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NOVEL MONOMERS AND SOLUTION POLYMERIZATION METHODS FOR
POLYBENZIMIDAZOLE POLYMERS

by

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ABSTRACT

The goal of this work was to identify and study various monomers and polymerization methods for polybenzimidazole polymers. Beginning with the solution polymerization of polybenzimidazole via a bisulfite adduct monomer, Chapter 2 describes the efforts to optimize and scale up this process. Chapter 3 then covers an alternative method to prepare polybenzimidazole in solution by using an orthoester monomer. Finally, in Chapter 4, the research to incorporate an adamantane moiety into the backbone of polybenzimidazole is described.

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CHAPTER 1: INTRODUCTION

1.1 INTRODUCTION TO POLYBENZIMIDAZOLE

Polybenzimidazole or PBI was first published by Vogel and Marvel in 1961 as a new class of thermally stable polymers.[1] These polymers derive their name from the benzimidazole moiety found in the repeat unit illustrated in **Scheme 1.1**. The most common way of synthesizing PBI is to condense a bis-o-diamine (**1**) and dicarboxylic acid or acid derivative (**2**) in which the R groups of these compounds can be changed. Depending on the specific R groups chosen for the polymer, the physical properties can vary; however, the glass transition temperature is usually about 430 °C and the decomposition temperature is upwards of 600 °C, making this material extremely thermally stable compared to other polymers. This polymer also exhibits excellent chemical stability as it is resistant to strong acids and organic solvents.[2] The combination of these properties allows for PBI to be a good material for numerous applications. The applications of PBI, which will be discussed in this paper, are hydrogen fuel cells, gas separation, and fibers.
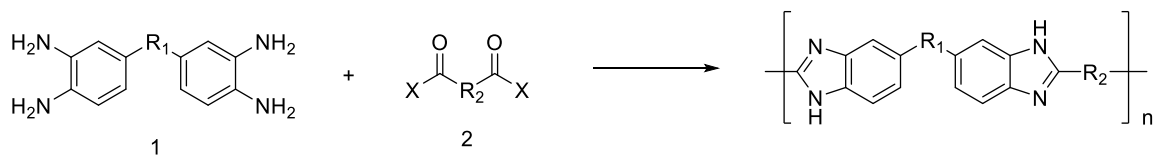
Scheme 1.1: General synthesis of polybenzimidazole.

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1.2 POLYBENZIMIDAZOLE FIBERS

Due to the high thermal stability of PBI, this material is a good choice for use in flame resistant textiles. The PBI fiber offers good dimensional and physical stability at high temperature. The polymer does not melt or burn and is not a fuel source. It forms a tough char, which is important in flame resistant applications. Additionally, the polymer is chemically resistant to acids and organic solvents.[2] For these reasons, PBI fibers have been used in firefighting suits, space suits, and various other products in which high temperature stability is needed.

The current method of production for these fibers is energy and time intensive, however. The polymer is first synthesized in a two-step bulk polymerization. In the first step, the monomers are heated to form a low molecular weight polymer. As this polymer is formed, water and phenol are produced as byproducts and must not only be removed but also cause the polymer to form a hard foam. This foam must then be crushed and heated in the second stage of polymerization which requires temperatures upwards of 400 °C to produce a high molecular weight polymer. Once the polymer is synthesized, it must be dissolved in an organic solvent for fiber spinning. Dissolving the polymer requires the use of high temperature and pressure. Overall this process is unconventional and inefficient. If a way to synthesize the polymer in solution was developed, the high energy and time requirements could be relieved and the fibers could be spun directly from the polymerization solution.

Recently, it has been shown that by using a bisulfite adduct of isophthalaldehyde with a bis-o-diamine, m-PBI can be synthesized in DMAc at high concentration and high inherent viscosity can be achieved.[3] **Figure 1.1** shows the resulting inherent viscosity of

m-PBI when synthesized at various polymer concentrations. In industry the current method of production requires that the PBI have an inherent viscosity of approximately 0.7 dL/g with solution concentrations of 26 wt.% polymer content. Considering the data in **Figure 1.1**, the possibility of producing a PBI solution with these properties is promising. However, additional work is required to scale up this polymerization method and perform fiber spinning trials.
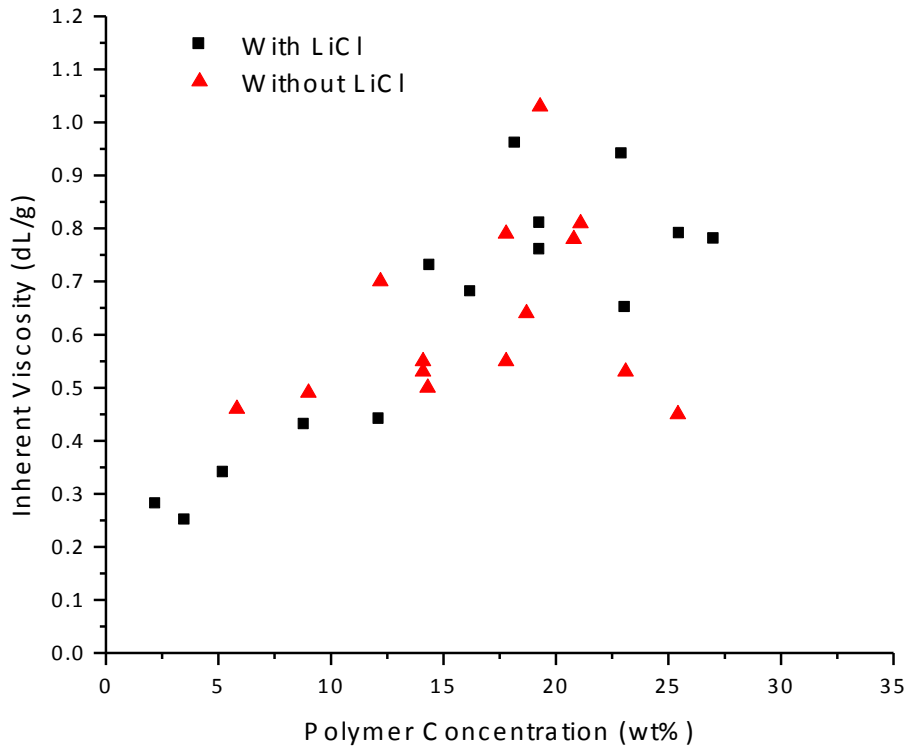
Figure 1.1: Inherent viscosity of PBI synthesized at various concentrations in solution.

1.3 POLYBENZIMIDAZOLE FOR USE AS POLYMER ELECTROLYTE MEMBRANES

As global energy demands increase, the need for alternative energy sources becomes more important. Hydrogen fuel cells have become an emerging technology, which can provide a clean source of energy. Polymer electrolyte membrane (PEM) fuel

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cells are electrochemical devices, which convert chemical energy directly into electrical energy so long as fuel and an oxidant are supplied. **Figure 1.2** illustrates the basic components of the PEM fuel cell. The fuel, typically hydrogen, is supplied to the anode side where the hydrogen can associate with a platinum catalyst and be split into its constituent protons and electrons. The electrons are supplied to the external circuit while the protons are conducted through the PEM. On the cathode side of the fuel cell oxygen or air is supplied and protons from the PEM are able to combine on another platinum catalyst with oxygen to create water and heat. Since the only byproducts of this process are water and heat, the hydrogen fuel cell is a good source of clean energy.
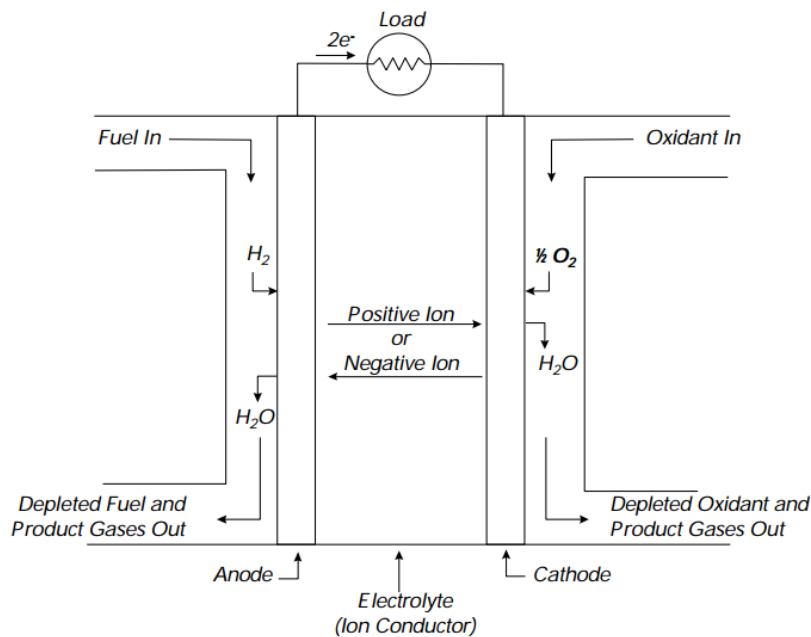
Figure 1.2: Schematic of PEM fuel cell taken from Fuel Cell Handbook.[4]

At the heart of the fuel cell is the PEM which is a polymer membrane doped with an electrolyte. Historically water has been used as the electrolyte in the membrane, which limits the operating temperature of the fuel cell. Operating above 100 °C will vaporize the electrolyte and cause the fuel cell to fail. Polybenzimidazole has become an attractive

polymer for use in the PEM due to its high thermal stability and chemical resistance. PBI has the added benefit that it can be doped with electrolytes such as phosphoric or sulfuric acid. The combination of these properties allow for increased operating temperatures above 120 °C as water is not required for proton conductivity. The higher operating temperature in turn allows for better electrode kinetics, higher impurity tolerance, and eliminates the need to humidify the fuel. Proton conductivity of the PBI membrane is dependent on polymer architecture and is one of the motivations for this research.[5]

1.4   POLYBENZIMIDAZOLE FOR USE IN GAS SEPARATION DEVICES

Another application in which PBI is used is gas separation for the capture or purification of hydrogen gas. In these devices, a polymer membrane is used to perform the separation but the major consideration in selecting a polymer membrane is the trade-off between selectivity and permeability of the membrane. For a particular polymer membrane, the selectivity for hydrogen over other gases may be high but the permeability will be low and the opposite can be true as well. The performance of the membrane is dependent primarily on free volume of the polymer, polymer chain packing in the membrane, and polymer chain mobility.[6] Investigation into new PBI chemistries for use in gas separation devices is important in understanding the relationship between polymer architecture and membrane performance.

1.5   THESIS OUTLINE

In this thesis, Chapter 2 describes the efforts to prepare the bisulfite adduct polymerization method for scale up and fiber spinning trials. First, optimizations were studied to ensure that time and temperature profiles were understood and the results of these findings are presented. Also, the addition of sodium bisulfite to the reaction prior to

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polymerization was studied to ensure that any remaining aldehyde functionalities were converted to the bisulfite adduct in situ and that high molecular weight polymer was synthesized. Then, as a way to modify polymer solution viscosity, an important parameter for fiber spinning, lithium chloride and sodium bisulfite were added to polymer solutions to determine the effect these salts had on the solution viscosity.

Once these optimizations were completed, the monomer synthesis was scaled from ~12 g batches to >500 g batches and the solvent use in the monomer synthesis was reduced. Next, the polymer synthesis was scaled from ~20 g scale to multi-kilogram scales in several steps. Starting with larger laboratory scale reactions, the polymerization was studied to ensure high inherent viscosity polymer could be synthesized at high concentration. Once these laboratory scale-up polymerizations had proved successful, an industrial pilot reactor was then used to do the polymerization on a multi-kilogram scale. This scale polymerization presented challenges and resulted in more laboratory experiments being conducted to determine the cause.

In Chapter 3, the efforts to produce meta-PBI in DMAc are described utilizing a different chemistry, a bisorthoester. This chapter begins by describing the monomer synthesis, which when compared to the bisulfite adduct synthesis has many more steps and is not as efficient. However, the polymerization is very similar to the bisulfite adduct synthesis and meta-PBI was synthesized at several concentrations, all of which were much higher than previously reported. The polymer inherent viscosity was then measured and plotted as a function of concentration. The initial findings from this set of studies proved to be promising for this chemistry to produce meta-PBI in DMAc.

Chapter 4 then describes the synthesis of an adamantane-PBI. This work was done to study the gas separation properties of this polymer as well as for use as a proton exchange membrane. In this chapter, it was found that the adamantanedicarboxylic acid monomer was sensitive to the polymerization solvent and another solvent was identified. The adamantane-PBI also presented solubility issues, and modifications to the adamantane monomer were performed in an effort to increase the solubility of the polymer in organic solvents as well as stabilize the monomer in polymerization solvents.

1.6 REFERENCES

1. Vogel, H.; Marvel, C. S., Polybenzimidazoles, new thermally stable polymers. *Journal of Polymer Science* **1961,** *50*, 511-539.

2. Powers, E. J.; Serad, G. A., History and Development of Polybenzimidazole. *High Performance Polymers: Their Origin and Development* **1986**.

