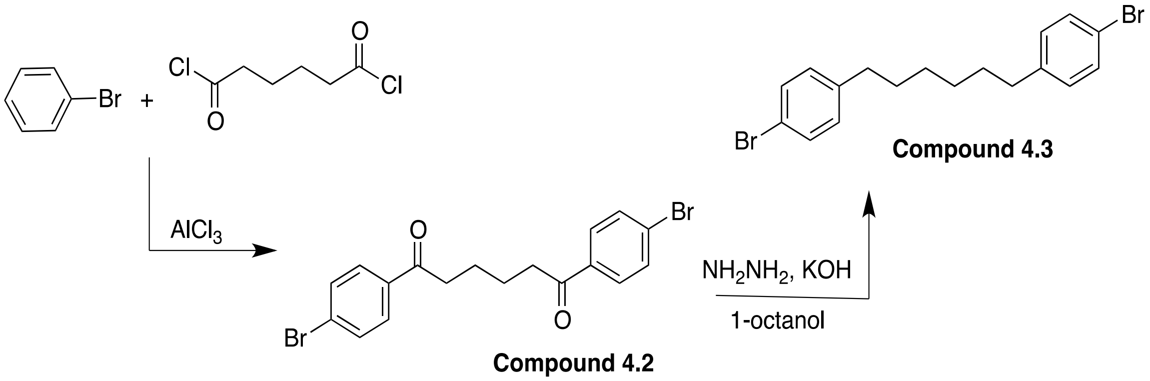
Scheme 4.1: Synthesis of flexible diboronic acids from 4-carboxyphenyl diboronic acid through nucleophilic substitution of a diamine with n=4, 6, 8 or 12.

Trimer 4.1 was synthesized to see if **Compound 4.1** could indeed be converted into a boronate ester. **Compound 4.1** was combined with neopentyl glycol via a condensation reaction in a solution of toluene with 1% methanol. The methanol was required to ensure that the monomers completely dissolved in solution. **Trimer 4.1** successfully synthesized with n= 4, 6, 8, 12 and confirmed by NMR analysis performed using deuterated chloroform. The individual mono mers are not soluble in chloroform and the fact that **Trimer 4.1** does dissolve further supports the formation of the more soluble boronate ester. Because of this promising result, we next set out to synthesize Polymer 4.1 using the same reaction conditions, but replacing the neopentyl glycol with pentaerythritol (**Scheme 4.2**). Unfortunately, we were unable to confirm synthesis of the polymer because we only obtained an insoluble powder, which could be the result of the formation of an extensive hydrogen-bonding network.



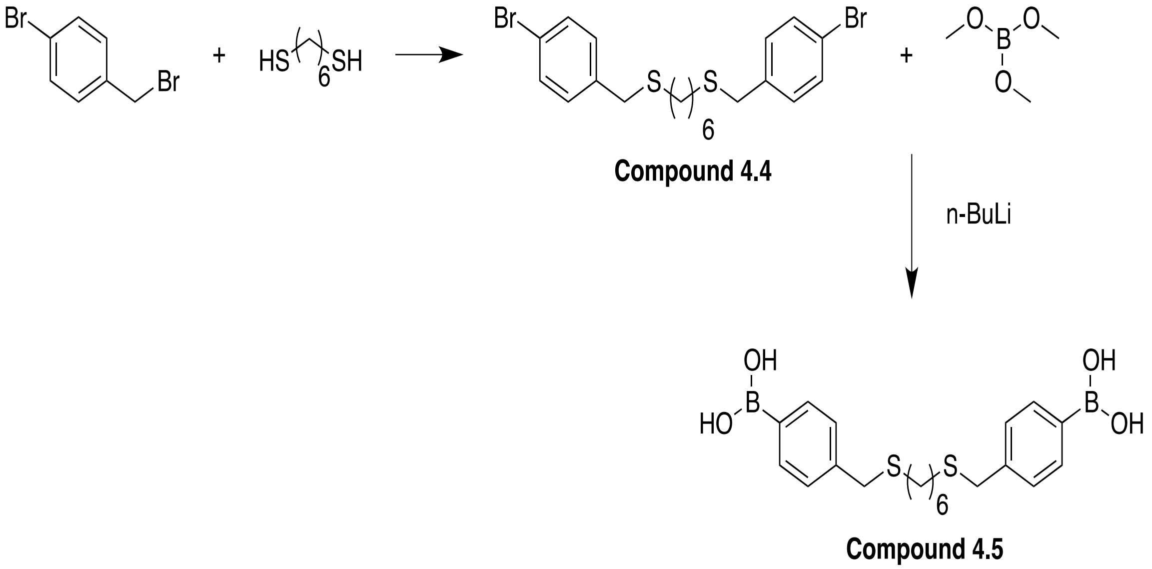
Scheme 4.2: Trimer was synthesized by azeotropic removal of water from Compound 4.1 and neopentyl glycol in a 1% methanol/toluene solution. The polymer only formed an insoluble compound.