3. Gulledge, A. L. Advancements in the Design, Synthesis and Applications of Polybenzimidazoles. Ph.D. Thesis, University of South Carolina, 2014.

4. Hirschenhofer, J. H.; Stauffer, D. B.; Engleman, R. R.; Klett, M. G., *Fuel Cell Handbook*. Fourth ed.; Parsons Corporation: Reading, PA, 1998.

5. Xiao, L.; Zhang, H.; Jana, T.; Scanlon, E.; Chen, R.; Choe, E. W.; Ramanathan, L. S.; Yu, S.; Benicewicz, B. C., Synthesis and Characterization of Pyridine-Based Polybenzimidazoles for High Temperature Polymer Electrolyte Membrane Fuel Cell Applications. *Fuel Cells* **2005,** *5*.

6. Kanchan, G.; Benny, D. F., Gas separation using polymer membranes: an overview. *Polymers for Advanced Technologies* **1994,** *5*.

CHAPTER 2: OPTIMIZATION AND SCALE-UP OF SOLUTION POLYMERIZATION OF POLYBENZIMIDAZOLE

2.1 INTRODUCTION

After the conclusion of the initial studies to demonstrate that a bisulfite adduct monomer could be used to produce meta-PBI in solution at high polymer concentration, additional work was required to optimize and scale up the process for fiber spinning trials.[1] First, to optimize the process, time and temperature studies were performed to determine the optimal conditions for this polymerization. Additionally, to be able to spin fibers, the polymer solution should have a viscosity of approximately 2100 Poise and thus solution viscosity modifiers were investigated. Additional measures were also studied to ensure target inherent viscosity was achieved in the polymerization.

Once these parameters were determined, both the monomer and polymer synthesis was scaled up to determine if this method of polymerization could be used to create a polymer solution which could be spun into fibers. Monomer scale-up involved optimization of solvent use and monomer slurry processing. The polymer scale-up was performed in steps going from the 20 g scale up to a 6 Kg in an industrial pilot reactor.

2.2 MATERIALS

3,3',4,4'-Tetraaminobiphenyl (TAB) was donated by BASF. Isophthalaldehyde was purchased from TCI America and Combi-Blocks. Sodium Bisulfite was purchased

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from VWR. Dimethylacetamide was purchased from Acros Organics and Oakwood Chemicals. Methanol was purchased from MACRON Fine Chemicals.

2.3 CHARACTERIZATION

2.3.1 INHERENT VISCOSITY

Approximately 0.050 g of recently dried polymer was added to a 25 mL volumetric flask. The flask was partially filled with concentrated sulfuric acid and shaken on a mechanical wrist-action shaker overnight to dissolve the polymer. Once all polymer was dissolved, the flask was completely filled with concentrated sulfuric acid to achieve a final polymer concentration of 0.2 g/dL. The polymer solution was filtered through a 0.4 µm filter to remove any undissolved particles and the filtered solution was added to a 200 µm Ubbelohde viscometer. The viscometer was placed into a 30 °C water bath for 30 minutes. Three flow times between the calibrated marks on the viscometer were measured. The average of these times was used in **Equation 3.1** as the solution time *t*.

Equation 2.1

$$\eta_{inh} = \frac{\ln\left(t/t_0\right)}{C}$$

η_{inh} (dL/g): inherent viscosity

t (sec): solution flow time

t_0 (sec): solvent flow time

C (g/dL): solution concentration

2.3.2 THERMOGRAVIMETRIC ANALYSIS (TGA)

TGA was performed using a TA Instruments Q-5000 with heating rate of 10 °C/min under nitrogen. Weight loss of polymer as a function of temperature was compared to commercial samples of m-PBI to confirm presence of desired product.

2.3.3 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FTIR spectra were recorded on a Perkin Elmer Spectrum 100 using an attenuated total reflection (ATR) diamond cell attachment. Monomer spectra were used to detect impurities and polymer spectra were compared to commercial polymer spectra.

2.3.4 NUCLEAR MAGNETIC RESONANCE (NMR)

NMR spectra were recorded using a 300 MHz Varian Mercury 300 Spectrometer using dimethyl sulfoxide-d_6. ^{1}H-NMR spectra of monomer samples were used to confirm the presence of the desired product and detect impurities.

2.3.5 SOLUTION VISCOSITY

Samples of polymer solution were sent to an industrial lab for viscosity measurements. The industrial lab used a Brookfield Rheometer, Model R/S-CPS with a 25 mm diameter cone spindle with 2° angle. Viscosity measurements were made at the end of 60 seconds in a constant sheer stress mode set to 1000 Pa.

2.4 TIME AND TEMPERATURE POLYMERIZATION STUDIES

The initial studies using the bisulfite adduct monomer to make meta-PBI were all performed in DMAc at reflux conditions for 24 hours.[1] These trials showed that under these conditions, meta-PBI could be synthesized at high polymer concentration and give a high inherent viscosity. Further studies were conducted to determine whether the

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polymer could be synthesized under milder conditions and if 24 hours of reaction time was needed. To answer these questions, polymerizations were conducted at various temperatures (140, 150, 160 °C) and reaction times (6, 12, 18, 24 hours).

2.4.1 EXPERIMENTAL

2.4.1.1 SYNTHESIS OF ISOPHTHALALDEHYDE BISULFITE ADDUCT (IBA)

Isophthalaldehyde (5.00 g, 0.0372 moles) and sodium bisulfite (7.76 g, 0.0745 moles) were added to a 1 L round bottom flask. Methanol (500 mL) and water (75 mL) were poured over the starting materials. The solution was slurried for 24 hours before filtering the IBA and washing with methanol. IBA was dried under vacuum at 60 °C overnight before use. Collected 12.47 g of IBA (98 % yield). ^{1}H-NMR (DMSO-d$_6$), ppm: 4.95 (2H, s, OH); 5.85 (2H, s, CH), 7.09-7.51 (3, m, Ar-H).

2.4.1.2 SYNTHESIS OF M-PBI

Isophthalaldehyde bisulfite adduct (4.00 g, 0.01168 moles), 3,3',4,4'-tetraaminobiphenyl (2.504 g, 0.01168 moles), and dimethylacetamide (17.5 mL) were added to a 100 mL round bottom flask fitted with nitrogen flow, mechanical stirrer, and reflux condenser. The flask was placed in a preheated oil bath and stirred at 30 RPM. Polymerization time and temperature was varied between 6, 12, 18, and 24 hours and temperatures of 140, 150, and 160 °C.

2.4.2 RESULTS

Three polymerizations for each of the times (6, 12, 18, and 24 hours) at each of the temperatures (140, 150, and 160 °C) were conducted. After each polymerization, the inherent viscosity of the polymer was measured. The results for all polymer samples are

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plotted in **Figure 2.1**. In general, there was no trend for any of the times or temperatures
except that all but two of the polymer samples were under the required 0.7 dL/g inherent
viscosity. This indicates that the polymerization does require reflux conditions and 24
hours of reaction time to achieve high inherent viscosity. The two outlying data points,
which did achieve the target inherent viscosity, are likely the result of experimental error
but could be an indication that the polymerization can be performed at these lower
temperatures and shorter times. As with all new reactions, unknown variables could have
sizeable affects on the polymerization (e.g., variations in monomer purity with different
lots of monomer).
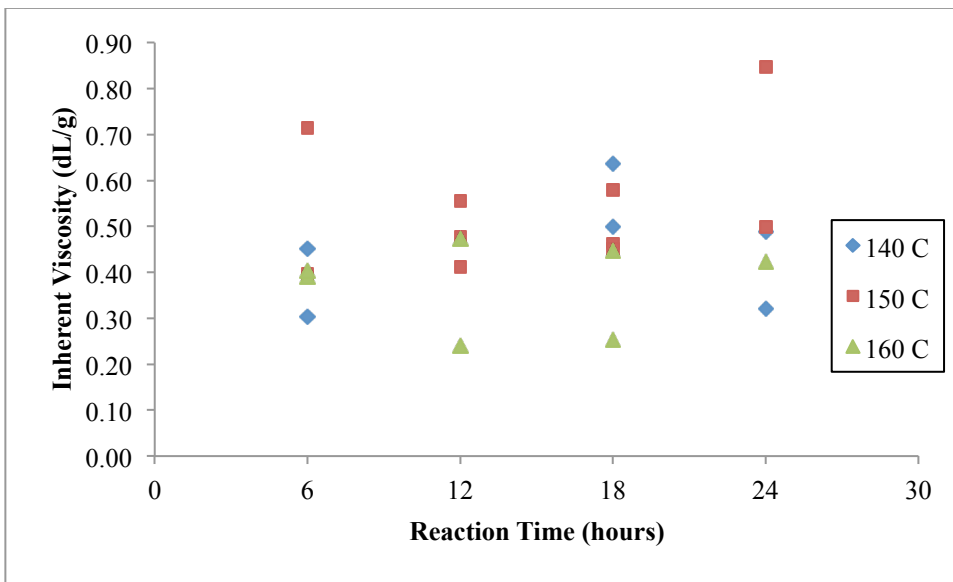
Figure 2.1: Inherent viscosity of polymer samples plotted with respect to reaction time.
Polymerizations are color coded 140 °C (blue diamonds), 150 °C (red squares), and 160
°C (green triangles).

Thermogravimetric analysis of some of the polymers produced under these
conditions was performed. Results from this analysis are shown in **Figure 2.2**. Plotted in
this figure are a commercial m-PBI sample and three polymer samples polymerized at
140, 150, and 160 °C for 24 hours. Although there are differences in moisture content

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between the commercial sample and the solution polymerized samples, all of the polymers are thermally stable up to 600 °C at which point they begin to degrade. The major differences among the samples are the char yield. For the commercial m-PBI and 160 °C sample, approximately 70 % of the initial weight remains at 1000 °C. In the case of the 150 °C and 140 °C samples, however, significantly less material is present at the end of the experiment. The 140 °C sample is almost completely degraded at 1000 °C. These results are indicative of incomplete ring closure to form the benzimidazole in the backbone of the polymer due to the lower reaction temperatures.
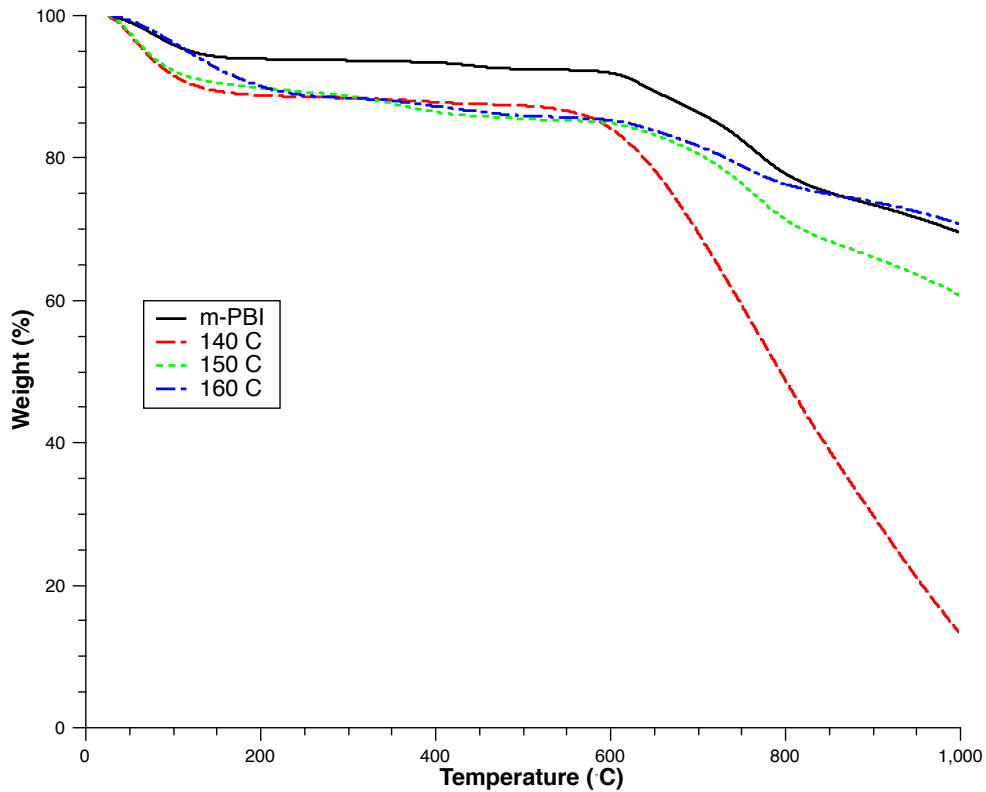
Figure 2.2: TGA of commercial m-PBI (solid black) and polymer samples synthesized at 140 °C (red dashes), 150 °C (green dots), and 160 °C (blue dash-dots).

2.4.3 CONCLUSIONS

By utilizing the bisulfite adduct of isophthalaldehyde, m-PBI was synthesized in solution below reflux temperature and over shorter reaction times. The inherent viscosities for the resulting polymers synthesized under these conditions were generally much lower than the targeted 0.7 dL/g necessary to produce m-PBI fibers. Also, the thermal stability of the polymer synthesized at these lower temperatures is severely reduced. These results suggest that reaction time must be at least 24 hours or more at reflux temperature of DMAc to achieve high molecular weight m-PBI. Lower polymerization temperatures are likely to result in incomplete ring closure of the benzimidazole ring system.

2.5 ADDITIONAL SODIUM BISULFITE POLYMERIZATIONS

Although the synthesis to make the bisulfite adduct monomer is an efficient reaction which gives high yield and purity, there is still a small amount of the aldehyde present as seen by NMR.[1] To ensure that all aldehyde functionalities were converted to the bisulfite adduct, it was proposed to add additional sodium bisulfite to the polymerization solution to form the bisulfite adduct in situ. In practice, three different amounts of additional sodium bisulfite were used; 4 % by weight of the bisulfite adduct monomer, and 2 and 4 mole percent additional sodium bisulfite. The inherent viscosity of the polymer was then measured to determine the effect of the additional salt.

2.5.1 EXPERIMENTAL

2.5.1.1 POLYMERIZATION OF m-PBI IN DMAc WITH 2 WEIGHT PERCENT ADDITIONAL SODIUM BISULFITE

Isophthalaldehyde bisulfite adduct (4.00 g, 0.01168 moles), 3,3',4,4'-tetraaminobiphenyl (2.504 g, 0.01168 moles), sodium bisulfite (0.080 g, 0.00076 moles) and dimethylacetamide (17.5 mL) were added to a 100 mL round bottom flask fitted with nitrogen flow, mechanical stirrer, and reflux condenser. The solution was stirred and heated to reflux for 24 hours. After allowing the solution to cool, a portion of the polymer solution was poured into 500 mL water and the precipitated polymer was washed in a blender twice with water and twice with methanol. The polymer was then dried overnight under vacuum at 200 °C.

2.5.1.2 POLYMERIZATION OF m-PBI IN DMAc WITH 2 OR 4 MOLAR PERCENT ADDITIONAL SODIUM BISULFITE

Isophthalaldehyde bisulfite adduct (4.00 g, 0.01168 moles), 3,3',4,4'-tetraaminobiphenyl (2.504 g, 0.01168 moles), sodium bisulfite (0.024 g, 0.00023 moles, 2% or 0.048 g, 0.00046 moles, 4%), and dimethylacetamide (17.5 mL) were added to a 100 mL round bottom flask fitted with nitrogen flow, mechanical stirrer, and reflux condenser. The solution was stirred and heated to reflux for 24 hours. After allowing the solution to cool, a portion of the polymer solution was poured into 500 mL water and the precipitated polymer was washed in a blender twice with water and twice with methanol. The polymer was then dried overnight under vacuum at 200 °C.

2.5.2 RESULTS

Beginning with the large excess of sodium bisulfite polymerization, which was the 2 weight percent additional salt, the solution initially behaved normally. Once the solution reached a temperature of 120 °C, however, there was a gas produced and the solution began foaming. This off gassing subsided fairly quickly but did cause some of the undissolved monomer to be pushed onto the side of the reaction vessel. Once the solution reached the final reflux temperature of 168 °C, the all of the monomer dissolved and the polymerization behaved as expected resulting in a viscous polymer solution. The inherent viscosity of the polymer was 0.72 dL/g.

In the case of the 2 and 4 molar percent additional sodium bisulfite, a similar off gassing was observed when the solution reached a temperature of 120 °C but these episodes were much more brief. Again, once the solution reached reflux temperature, the polymerization behaved normally and produced a viscous polymer solution at the end of the reaction time. Inherent viscosity measurements of the polymers with the 2 and 4 molar percent additional sodium bisulfite were 0.64 dL/g and 0.75 dL/g respectively. Given these data, it was evident that the 4 molar percent additional salt would ensure that any unreacted aldehyde would be converted to the bisulfite adduct in situ but also minimize the amount of foaming in the solution.

2.5.3 CONCLUSIONS

Polymerizations using the bisulfite adduct monomer were conducted with 2 weight percent, 2 molar percent, and 4 molar percent additional sodium bisulfite. In all cases, some off gassing was observed but once the solution reached the final polymerization temperature the off gassing had subsided. The polymerization with 4

molar percent additional salts achieved the highest inherent viscosity of all the polymerizations and minimized the amount of foaming in the solution.

2.6 VISCOSITY MODIFIERS

Currently, the method of spinning PBI fibers requires that PBI of ~0.7 dL/g inherent viscosity be dissolved in DMAc with 2 wt.% lithium Chloride at 26 wt.% polymer content. This makes a PBI solution with a viscosity of 2100 Poise, ideal for the current equipment to spin fibers. In order to match these solution specifications, a method for adjusting the solution viscosity would need to be identified. Lithium chloride is known in industry to not only be a solution stabilizer but also increases the polymer solution viscosity. Lithium chloride is corrosive and is therefore less desirable from an industrial viewpoint so alternatives to this salt would be preferred. Adjusting the viscosity with other salts such as sodium bisulfite would therefore be studied in this work.

2.6.1 EXPERIMENTAL

PBI/DMAc solution (25.0 g) with known inherent viscosity and polymer content was measured into a 100 mL resin kettle. Lithium chloride (0.5 g, 0.0118 moles) or sodium bisulfite (0.5 g, 0.0048 moles) was added to the polymer solution and stirred overnight at 80 °C. The solution is then cooled and collected for viscosity measurements.

2.6.2 RESULTS

After tabulating the viscosity results from samples with a variety of inherent viscosities and polymer content (**Table 2.1**), it was apparent that the solution viscosity is very sensitive to these factors. Sample AG2-201 was the only sample to exceed the desired viscosity of 2100 poise; however, according to industry sources, this solution

viscosity would be too high to spin fibers from using the current equipment. The majority of the polymer solutions were far too low viscosity for fiber spinning and those marked with asterisk had viscosities too low to measure on the instrument. One interesting result is the effect polymer content had on the solution viscosity with additional salts added. Most of the lower solids content solutions did not increase in viscosity or increased marginally with the addition of lithium chloride or sodium bisulfite. The higher solids content solutions had a much more pronounced response to the additional salts as seen in sample AG2-201.

Table 2.1: Viscosity of polymer solutions before and after adding viscosity modifiers.

	Sample	I.V. (dL/g)	% Solids	Viscosity (poise)		
				No Salt	+ 2% LiCl	+2% NaHSO$_3$
§	AG2-201	0.32	23	450	3004	3101
	AG2-209	0.36	17.8	*	*	*
Standard Formulation	JH1-96	0.33	17.8	*	87	*
	WPS1-142	0.42	17.8	*	*	*
	AG2-210	0.62	17.8	*	27	6
2 wt.% Excess NaHSO$_3$	JH1-97	0.62	17.8	*	*	191
	WPS1-143	0.77	17.8	693	253	29
8 L Run		0.39	22	3.4	*	*
2% Molar XS	JH1-116	0.64	22	*	*	6.5
4% Molar XS	JH1-117	0.75	22	370	274	1233

Another area of interest from these data is the relationship between inherent viscosity and solution viscosity. In the case of AG2-201, the I.V. is only 0.32 dL/g but the solution viscosity can be adjusted to well over the target 2100 poise. By contrast, the solutions that had higher I.V. but lower solids content did not increase in viscosity at all or very little with additional salts. These data suggest the solution viscosity has a

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complex relationship with inherent viscosity and polymer content and more data would be needed to fully understand the relationships between the key variables of I.V., polymer concentration, and added salts.

2.6.3   CONCLUSIONS

Based on the results from the viscosity measurements, it was apparent that the polymer solution viscosity is sensitive to a number of factors. The polymer content of the solution plays a significant role as all of the 17 % polymer solutions were very low viscosity. Some of the higher polymer content solutions were able to come close to the target 2100 poise but there was not enough data to draw a trend for the amount of viscosity modifier would be needed for a particular polymer solution. In the production runs, the viscosity will need to be adjusted by trying several amounts of viscosity modifier. Additionally, both salts (lithium chloride and sodium bisulfite) were able to modify the viscosity so there is still the possibility to eliminate the corrosive lithium chloride from the fiber spinning process.

2.7   MONOMER SCALE-UP AND OPTIMIZATION

Monomer production is an important aspect to this process since the isophthalaldehyde bisulfite adduct monomer is not commercially available. The published synthesis,[2] requires 500 mL of methanol to produce 12.7 g of isophthalaldehyde bisulfite adduct. This means for every kilogram of the bisulfite adduct, nearly 40 L of methanol would be required and multiple kilograms of monomer are needed to make enough of the polymer solution to attempt a fiber spinning trial. While the methanol could be recycled this would be tedious and so a more solvent efficient synthesis was studied.

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2.7.1 EXPERIMENTAL

2.7.1.1 SYNTHESIS OF ISOPHTHALALDEHYDE BISULFITE ADDUCT AT 6X CONCENTRATION OF PREVIOUSLY PUBLISHED WORK

Isophthalaldehyde (29.937 g, 0.2232 moles) was dissolved in methanol (500 mL) and sodium bisulfite (46.514 g, 0.447 moles) was dissolved in water (75 mL). Once dissolved the aqueous sodium bisulfite solution was added dropwise to the methanol solution and stirred overnight. A white precipitate formed which was then filtered off, washed with methanol, and the product was dried overnight under vacuum at 60 °C. Collected 74.08 g of IBA (97 % yield). ^{1}H-NMR (DMSO-d$_6$), ppm: 4.95 (2H, s, OH); 5.85 (2H, s, CH), 7.09-7.51 (3, m, Ar-H).

2.7.1.2 SYNTHESIS OF ISOPHTHALALDEHYDE BISULFITE ADDUCT ON MULTI-KILOGRAM SCALE

Isophthalaldehyde (208.57 g, 1.555 moles) was dissolved in methanol (3478 mL) and sodium bisulfite (332.26 g, 3.193 moles) was dissolved in water (521 mL). The aqueous sodium bisulfite solution was added to the methanol solution dropwise while being stirred. The solution was stirred overnight and a white precipitate formed. The product was filtered off, washed with methanol, and dried under vacuum at 60 °C. Collected 521.5 g of IBA (98 % yield). ^{1}H-NMR (DMSO-d$_6$), ppm: 4.94 (2H, s, OH); 5.86 (2H, s, CH), 7.10-7.51 (3, m, Ar-H).

2.7.2 RESULTS

After attempting several increased concentrations, it was found that the 6 times concentration over the original formulation was ideal from a processing perspective. At 7

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times the original concentration, as the bisulfite adduct began to precipitate, the slurry became too thick and adequate stirring was not achieved. This sub-optimal stirring led to a slight increase in mono-adduct formation and the work-up of the material became more difficult because the monomer could no longer be poured out of the flask. At the 6 times concentration, the solution could be slurried effectively and the product was easily poured for filtration and washing. Additionally, when this synthesis was scaled to a multi-kilogram level, the monomer slurry could still be stirred effectively and there was not an increase in mono-adduct formation. The NMR of the product (**Figure 2.3**) synthesized on the multi-kilogram scale had a very small peak at 10 ppm from the aldehyde proton but integration calculated that the product was >98% pure.
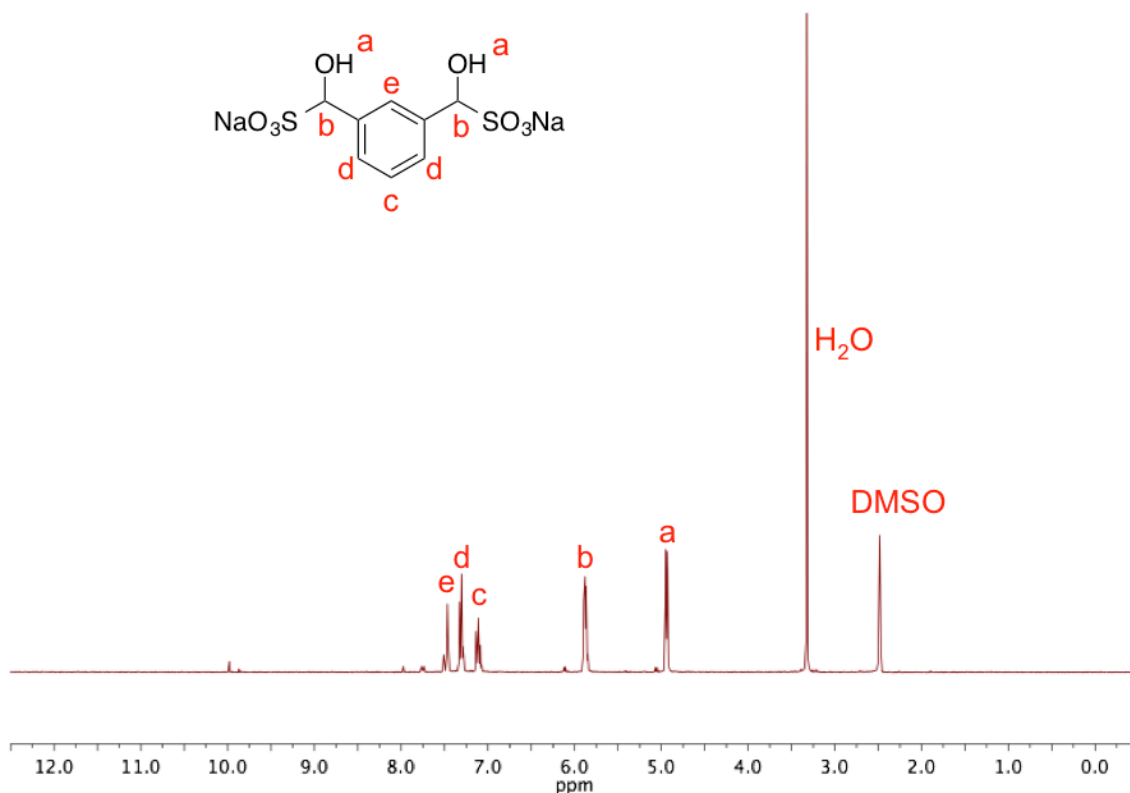
Figure 2.3: ^{1}H-NMR of isophthalaldehyde bisulfite adduct made at 6 times original concentration on multi-kilogram scale.