As a method of testing our hypothesis, we decided to synthesize a version of **Compound 4.1** without the amide functional group. By replacing decanoyl chloride with adipoyl chloride and reacting with bromobenzene (**Scheme 4.3**), we were able to successfully synthesize and purify **Compound 4.2**.[6] The next step, a Wolf-Kishner reduction to obtain **Compound 4.3** was unsuccessful based on TLC analysis, preventing us from moving forward with the synthetic scheme.



Scheme 4.3: Synthetic route to synthesis the dibromo precursor before borylation

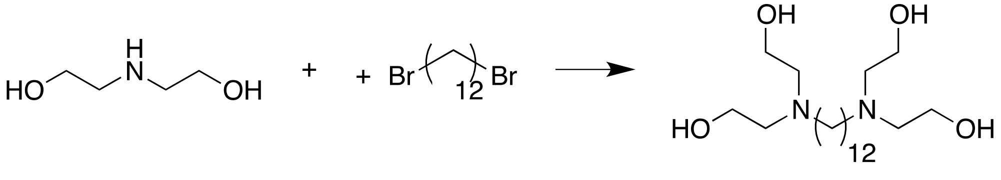
Our final attempt to synthesize a flexible aromatic diboronic acid involved reacting 1-bromo-4-(bromomethyl)benzene with hexane-1,6-dithiol in isopropyl alcohol in the presence of potassium hydroxide to allow nucleophilic substitution of the thiol (**Scheme 4.4**).[7] **Compound 4.4** was purified by subliming excess 1-bromo-4-(bromomethyl)benzene and removing excess thiol by reacting with N-phenylmalieimide. The final step was the boroylation of bromines using trimethy borate and n-butyl lithium. After the boroylation, we were unable to recover pure diboronic acid. After several unsuccessful attempts to produce flexible diboronic acids, we decided that the synthesis of the tetrol should be investigated.



Scheme 4.4: Synthesis of Compound 4.5 using nucleophilic substitution and boroylation.