2.7.3   CONCLUSIONS

In this work, several batches of isophthalaldehyde bisulfite adduct were synthesized at higher concentrations than originally reported and on multi-kilogram scales. These monomer preparations at higher concentrations showed that this synthesis could be more solvent efficient than before without sacrificing monomer quality. Also, this process proved to be easily scaled which is important to make this a viable industrial process.

2.8   LAB SCALE-UP POLYMERIZATIONS

Before attempting a polymerization in the industrial pilot reactor, several polymerizations were performed at intermediate scales to identify potential challenges. Based on the viscosity data, these polymerizations would first be attempted at 26 % polymer content which is the same concentration as the polymer solution used currently to spin fibers.

2.8.1   EXPERIMENTAL

2.8.1.1   26 % POLYMER SOLUTION POLYMERIZATION ON 600 GRAM SCALE

Isophthalaldehyde bisulfite adduct (172.04 g, 0.5026 moles), 3,3',4,4'-tetraaminobiphenyl (107.71 g, 0.5026 moles), sodium bisulfite (2.092 g, 0.0201 moles) and dimethylacetamide (475 mL) were added to a 2 L resin kettle. The kettle was equipped with an overhead mechanical stirrer, nitrogen flow and reflux condenser. The kettle was placed in an oil bath and the solution was heated to reflux over 1 hour. The solution was stirred and refluxed for 24 hours at which point the solution was allowed to cool and was collected. A portion of the polymer solution was poured into excess water,

powdered in a laboratory blender, and washed with water and methanol twice. The polymer powder was then dried at 200 °C under vacuum overnight for inherent viscosity measurements.

2.8.1.2 17.8 % POLYMER SOLUTION POLYMERIZATION ON 200 GRAM SCALE

Isophthalaldehyde bisulfite adduct (24.58 g, 0.1147 moles), 3,3',4,4'-tetraaminobiphenyl (39.26 g, 0.1147 moles), sodium bisulfite (0.477 g, 0.0045 moles) and dimethylacetamide (175 mL) were added to a 500 mL three-neck round-bottom flask. The flask was equipped with an overhead mechanical stirrer, nitrogen flow and reflux condenser. The flask was placed in an oil bath and the solution was heated to reflux over 1 hour. The solution was stirred and refluxed for 24 hours at which point the solution was allowed to cool and was collected. A portion of the polymer solution was poured into excess water, powdered in a laboratory blender, and washed with water and methanol twice. The polymer powder was then dried at 200 °C under vacuum overnight for inherent viscosity measurements.

2.8.2 RESULTS

The 600 g scale polymerization started off with similar observations to those seen in the additional sodium bisulfite polymerizations. As the solution reached a temperature of 120 °C, the solution began to foam but due to the differences in scale and reactor design the foaming did not subside as quickly. To control the foaming, the kettle was lifted out of the oil bath and allowed to cool down which stopped the foaming. Once the foaming subsided the kettle was lowered back into the oil bath and resumed heating. Again, as the solution heated foaming started again and the kettle had to be removed from the oil bath. This process was repeated several times until all foaming subsided and the

solution was heated to reflux. Once reflux was achieved the reaction was stable and after 24 hours the solution was dark brown and viscous.

The inherent viscosity of the polymer from this reaction was only 0.32 dL/g. Since the polymerization was conducted at a high polymer concentration, it was thought that this polymerization was at the upper limit of polymer concentrations that would produce high I.V. PBI by this process. Thus, the next set of polymerizations was conducted at the 17.8% concentration, which had shown to produce the highest inherent viscosities on small-scale tests.

Because the 600 gram polymerizations used a large amount of monomer for each run, the next set of polymerizations was done on 200 gram scales at 17.8 % polymer content; 10 times the original scale. During these polymerizations, the solution foamed in same way as the previous polymerizations and the solution had to be cooled and heated slowly to control the foaming. After the foaming stopped, the polymerization was stable at reflux conditions and after 24 hours of reaction time the solution was dark brown and viscous. The resulting inherent viscosity of the polymer from this solution was 0.62 dL/g.

2.8.3 CONCLUSIONS

Two sets of scaled-up polymerizations were conducted at 26 % and 17.8 % polymer content. The higher polymer concentration polymerization produced low I.V. polymer and it was concluded that the concentration would need to be decreased. At 17.8 % polymer content, the polymerization was able to produce polymer with a 0.62 dL/g inherent viscosity. This result was much closer to the target 0.7 dL/g inherent viscosity necessary for fiber spinning and would therefore be the starting point for the polymerization in the pilot reactor at the industrial site.

2.9   INDUSTRIAL SITE SCALE-UP POLYMERIZATIONS

After several intermediate scale polymerizations had been conducted and inherent viscosities of the resulting polymer were close to the target 0.7 dL/g, the next step of the project was to attempt a polymerization in the pilot reactor at an industrial site. The pilot reactor is an 8 L steel reactor with a band heater, condenser attachment, nitrogen purge, and thermocouples inside the reactor and on the outside wall between the band heater. The reactor is controlled by a PID controller able to control the temperature set point and stir rate. The controller also displays solution temperature, heater temperature, heater output, and amperes to maintain stir speed. The nitrogen out line would also be bubbled through a water scrubber to remove any sulfur dioxide gas produced during the polymerization and catch any condensate not returned by the condenser.

2.9.1   EXPERIMENTAL

2.9.1.1   PILOT REACTOR POLYMERIZATION 1

3,3'4,4'-Tetraaminobiphenyl (607.56 g, 2.835 moles, TAB) was dissolved in dimethylacetamide (3330 mL) the day prior to the polymerization and stored in glass bottles. Isophthalaldehyde bisulfite adduct (970.45 g, 2.835 moles) and sodium bisulfite (11.8 g, 0.1134 moles) were added to the pilot reactor and then TAB/DMAc solution was poured in the reactor. The reactor was set to heat to 162 °C and stir at 60 RPM for 24 hours. After this time, the polymer solution was cooled and discharged into 1 L containers for analysis.

2.9.1.2 PILOT REACTOR POLYMERIZATION 2

3,3,4,4'-Tetraaminobiphenyl (897.54 g, 4.189 moles, TAB) was dissolved in dimethylacetamide (3948 mL) the day prior to the polymerization and stored in glass bottles. Isophthalaldehyde bisulfite adduct (1433.62 g, 4.189 moles) and sodium bisulfite (17.44 g, 0.1675 moles) was added to the pilot reactor and the TAB/DMAc solution was poured in the reactor. The reactor was set to heat to 162 °C and stir at 90 RPM for 24 hours. After this time, the polymer solution was cooled and discharged into 1 L containers for analysis.

2.9.1.3 PILOT REACTOR POLYMERIZATION 3

3,3,4,4'-Tetraaminobiphenyl (718.03 g, 3.352 moles, TAB) was dissolved in dimethylacetamide (3159 mL) the day prior to the polymerization and stored in glass bottles. Isophthalaldehyde bisulfite adduct (1146.90 g, 3.352 moles) and sodium bisulfite (13.95 g, 0.1340 moles) was added to the pilot reactor and the TAB/DMAc solution was poured in the reactor. The reactor was set to heat to 162 °C and stir at 90 RPM for 24 hours. After this time, the polymer solution was cooled and discharged into 1 L containers for analysis.

2.9.2 RESULTS

For the first polymerization in the pilot reactor, it was decided to use a 22 % polymer content solution to compromise for final solution viscosity and inherent viscosity of the polymer. In this polymerization, the solution of monomers was heated from ambient to 170 °C in about 1 hour. During this time, it was noticed that once the solution reached a temperature of 130 °C, the nitrogen bubble rate through the water scrubber became irregular and turned the water cloudy. As the solution continued to

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increase in temperature, what appeared to be DMAc began coming out through the nitrogen out line into the water scrubber so the nitrogen flow rate was reduced. Once the solution reached a temperature of 175 °C, the fluid level in the water scrubber had increased from 1 L at the start of the reaction to 2 L. This would mean that if all of the liquid that came off the reaction was DMAc, then the polymer concentration would be in the region of 28 % polymer content, which is sub-optimal for achieving high I.V. polymer. To correct this, the solution was cooled back down to below 100 °C so that additional DMAc could be added to the reactor and a larger condenser could be installed.

Once 1 L of DMAc had been added back into the reactor, the solution was again heated but instead of heating directly to the final temperature the set point was increased in steps. **Figure 2.4** illustrates the temperature profile used for the entire reaction. In this figure, an overshoot was apparent when from when the temperature set point was changed. The cause for this overshoot can be seen in **Figure 2.4**. When the solution temperature is lower than the set point, the PID controller sets the heaters to 100 % output to quickly increase the temperature. The overshoot then occurs when the PID controller does not decrease the power output of the heater until the set point was reached and even continues to supply power once the set point is exceeded. Due to this overshoot, an oscillation in solution temperature occurred and to prevent DMAc from escaping the condenser the set point was set to 162 °C. This oscillation had a peak temperature of 165 °C and trough of 158 °C for the durations of the polymerization.
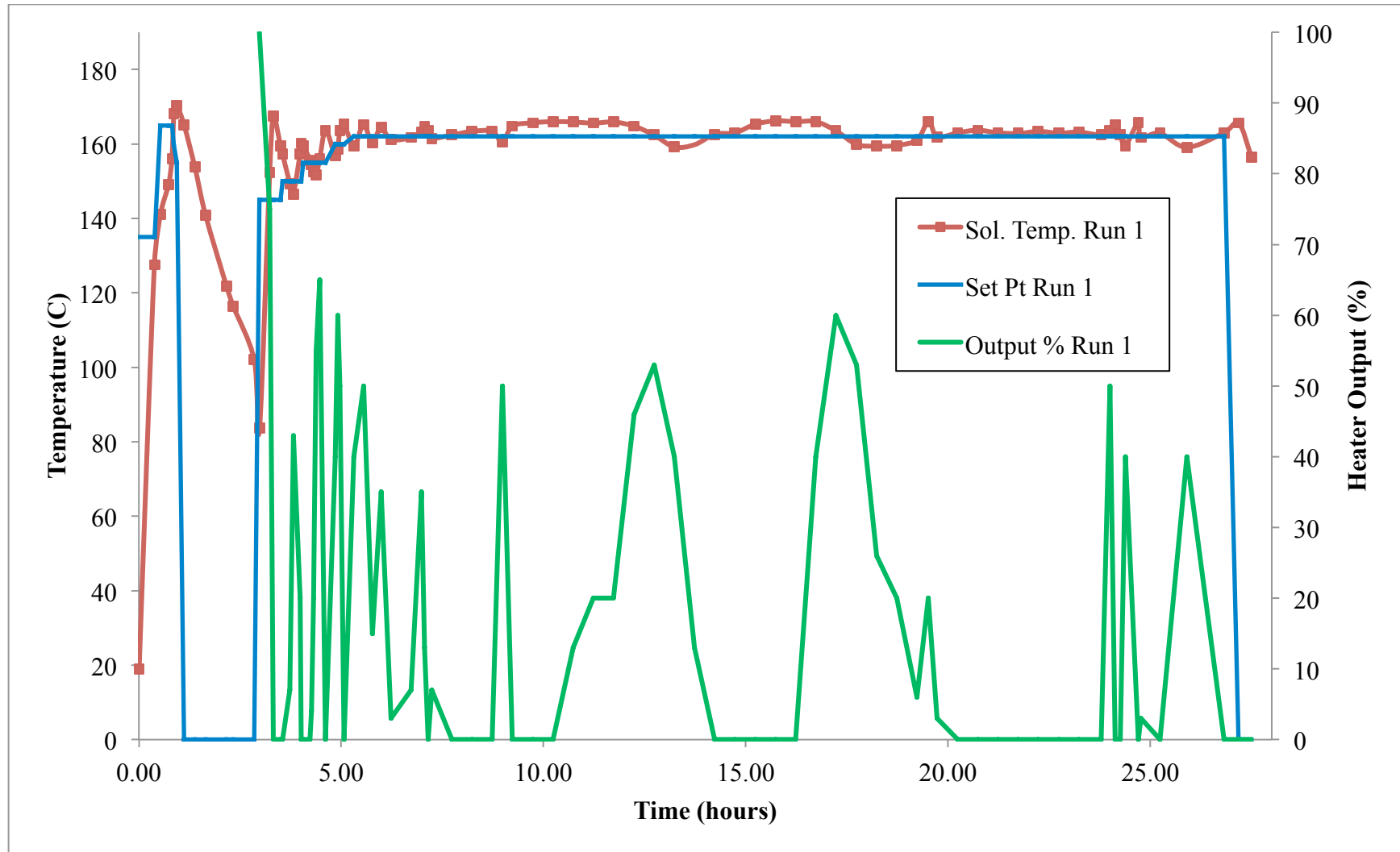
Figure 2.4: Plot of solution temperature, temperature set point, and heater output for pilot reactor polymerization 1.

After the solution temperature stabilized and the oscillation was minimized, the polymerization continued for another 24 hours. Once the solution cooled, the reactor was discharged and a dark brown liquid was collected. The final solution viscosity was only 3.4 poise and the inherent viscosity was 0.39 dL/g. FTIR characterization was performed and confirmed that the reaction did produce meta-PBI (**Figure 2.5**). Compared to the commercially produced PBI, the first pilot reactor polymer appears to be the same material.
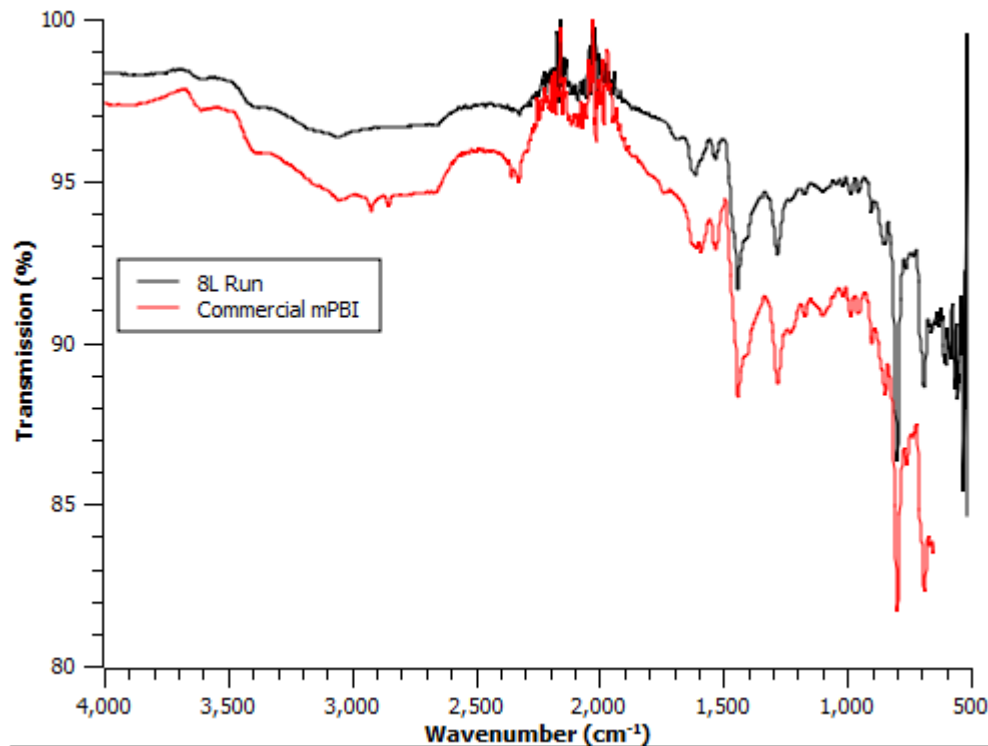
Figure 2.5: FTIR spectrum of commercial PBI (bottom curve) and PBI from first pilot reactor polymerization (top curve).

In the second pilot reactor polymerization, some conditions and reaction methods were altered. The first condition to be altered was the temperature profile which was initially be set to 140 °C then gradually increased to the final polymerization temperature to minimize temperature overshoot and DMAc loss. Also, the polymer content was

increased to 26 % because several small scale trials had shown the ability to achieve high I.V. at this concentration. Finally, the total reaction volume was increased because the stirrer in the pilot reactor did not fully submerge in the first reaction and optimal stirring did not occur.

The second pilot reactor polymerization initially showed promising improvement over the previous. As the solution heater reached 130 °C, the gas flow out increased rapidly but subsided almost immediately. Again, the water scrubber became cloudy at this point. When the solution temperature reached 150 °C, the volume of liquid in the water scrubber began to increase again. To avoid opening the reactor and exposing the reaction to air, the reaction was allowed to continue without replacing lost DMAc. The temperature continued to increase to the final set point temperature of 162 °C. A plot of the temperature profile is shown in **Figure 2.6**. As in the first polymerization, an oscillation around the set point lasted for the duration of the reaction.
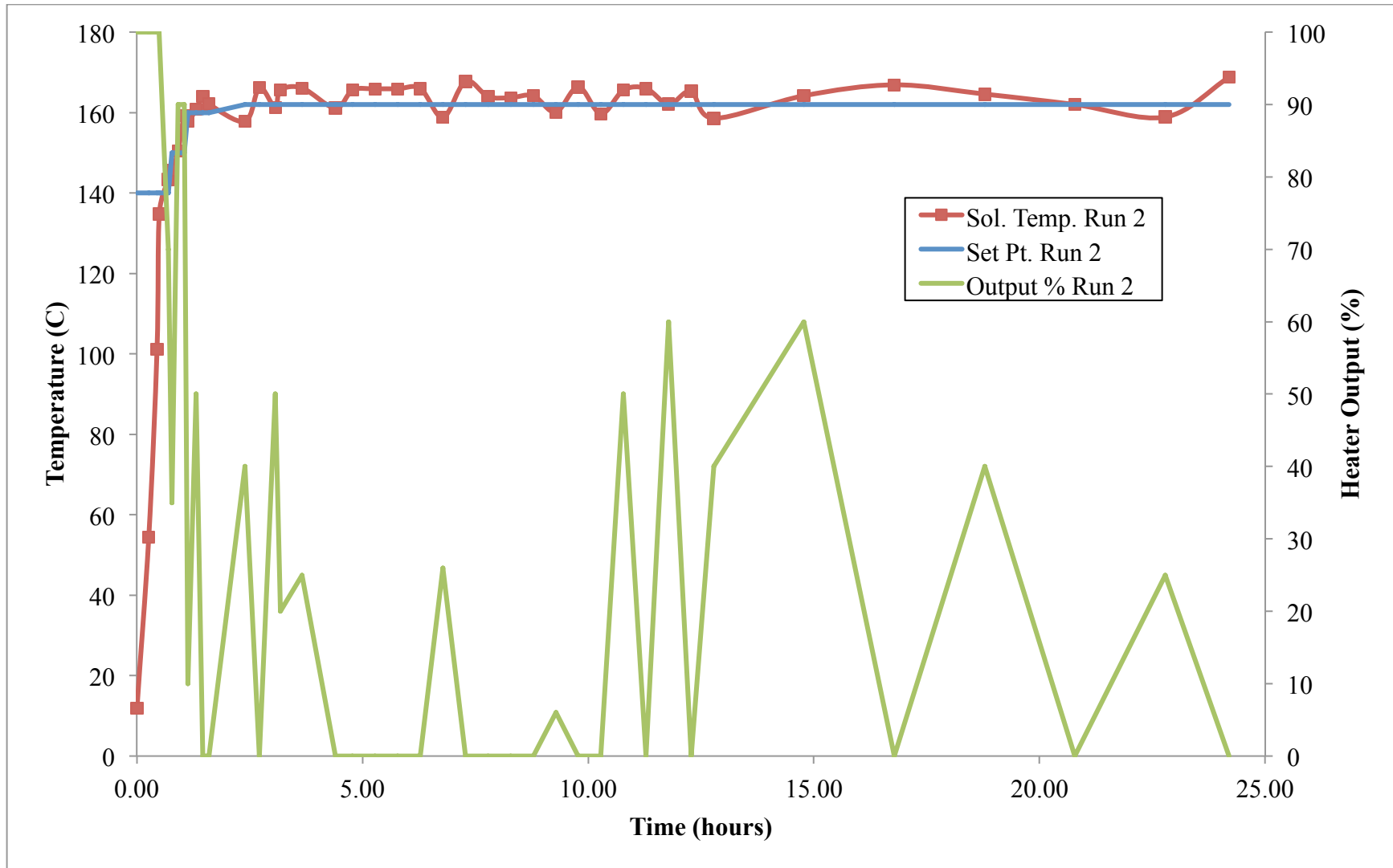
Figure 2.6: Plot of solution temperature, temperature set point, and heater output for pilot reactor polymerization 2.

Once the polymerization was completed, the solution was again allowed to cool and the reactor was discharged into 1 L containers. The resulting polymer solution had a much higher viscosity due to the higher solids level. The final concentration for this polymer solution was 32 % polymer with viscosity of 10300 poise. The inherent viscosity of this polymer was 0.51 dL/g, which was an improvement over the first pilot reactor polymerization.

In the third pilot reactor polymerization, two main parameters were adjusted to compensate for the results of the second pilot reactor polymerization. The first was the reaction volume was decreased. In the second pilot reactor polymerization, the thermal expansion of the DMAc was not accounted for and some polymer and monomer were pushed into the condenser. The second parameter to be adjusted was the temperature overshoot. Due to the programming of the temperature controller for this reactor, the solution temperature significantly overshoots the set point. To avoid this problem, the heater output would manually be adjusted to reach the desired temperature then the controller would be switched back to automatically control the temperature for the remainder of the polymerization.

Before starting the polymerization, it was found that the gain on the controller could be adjusted so the gain was reduced significantly. The idea was that if the gain were reduced then the temperature overshoot would not be as severe or would be eliminated. In practice this was not the case. The solution temperature still went above the set point and the reactor was sealed in order to contain the solvent. Once the seal was released however the solvent again began to come out of the reaction and was collected

in the water scrubber. At this point, the amount of DMAc lost was added back to the reaction via a port, which allowed the reaction to remain under nitrogen.

After adding the DMAc back, the power output of the heater was controlled manually. This allowed for precise control of the solution temperature and ensured the solution temperature did not exceed the desired set point. Using only 40 % output on the heaters, the solution temperature was carefully increased to the final temperature around 162 °C. Once the solution temperature was stable, the temperature controller was set back to automatic and controlled the heaters automatically. **Figure 2.7** illustrates the temperature profile of the polymerization. It is evident from the temperature data that controlling the heater output manually gave much better temperature control and completely eliminated the temperature overshoot. Once the final temperature was reached and the automatic control switched back on, the temperature was stable for the entirety of the polymerization still with some oscillation.
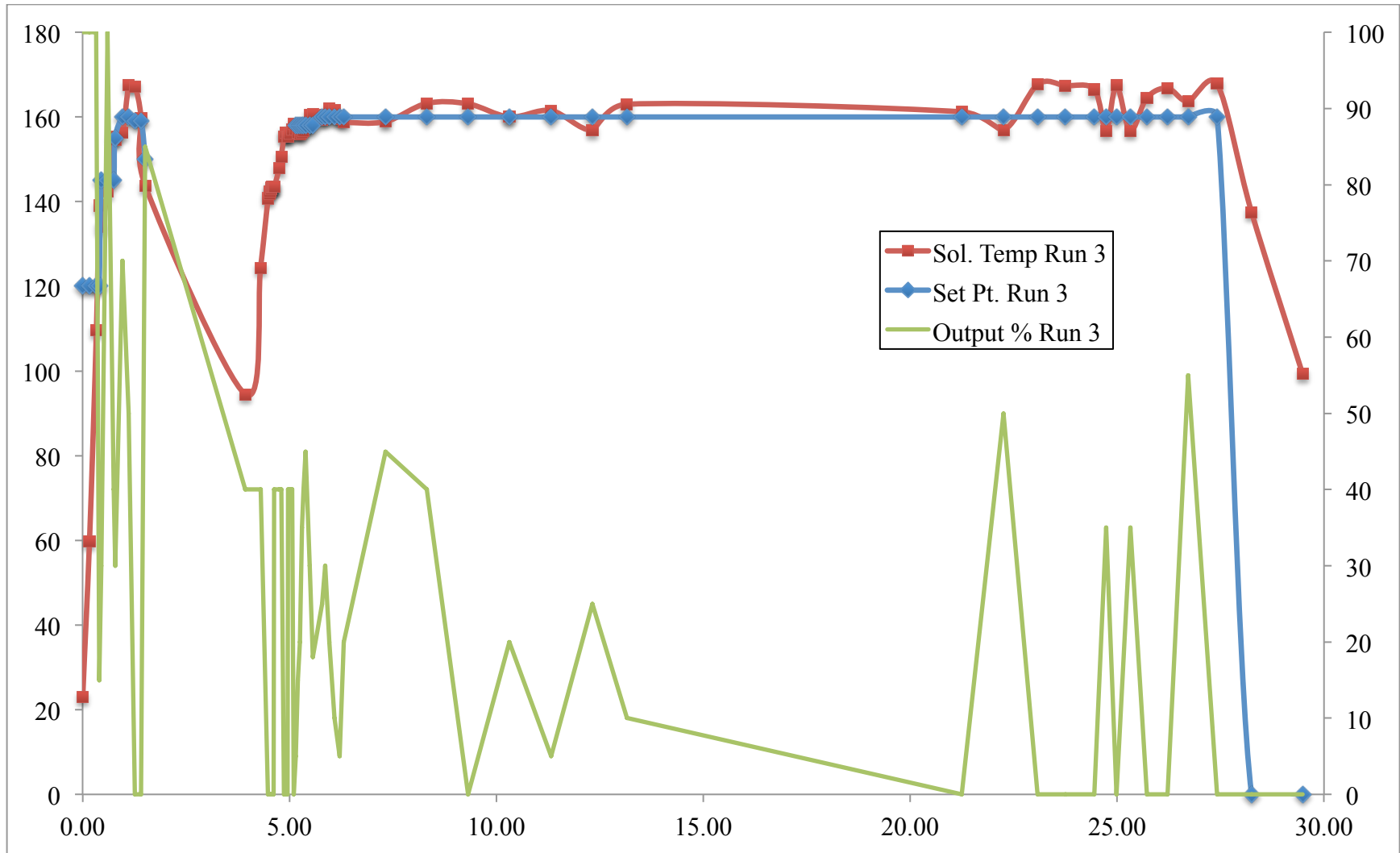
Figure 2.7: Plot of solution temperature, temperature set point, and heater output for pilot reactor polymerization 3.