4.3 SYNTHESIS OF TETRAOL MONOMERS

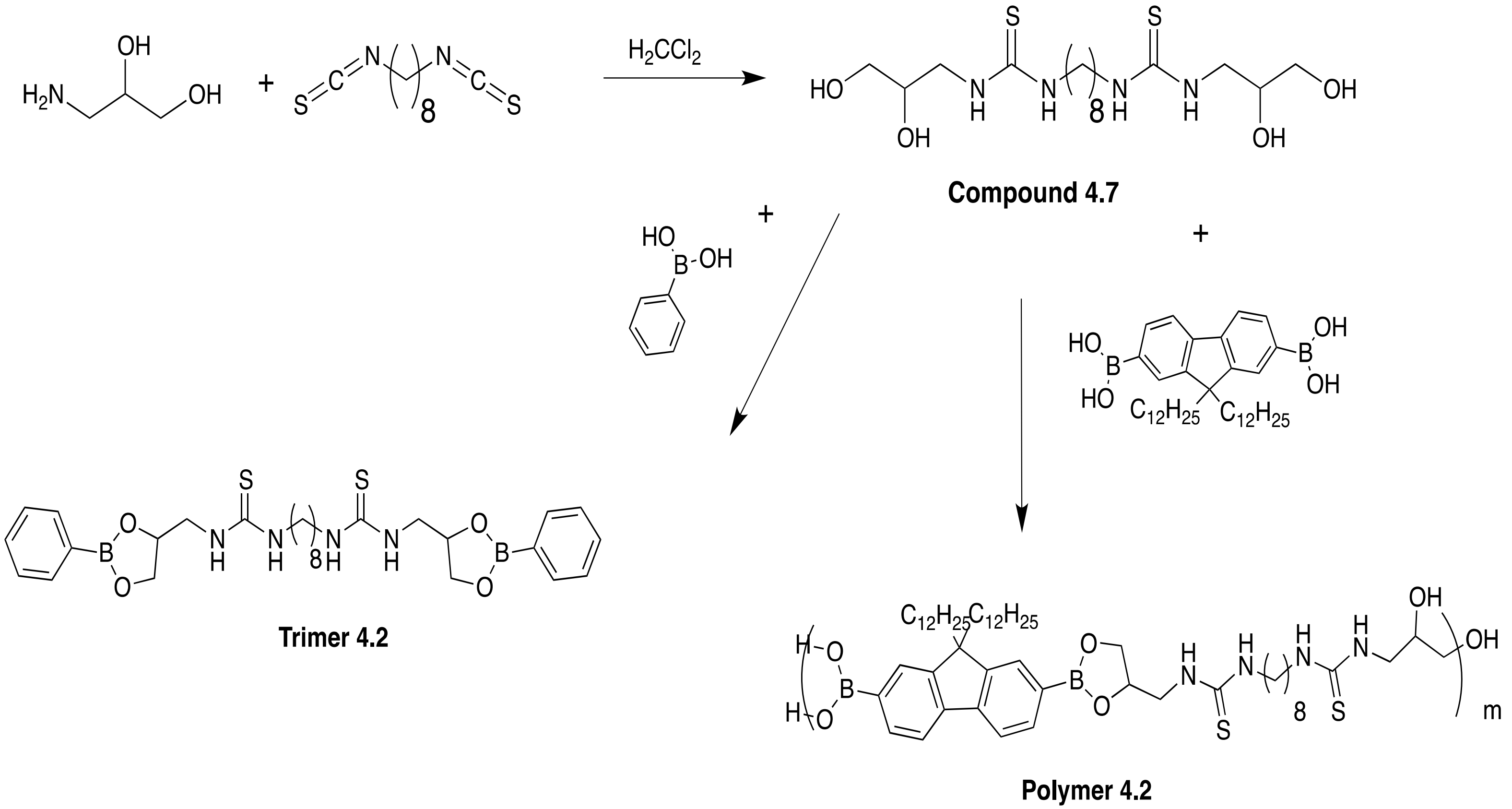
There are several literature references on the alkylation of ethanolamines.[8] Diethanol amine was treated with 1,12-dibromondodecane in the presence of triethyl amine in tetrahydrofuran to form **Compound 4.6** (**Scheme 4.5**. After a four-hour reaction, a brown viscous solution was obtained and after solvent removal we obtained a brown solid, which was purified through an organic extraction. **Compound 4.6** was synthesized in 10.8% yield. Through NMR analysis we were unable to conclude that the conversion was successful due to the overlapping of the alkyl peaks. Therefore we switched to the alkylating ethanolamine with 4,4'-dibromo -1-1'-biphenyl so simplify characterization. Because the bromo-substituents are aromatic, we adapted the amine alkylation method published by the Wang group, which consists of adding potassium carbonate, potassium iodide and reacting the reagents in a refluxing solution of methyl acetonitrile and chloroform.[9] Results of NMR, mass spectrum, and FT-IR analyses support that the alkylation was unsuccessful. To stay in line with facile synthesis of the poly(dioxaborolane)s, we also wanted to keep our monomer synthesis simple.



Compound 4.6

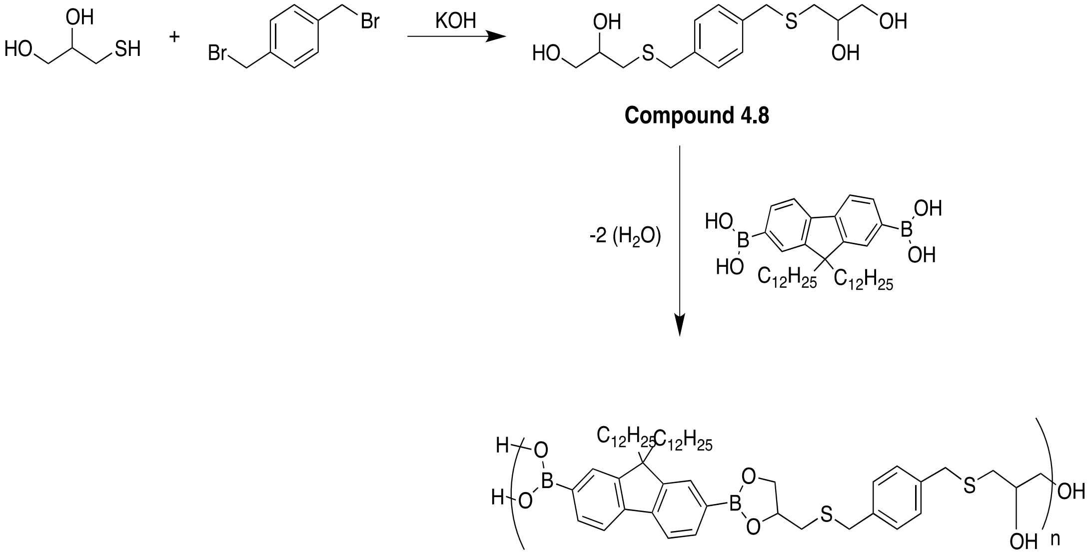
Scheme 4.5: N-alkylation of diethanol amine using 1,12-dibromododecane.

Instead of alkylating the amine group, we tried a more direct route which is treating 3-aminopropane-1,2-diol with 1,8-octane diisocynate for 3 hours in a dichloromethane/triethyl amine mixture (**Scheme 4.5**). Within the first hour of the reaction, a white solid starts form. The desired compound was purified through sublimation and recrystallization with a 23.4% yield. NMR analysis indicates **Compound 4.7** was synthesized, but because of stereochemistry, peak assignment was difficult. Mass spectrometry analysis with negative ion electron spray ionization shows a parent peak with the m/z value of 409, which supports the expected formula weight of 411 g/mol. The diboronate ester (**Trimer 4.2**) was synthesized by treating Compound 4.6 with two equivalents of phenylene boronic acid producing the diester as a clear, colorless film. This resulted in the synthesis of the polymer by reacting with 9,9-didodecylfluorene-2,7-diboronic acid in distilled dioxane. After the polymerization and solvent removal, the film was dropcast from benzene. The resulting material; however, lacked ductility. Because the 1,-8-octane diisocynate is not cost efficient, we decided to revisit the thiol chemistry, but this time synthesize tetrols from dithiols.



Scheme 4.6: Synthesis of a thiourea tetraol. Formation of a diester by reacting with a monofunctional boronic acid and formation of the polymer by reacting with a diboronic acid.

We reacted 1-mercapto-2,3-propanediol with *p*-dibromoxylene and treated in KOH in isopropyl alcohol to form **Compound 4.8**.[10] After synthesis of the newly formed tetraol, was reacted with phenylene boronic acid to form the diester. **Polymer 4.3** was obtained by a step-growth polymerization **Compound 4.8** and 9,9-didodecylfluorene-2,7-diboronic acid. The resulting polymer was more "sticky" that previous synthesized polymers, which all formed hard films. To see if we could synthesize a polymer that possesses some of the sticky quality as well as some of the hardness, we replaced the diboronic acid with 1,4-phenylene diboronic acid. The resulting polymer was a chalky material. Being that we are able to successfully incorporate longer alkyl portions in difuctional monomers, it seems that more research needs to be done to determine the combination of diboronic acid and tetraol to synthesize reproducible ductile films.