After the 24 hours of polymerization time at 162 °C, the solution was cooled and collected in 1 L containers. The resulting inherent viscosity of this polymer was 0.46 dL/g. The low inherent viscosity was in part due to the poor temperature control at the beginning of the reaction but it is likely there is another factor affecting the final polymer inherent viscosity.

2.9.3 CONCLUSIONS

Three polymerizations were conducted in an 8 L pilot reactor at an industrial site and it was shown that this solution polymerization process could be scaled-up to produce PBI. The inherent viscosity of the final polymer in all of the reactions was too low to spin into useable fibers, however. Temperature overshoot issues plagued all three polymerizations but the problem was solved in the last polymerization by manually controlling the heater output. In order to have better control of the process and be able to more carefully monitor the reaction, the next polymerizations would be conducted in the laboratory setting.

2.10 LABORATORY PRODUCTION

In an attempt to better control the polymerization, the production of PBI solution would be moved back into the laboratory setting. Not only would this give better control over the solution temperature but using glass would give better insights into the nature of this process. To do these polymerizations in the lab, a 5 L glass round bottom reactor would be used with a stainless steel stirrer, which has a helical stir arm and half moon paddle at the bottom. A mantle would heat the solution and the temperature controller could be tuned using neat DMAc.

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2.10.1 EXPERIMENTAL

2.10.1.1 SYNTHESIS OF M-PBI IN 5 L REACTOR

Isophthalaldehyde bisulfite adduct (860.17 g, 2.513 moles), 3,3',4,4'-tetraaminobiphenyl (538.52 g, 2.513 moles), sodium bisulfite (10.46 g, 0.1005 moles), and dimethylacetamide (2370 mL) were added to a 5 L round bottom flask. The flask was fitted with a stainless steel stirrer, reflux condenser, and nitrogen flow. The flask was then placed in a heating mantle, which was controlled by a thermocouple inside the solution. The solution was then refluxed and stirred for 24 hours. Some of the resulting polymer solution was precipitated in water, washed with methanol, and dried at 200 °C under vacuum.

2.10.1.2 SYNTHESIS OF M-PBI IN 2 L REACTOR

Isophthalaldehyde bisulfite adduct (229.38 g, 0.6702 moles), 3,3',4,4'-tetraaminobiphenyl (538.52 g, 0.6702 moles), sodium bisulfite (2.790 g, 0.0.0268 moles), and dimethylacetamide (632 mL) were added to a 2 L round bottom flask. The flask was fitted with a stainless steel stirrer, reflux condenser, and nitrogen flow. The flask was then placed in a heating mantle, which was controlled by a thermocouple inside the solution. The solution was then refluxed and stirred for 24 hours. Some of the resulting polymer solution was precipitated in water, washed with methanol, and dried at 200 °C under vacuum.

2.10.2 RESULTS

The first trial of the lab production produced an important observation almost immediately. As the mantle was heating the solution, the thermocouple reading the

solution temperature increased quickly to 130 °C, which was far above the oil temperature and a liquid refluxed in the reactor. There also was a ring of precipitate around the edges of the reactor where this liquid was condensing back into the solution. The precipitate had a yellow color and it was then hypothesized that water was being produced as a by-product of the reaction causing precipitation of PBI on the sides of the reactor. To confirm this hypothesis, a distillation column was attached to the reactor where the condenser had been. At this point, the head temperature climbed to 100 °C and around 200 mL of water was distilled from the reaction. As the water was removed, the precipitate went back into solution. Once the headspace temperature began to rise above 100 °C, the condenser was reinstalled and the polymerization proceeded for the remainder of the reaction time under reflux conditions. The inherent viscosity of the polymer was 0.59 dL/g; an improvement over all of the trials in the pilot reactor.

The next measures to improve the I.V. of the polymer were then focused on ensuring that all water was removed from the polymerization to drive the reaction towards the product. In the two proceeding polymerizations, similar results were observed. As the solution was heated, water was distilled off until the headspace temperature increased to the reflux temperature of DMAc. At this point the polymerizations would be transitioned to reflux mode and remained this way until the end of the reaction. These two subsequent reactions were both aborted, however, when the glass reactor cracked and caused the heating mantle to short.

Exhausting the supply of 5 L reactors and heating mantles, the next polymerizations were attempted in 2 L reactors in oil baths. Again, water was distilled from the reaction until the headspace temperature rose to 148 °C. The reflux condenser

was then reattached and these polymerizations were able to go to completion. Even with the distillation of the water, the resulting inherent viscosities were only 0.56 and 0.40 dL/g.

2.10.3 CONCLUSIONS

An important observation was made for this particular polymerization. Water is a byproduct of the reaction and must be removed to drive the reaction to completion. Distilling the water also eliminates any PBI from precipitating on the walls of the reactor, which prematurely stops that polymer from increasing in molecular weight. While the elimination of water did not completely solve the problem of low inherent viscosity, it did add to the knowledge of this polymerization method and distillation will be used for all future polymerizations using the bisulfite adduct monomer.

2.11 PROJECT CONCLUSIONS AND FUTURE DIRECTIONS

Beginning with time and temperature studies, it was shown that the optimum conditions for this polymerization method were reflux temperature for 24 hours or more. Additional sodium bisulfite salts added to the polymerization were shown to increase polymer inherent viscosity to meet the required 0.7 dL/g for fiber spinning. Viscosity modifiers were also studied and both lithium chloride and sodium bisulfite proved to be effective. The final viscosity was very sensitive to inherent viscosity and solids content so it was concluded that viscosity would be adjusted on a per batch basis.

Next, scale-up of all the processes was attempted. Monomer synthesis proved to be a very scalable reaction and the reaction could be optimized for lower solvent use as well. The polymer synthesis presented many more challenges. In the pilot reactor, polymerization solution temperature was difficult to control and all of the polymer

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produced was low I.V. Another set of laboratory experiments was conducted, which provided new insights into the reaction as it was found that water was produced during the polymerization. Although moderate I.V. polymers were produced, further experiments will be needed to achieve higher inherent viscosities at the appropriate polymer concentrations need for fiber spinning trials.

In future work, the focus will certainly be to resolve the issue of low I.V. polymer being produced. Monomer purity and contaminants should be investigated since the monomer can be hygroscopic. Additionally, most reactions have only lasted for 24 hours so longer polymerization times could be beneficial for larger scale reactions.

2.12 REFERENCES

1.   Gulledge, A. L. Advancements in the Design, Synthesis and Applications of Polybenzimidazoles. Ph.D. Thesis, University of South Carolina, 2014.

2.   Higgins, J.; Marvel, C. S., Benzimidazole polymers from aldehydes and tetraamines. *Journal of Polymer Science Part A-1: Polymer Chemistry* **1970,** *8* (1), 171-177.

3.   Kissane, M. G.; Frank, S. A.; Rener, G. A.; Ley, C. P.; Alt, C. A.; Stroud, P. A.; Vaid, R. K.; Boini, S. K.; McKee, L. A.; Vicenzi, J. T.; Stephenson, G. A., Counterion effects in the preparation of aldehyde–bisulfite adducts. *Tetrahedron Letters* **2013,** *54* (48), 6587-6591.

CHAPTER 3: SYNTHESIS AND CHARACTERIZATION OF

POLYBENZIMIDAZOLE FROM ORTHOESTER MONOMERS

3.1 INTRODUCTION

In the search for methods to prepare polybenzimidazole in solution, only one article in the literature presented a procedure to do so in dimethylacetamide (DMAc) other than by the bisulfite adduct method.[1] This alternative procedure utilizes a bisorthoester monomer in conjunction with the tetraamine to synthesize polybenzimidazole in DMAc (**Scheme 3.1**).[2] Orthoesters have been known to be highly reactive intermediates for the synthesis of heterocycles,[3] which make them an attractive chemistry to investigate for this application. In Dudgeon and Vogl's article[2] on orthoester monomers, polymerizations were conducted at very low concentrations below 2% polymer content and the inherent viscosity of the polymer was 0.32 dL/g. To be a viable route in a fiber spinning application, the resulting polymer would need to have an inherent viscosity above 0.70 dL/g and the polymer content of the solution is typically targeted at around 26%. Thus, preliminary investigations were conducted to produce polybenzimidazole from these bisorthoester monomers at high polymer concentration.
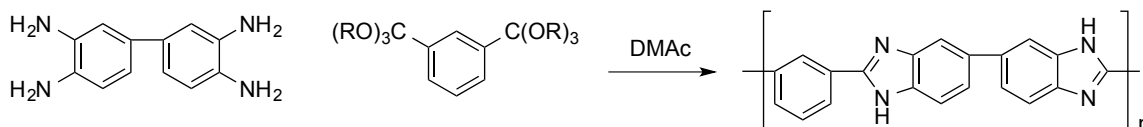
Scheme 3.1: General synthesis of m-PBI from an orthoester monomers.

3.2 MATERIALS

α,α,α,α', α', α'-hexachloro-m-xylene (HCMX) was purchased from TCI America and used without further purification. Sodium was purchased from Alfa Aesar and used as received. 3,3',4,4'-Tetraaminobiphenyl (TAB) was donated by BASF. Methanol was purchased from MACRON Fine Chemicals and distilled before use. Dimethylacetamide was purchased from Acros Organics.

3.3 EXPERIMENTAL

3.3.1 SYNTHESIS OF HEXAMETHYLORTHOISOPHTHALATE (HMOI)

Sodium (3.84 g, 0.167 moles) was added to 300 mL of distilled methanol in a 500 mL round bottom flask. The flask was cooled in an ice bath as the sodium dissolved. Once the sodium completely dissolved and the solution had cooled to 5 °C, HCMX (7.82 g, 0.025 moles) was added dropwise. The solution was refluxed for 5 days. Once cooled to room temperature, the solution was filtered and the methanol was removed by vacuum distillation. The crude product was then mixed with water and extracted with chloroform (10x50 mL). The chloroform extracts were washed with saturated aqueous sodium bicarbonate solution and dried over anhydrous magnesium sulfate. The chloroform was removed by vacuum distillation resulting in 5.795 g HMOI (80% yield), m.p. 91 °C (lit.[3] m.p. 95.4-96.6 °C). ^{1}H-NMR (DMSO-d_6), ppm: 3.16 (6H, s, OCH$_3$), 7.28-7.77 (3H, m, Ar-H).

3.3.2 POLYMERIZATION OF POLY(2,2'-M-PHENYLENE-5,5'BIBENZIMIDAZOLE) (M-PBI) USING HMOI

HMOI (1.726 g, 0.006 moles), TAB (1.280 g, 0.006 moles), and 9.88 mL of DMAc were added to a 100 mL three-neck round bottom flask. The flask was equipped with nitrogen flow, mechanical stirrer, and reflux condenser. The solution was heated from room temperature to reflux over 1 hour and held at this temperature for 24 hours. The solution was then cooled to room temperature and the polymer was precipitated in water. The polymer was washed several times with methanol to remove DMAc and dried overnight at 200 °C under vacuum.

3.4 CHARACTERIZATION

3.4.1 INHERENT VISCOSITY (I.V.)

Approximately 0.050 g of recently dried polymer was added to a 25 mL volumetric flask. The flask was partially filled with concentrated sulfuric acid and shaken on a mechanical wrist-action shaker overnight to dissolve the polymer. Once all polymer was dissolved, the flask was completely filled with concentrated sulfuric acid to achieve a final polymer concentration of 0.2 g/dL. The polymer solution was filtered through a 0.4 μm filter to remove any undissolved particles and the filtered solution was added to a 200 μm Ubbelohde viscometer. The viscometer was placed into a 30 °C water bath for 30 minutes. Three flow times between the calibrated marks on the viscometer were measured. The average of these times was used in **Equation 3.1** as the solution time *t*.