Polymer 4.3

Scheme 4.7: Synthetic scheme for **Compound 4.8** and **Polymer 4.3**.

4.4 SUMMARY AND OUTLOOK

We have determined the viscoelastic properties of our rigid poly(dioxaborolane)s, but the biggest disadvantage of these materials is the inability to consistently produce ductile films. Having longer alkyl groups as part of the integral structure of the monomers is one way to produce a more flexible polymer. Through the use of well-established chemistries, we have successfully synthesized several diboronic acid and tetraol monomers. However, using the more flexible monomers has not increased the quality of our polyboronate films.

We have shown that in the solid state, the boronate ester linkage is stable enough to withstand ambient conditions. The future of this project is going to be the ability to consistently produce films that are ductile. By synthesizing polyboronates that have both rigid and flexible main chains, we will be able to determine the relationship between properties such as toughness, hardness, and elasticity. Having this information will give us the advantage of being able to better design a real-world utility for these materials.

4.5 EXPERIMENTAL

Materials. Monomers were purchased and used without further purification unless otherwise indicated. Solvents were purchased and used without further purification unless otherwise indicated. Toluene was obtained from Innovative Technologies solvent purification system.

Instrumentation. The *in situ* NMR study was preformed on the 500 MHz NMR. The kinetic study and polymer analysis was performed on either the 400 MHz NMR in $DCCl_3$.

Synthesis of Compound 4.1: 4-carboxyphenylboronic acid was dried under vacuum overnight. To a 50 mL 2-neck round bottom flask, 2.1133 g (12.7 mmols) of the 3-carboxyphenylboronic acid and 32.2 mL (0.446 mmols) of $SOCl_2$ were added. An argon balloon was added and the reaction was heated to reflux for a period of 24 hours to form 4-chloroformyl phenylboronic acid. Excess SOCl2 was azeotroped off with benzene. The respective diamine was dissolved in 15 mL of dry methanol with 4 mL of triethyl amine and placed in an ice bath. The chloroformyl phenylboronic acid was added dropwise to the solution. The reaction mixture was allowed to warm to room temperature and stirred overnight. The desired product was precipitated out by adjusting the pH to ~4. ^{1}H NMR analysis NMR (400 MHz, $CDCl_3$, δ): N-H (8.36 ppm broad singlet); aromatics (8.15 ppm, 7.86 -7.78 ppm, 7.38 ppm); -CH2- (3.24-3.18 ppm, 1.50 ppm, 1.29 ppm).

Synthesis Trimer 4.1: To a round bottom flask, 10 mL of a 1% methanol/toluene solution was added along with 102.7 mg of Compound 4.1 and 52.1 mg of neopentyl glycol. The solvent was concentrated under reduced pressure and more 5 mL of toluene was added and the process was repeated an additional two times. Formation of boronate ester was confirmed by dissolving resulting material in chloroform. This trimer is to be used as a model for **Compound 4.1**.

Synthesis Polymer 4.1: Compound 4.1 was dissolved in a 1 % solution of methanol in 1,4-dioxane. A Dean Stark apparatus was attached and the reaction was heated to reflux for 3 hours. Reaction mixture was a yellow clear solution with a brown solid. Mixture was filtered to separate solvent and solid. The solvent was removed via rotary evaporation, producing an empty reaction vessel. We tried to dissolve the solid in chloroform, dichloromethane, DMSO, tetrahydrofuran, and dioxane but the material did not dissolve, making further analysis not possible.