Equation 3.1

$$\eta_{inh} = \frac{\ln\left(t/t_0\right)}{C}$$

η_{inh} (dL/g): inherent viscosity

t (sec): solution flow time

t_0 (sec): solvent flow time

C (g/dL): solution concentration

3.4.2 Thermogravimetric Analysis (TGA)

TGA was performed using a TA Instruments Q-5000 with heating rate of 10 °C/min under nitrogen. Weight loss of polymer as a function of temperature was compared to commercial samples of m-PBI to confirm presence of desired product.

3.4.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded on a Perkin Elmer Spectrum 100 using an attenuated total reflection (ATR) diamond cell attachment. Monomer spectra were used to detect impurities and polymer spectra were compared to commercial polymer spectra.

3.4.4 Nuclear Magnetic Resonance (NMR)

NMR spectra were recorded using a 300 MHz Varian Mercury 300 Spectrometer using dimethyl sulfoxide-d_6. ^{1}H-NMR spectra of monomer samples were used to confirm the presence of the desired product and detect impurities.

3.5 Results

Following the previously published synthesis[3], the desired orthoester monomer HMOI was synthesized in good yields and purity. Analysis of the monomer by FTIR

(**Figure 3.1**) showed a strong absorption peak at 1100 cm^{-1} corresponding to the C—O stretch of the orthoester.[3] A small peak at 1700 cm^{-1} (C=O stretch) is present in the spectrum indicating some of the orthoester was hydrolyzed to the methyl ester. As previously reported[3], orthoesters are sensitive to moisture and can convert to the ester. Aqueous work-up procedures and exposure to moisture in the air are likely the cause for these impurities.
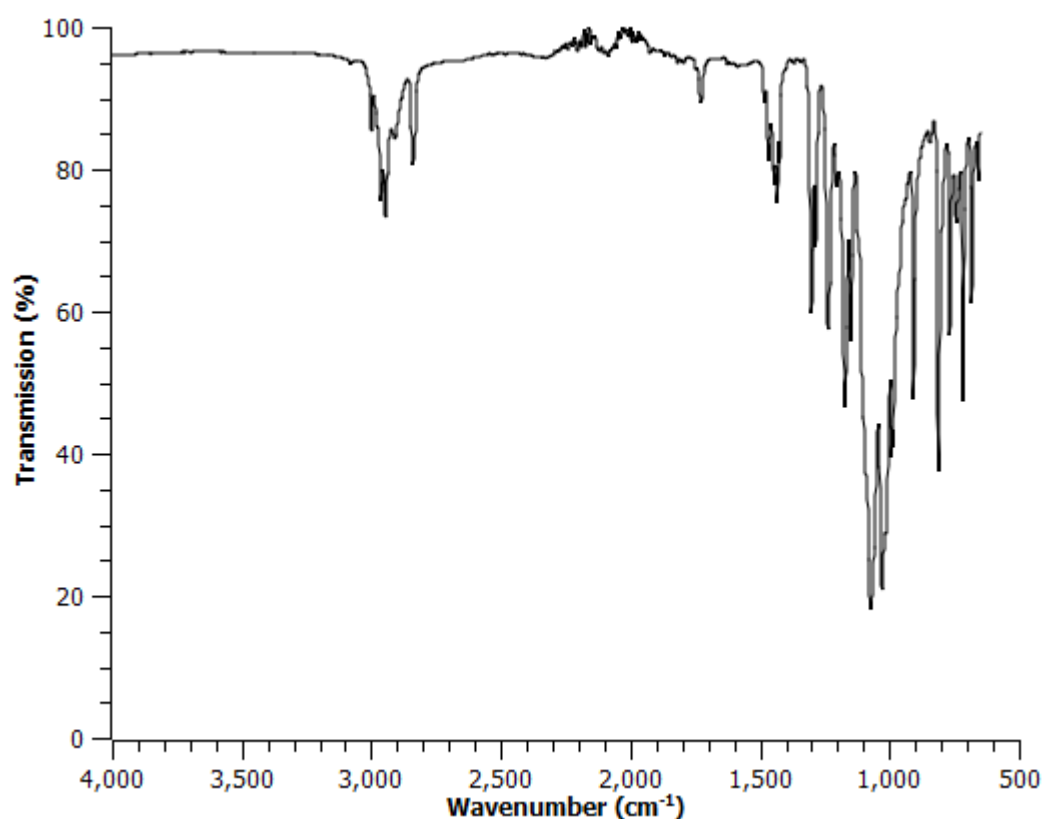
Figure 3.1: FTIR spectrum of synthesized HMOI.

Analysis of HMOI by ^{1}H-NMR (**Figure 3.2**) produced a singlet at 3.14 ppm from the methoxy protons (a) and three peaks between 7.2 and 7.8 ppm from the aromatic protons (b, c, d). The NMR spectrum along with the IR spectrum are strong evidence that the desired product was successfully synthesized. A small peak at 3.9 ppm also suggests hydrolysis of a small amount of the orthoester to the methyl ester.

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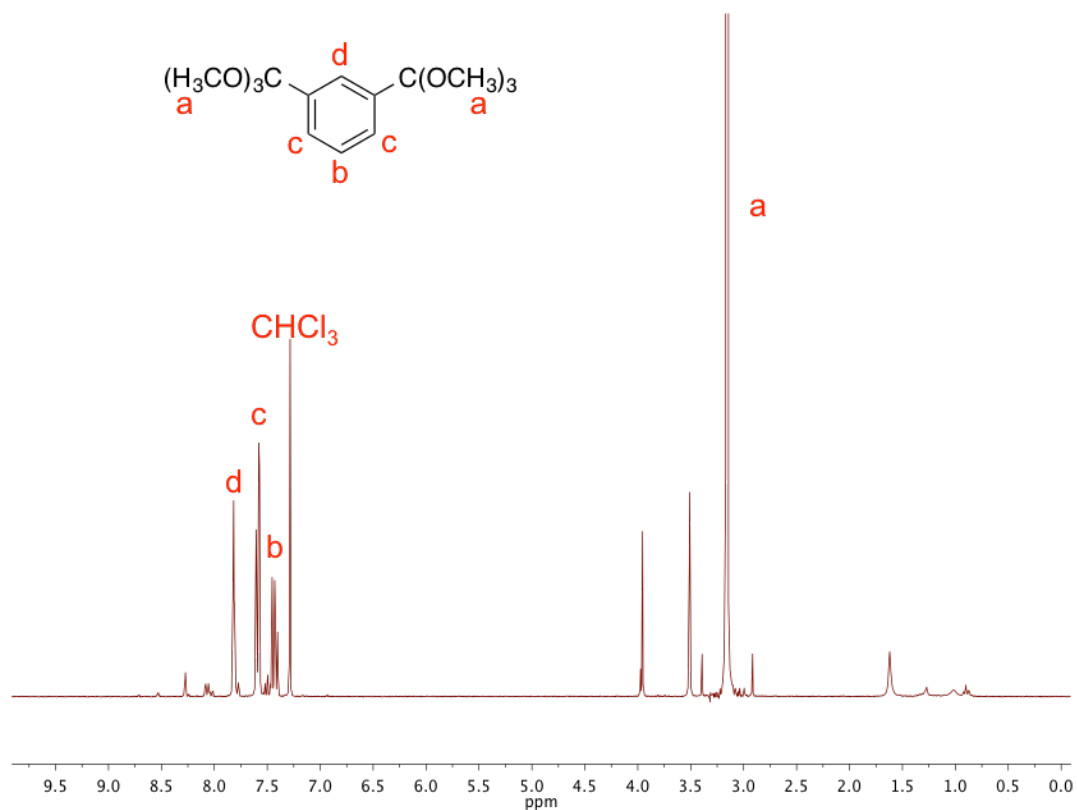
Figure 3.2: ^{1}H-NMR of HMOI in DMSO-d$_6$.

Despite the presence of some ester impurities, HMOI and TAB was polymerized at several concentrations in DMAc to determine the optimal conditions to achieve high polymer. Polymer concentrations ranged from 10 to 30 weight percent. The resulting inherent viscosities of the polymers synthesized are shown in **Figure 3.3**. While most polymer samples synthesized were of low I.V., the polymerization performed at 15% polymer concentration resulted in an I.V. of nearly 0.5 dL/g. The polymerization performed at 30 weight percent polymer content only produced a polymer powder and not a solution. The resulting powder did not dissolve in sulfuric acid to measure inherent viscosity.

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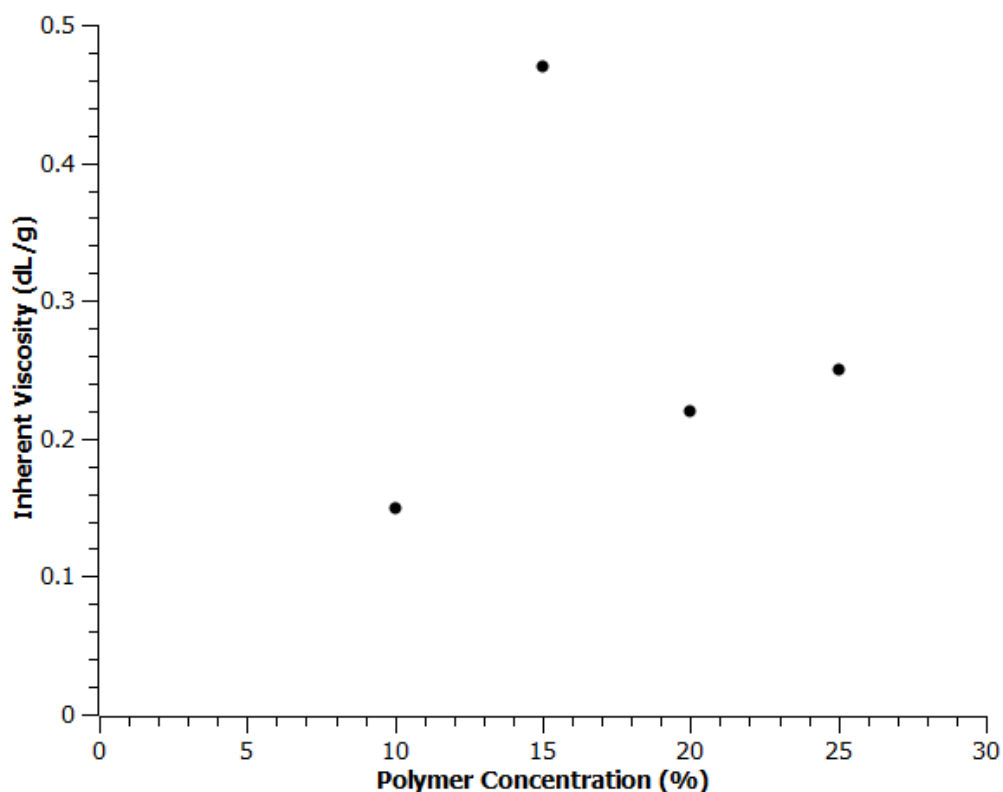
Figure 3.3: Inherent viscosity of m-PBI synthesized at several polymer concentrations.