Synthesis Compound 4.2 and 4.3: Glassware was dried overnight. Adipoyl chloride (2.65 mL, 18.1 mmol) was added drop wise to bromobenzene (3 mL). The catalyst, $AlCl_3$ (5.0620 g, 38 mmol) was added to 30 mL of dry benzene, a tan colored solution formed. Mixture of adipoyl chloride and bromobenzene were slowly added to $AlCl_3$ in the reaction vessel. A brown reaction mixture formed. The solution was stirred for 3 hours at 40 °C and turned a dark orange color. Mixture was poured into an Erylenmyer flask that contained crushed iced and concentrated HCl. Solid was removed through filtration and the solution was washed with H_2O. Dichloromethane was used to extract the organics. The solvent was removed through rotatory evaporation and recrystallized from DMF. Based on the reported ^1H NMR resonances,[6] pure **Compound 4.2** was obtained**.** Hydrazine (50 μL) and potassium hydroxide (80 mg) were dissolved in 3 mL of 1-octanol and heated to reflux. After 24 hours of heating, the solution was cooled to room temperature, diluted with 12 mL of diethyl ether, washed with a HCl and brine solution, and filtered. TLC analysis showed only starting material, indicating that **Compound 4.3** did not form.

Synthesis Compound 4.4 and 4.5: Mixed 5.1080 g of bromobenzyl bromide with 1,6-hexane dithiol in a solution of isopropyl alcohol. After allowing solution to stir, added 1.3957 g of potassium hydroxide. Reaction ran for 3 days and formed an orange mixture of solid and solution. Filtered solution and extracted the organic layer. Excess starting material was removed through sublimation and by reacting with N-phenylmaleimide. Filtered and concentrated mixture under reduced pressure and obtain **Compound 4.4** in 40% yield. ^{1}H NMR analysis NMR (400 MHz, $CDCl_3$, δ): aromatics (7.44-7.42ppm, 7.19-7.17 ppm); -CH_2-attached to the ring (3.63 ppm, S); S-CH2- (2.37ppm); S-CH_2-CH_2 (1.6-1.4 ppm);. S-CH_2-CH_2- CH_2 (1.38-1.21 ppm). The next step required the boroylation of Compound 4.4 using trimethyl borate and n-butyl lithium, but the boroylation step did not convert the bromide groups to boronic acids.

Synthesis of Compound 4.6: All reagents, ethanol amine, 1,12-dibromododecane, and triethyl amine were added to a reaction vessel with 15 mL of THF. The mixture was stirred and heated until everything solubilized. The reaction progress was monitored using TLC. After 16 hours, the mixture was removed from heat, washed with ether, concentrated under reduced pressure. ^{1}H NMR analysis shows mostly starting material remained.

Synthesis Compound 4.7: 3-amino-1,2-propanediol (134 µL, 1.51 mmol) and triethyl amine (351 uL, 2.52 mmol) were mixed together in 10 mL of dichloromethane. 3-amino-1,2-propanediol was added to the round bottom flask and the vessel was heated to 40 °C. After 50 minutes, the clear solution turned cloudy and product precipitated from the reaction mixture. Allowed the reaction to continue for 5 hours, before removing from heat and washing twice with dichloromethane. Dried product under reduced pressure for 1 hour. NMR analysis was inconclusive due to the splitting of peaks caused by the chiral carbons present in the structure of the material. **Compound 4.7** was polymerized by reacting with an equimolar amount of 9,9-didodecylfluorene-2,7-diboronic acid in 1,4-dioxane with a Dean Stark trap apparatus. Resulting material was extremely brittle and flaky.

Synthesis Compound 4.8: To an oil bath preheated at 50 °C, a reaction vessel containing 7.6615 g (70.8 mmols) of mercaptothiol and a stir bar was added. KOH (3.991 g) was dissolved in a minimum amount of water and added slowly to the reaction vessel. Added 8.9036 g (33.7 mmols) of dibromoxylene, reaction mixture formed two layers: the top layer was cloudy and colorless and the bottom layer was clear, with a yellowish color. After 4 days, the reaction was removed from heat, filtered and concentration under reduced pressure. Filtered through a silica plug and obtained 73.4% of the compound. ^{1}H NMR analysis NMR (400 MHz, $CDCl_3$, δ): aromatics (7.54-7.32ppm, 7.15-7.04 ppm); -CH_2-attached to the ring (3.54 ppm, S); S-CH2- (2.37ppm); S-CHOH- (2.6 ppm); -CHOH- CH_2 (2.7 ppm).

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