TGA was used to compare the thermal stability of the m-PBI produced by this method to a commercial sample of m-PBI (**Figure 3.4**). Initially the m-PBI made from the orthoester monomer has a much higher weight loss up to 100 °C however this is likely due to differences in work-up procedures as the commercial polymer is heated to 350 °C in the final stages of polymerization while the m-PBI from the orthoester was only dried at 200 °C after precipitation in water. The weight loss of the two samples above 100 °C is nearly identical and both samples begin to rapidly degrade at 600 °C.
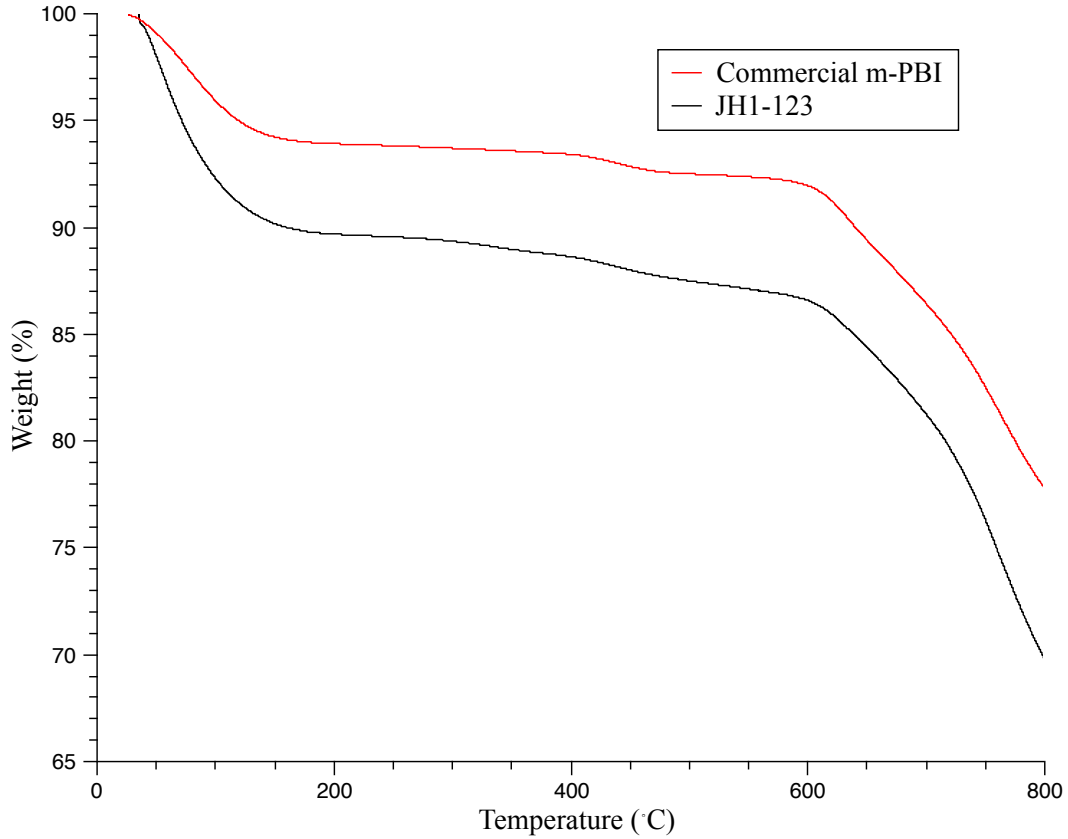
Figure 3.4: TGA of m-PBI from orthoester monomer (bottom curve) and commercial m-PBI (top curve).

The polymer prepared from the orthoester was also analyzed by FTIR and the spectrum was compared to a commercial sample of m-PBI (**Figure 3.5**). In these spectra, other than differences in intensity, the samples both appear to be the same material. Strong characteristic absorption peaks at 1300 and 1500 cm^{-1} appear in both spectra as well as several other weaker absorption peaks, which align between the two samples.
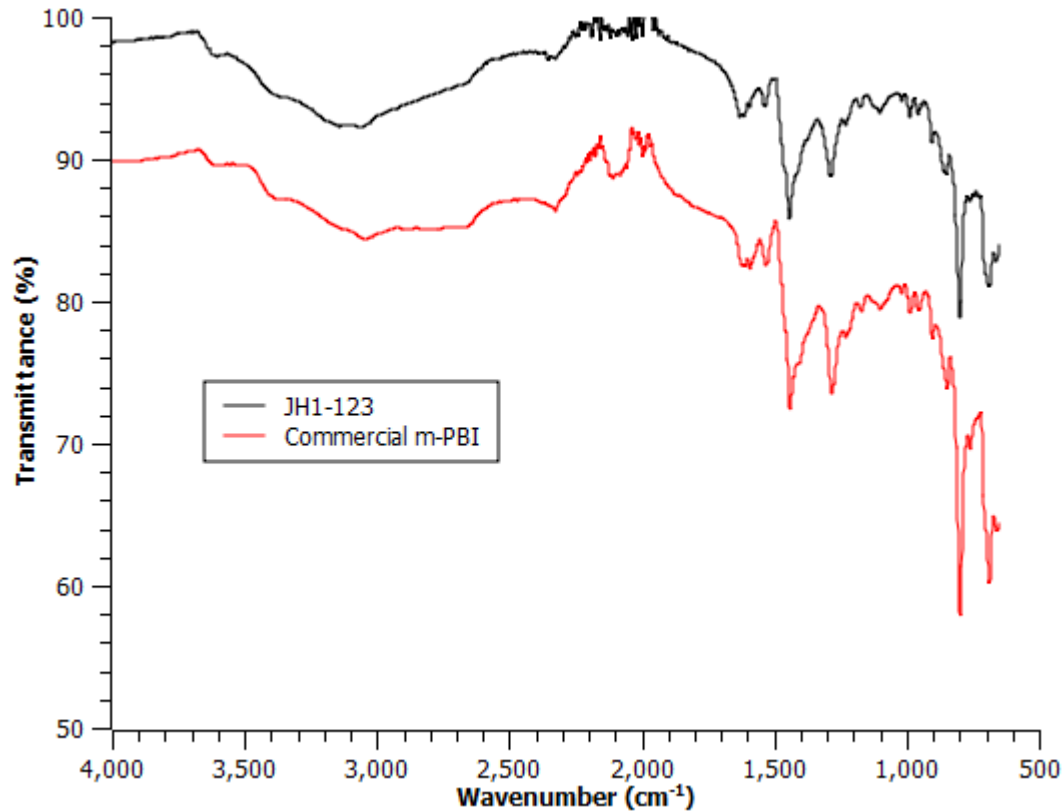
Figure 3.5: FTIR spectra of m-PBI from orthoester monomer (top curve) and commercial m-PBI (bottom curve).

3.6 CONCLUSIONS

The orthoester monomer HMOI was successfully synthesized and was able to be polymerized in solution to produce m-PBI. While this method is still in development and needs optimization of monomer and polymer synthesis, the initial results show a promising future for the production of m-PBI in solution at high polymer concentration. The 15 weight percent polymerization produced the highest reported I.V. to date with the use of HMOI. While the target I.V. was not met, other polymer concentrations between 10 and 20 weight percent could prove to meet or exceed 0.7 dL/g I.V. Further studies into other orthoester chemistries such as the propyl analog could also provide interesting results for the polymerization of m-PBI in solution. A critical parameter that could affect

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the polymerization and the resulting polymer molecular weight is the water content of the monomer. Future work in this area should be focused in minimizing aqueous work-up procedures and atmosphere moisture exposure as these affect monomer reactivity and the ultimate conversion during polymerization, as predicted by the Carothers Equation.[4]

3.7 REFERENCES

1.   Higgins, J.; Marvel, C. S., Benzimidazole Polymers from Aldehydes and Tetraamines. *Journal of Polymer Science: Part A-1* **1970,** *8*, 171-177.

2.   Dudgeon, C. D.; Vogl, O., Bisorthoesters as Polymer Intermediates. II. A Facile Method for the Preparation of Polybenzimidazoles. *Journal of Polymer Science: Polymer Chemistry Edition* **1978,** *16*, 1831-1852.

3.   Dudgeon, C. D.; Vogl, O., Bisorthoesters as Polymer Intermediates. I. Synthesis of Bisorthoesters. *Journal of Polymer Science: Polymer Chemistry Edition* **1978,** *16*, 1815-1830.

4.   Carothers, W. H., Polymers and polyfunctionality. *Transactions of the Faraday Society* **1936,** *32* (0), 39-49.

CHAPTER 4: SYNTHESIS AND CHARACTERIZATION OF AN ADAMANTANE CONTAINING POLYBENZIMIDAZOLE

4.1   INTRODUCTION

The cage-like structure of adamantane presents an interesting structure to investigate for gas separation membranes. When incorporated into the backbone of PBI, the adamantane would allow for the free volume of PBI to be increased and chain packing to be slightly disrupted. Compared to meta-PBI, this disruption could offer a higher membrane performance in gas separation devices. The adamantane-PBI has also never been tested for its performance as a fuel cell membrane. For these reasons, the synthesis and characterization of an adamantane containing PBI was studied.
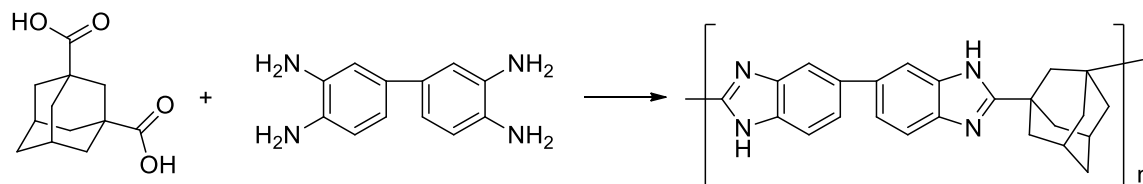
Scheme 4.1: General synthetic approach for synthesizing an adamantane containing PBI.

4.2   MATERIALS

1,3-Adamantanedicarboxylic acid and thionyl chloride were purchased from TCI and used as received. 3,3',4,4'-Tetraaminobiphenyl (TAB) and polyphosphoric acid (PPA) were donated by BASF. Methanesulfonic acid and Dimethylacetamide (DMAc) were purchased from Acros Organics. 3,4-Diaminobenzoic acid was supplied by Chem-Impex International Inc. and used as without further purification. Triethylamine, diethyl

ether, phosphorus pentoxide, and sulfuric acid were purchased from Fisher Chemical. Dimethylformamide (DMF), Dimethylsulfoxide (DMSO), and ammonium hydroxide were purchased from BDH. Chloroform was supplied by EMD. Ethanol was purchased from Decon Labs Inc.

4.3   CHARACTERIZATION

4.3.1   INHERENT VISCOSITY

Approximately 0.050 g of recently dried polymer was added to a 25 mL volumetric flask. The flask was partially filled with concentrated sulfuric acid and shaken on a mechanical wrist-action shaker overnight to dissolve the polymer. Once all polymer was dissolved, the flask was completely filled with concentrated sulfuric acid to achieve a final polymer concentration of 0.2 g/dL. The polymer solution was filtered through a 0.4 µm filter to remove any undissolved particles and the filtered solution was added to a 200 µm Ubbelohde viscometer. The viscometer was placed into a 30 °C water bath for 30 minutes. Three flow times between the calibrated marks on the viscometer were measured. The average of these times was used in **Equation 4.1** as the solution time *t*.

Equation 4.1

$$\eta_{inh} = \frac{\ln\left(t/t_0\right)}{C}$$

η_{inh} (dL/g): inherent viscosity

t (sec): solution flow time

t_0 (sec): solvent flow time

C (g/dL): solution concentration

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4.3.2 THERMOGRAVIMETRIC ANALYSIS (TGA)

TGA was performed using a TA Instruments Q-5000 with heating rate of 10 °C/min under nitrogen. Weight loss of polymer as a function of temperature was compared to reports in literature.

4.3.3 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FTIR spectra were recorded on a Perkin Elmer Spectrum 100 using an attenuated total reflection (ATR) diamond cell attachment. Polymer spectra were compared to commercial meta-PBI spectra.

4.3.4 NUCLEAR MAGNETIC RESONANCE (NMR)

NMR spectra were recorded using a 300 MHz Varian Mercury 300 Spectrometer using dimethyl sulfoxide-d_6. ^{1}H-NMR spectra of monomer samples were used to confirm the presence of the desired product and detect impurities.

4.4 ADAMANTANE CONTAINING POLYBENZIMIDAZOLE VIA PPA PROCESS

The Polyphosphoric Acid (PPA) Process was developed in 2005 as a convenient one pot synthesis to create phosphoric acid doped PBI membranes.[1] In this process, monomers are dissolved in PPA, which serves as the reaction solvent as well as a condensing agent, and upon heating to high temperature the PBI is formed. This process has proven to be effective for a wide range of monomers and for this reason it was the starting point for the research into the synthesis of an adamantane containing PBI.[1-2]

4.4.1 EXPERIMENTAL

1.524 g 1,3-adamantanedicarboxylic acid (0.0068 moles), 1.457 g TAB (0.0068 moles), and 97 g PPA were added to a 100 mL three-neck resin kettle. The reactor was

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fitted with an over-head mechanical stirrer and nitrogen flow. The kettle was placed into an oil bath and set to heat to 200 °C over 8 hours and allowed to remain at 200 °C for 16 hours. After this time, the solution was cast onto glass plates and the PPA was allowed to hydrolyze to phosphoric acid in a 55 % relative humidity chamber. A small amount of the PPA solution was poured into a large excess of water and neutralized to pH 7 with ammonium hydroxide.

4.4.2 RESULTS

During the polymerization, as the solution was being heated, the monomers initially dissolved making a homogeneous solution. Once the solution reached 80 °C, the solution began to foam as a gas was produced. By allowing the oil bath to continue to increase in temperature the foaming subsided and the solution became homogeneous again. After the oil bath had reached 200 °C and had remained at this temperature for 24 hours, the solution was dark brown in color but viscosity had not increased. By comparison, most PBI polymers when synthesized by the PPA process will have increased in viscosity once the solution has reached this temperature or even lower temperatures. Casting the solution onto glass plates and allowing the polyphosphoric acid to hydrolyze did not create a phosphoric acid doped PBI membrane.

To investigate why this set of monomers did not create polymer several steps were taken to study this phenomenon. The TAB was polymerized with other monomers known to synthesize PBI such as isophthalic and terephthalic acid. Using the same method of polymerization, these sets of monomers did produce PBI indicating that the TAB was not contaminated. The focus was then shifted to the adamantane monomer. Recrystallization of the monomer from ethanol did not eliminate gas formation and

foaming and NMR of the monomer (**Figure 4.1**) did not indicate any contaminants were present.
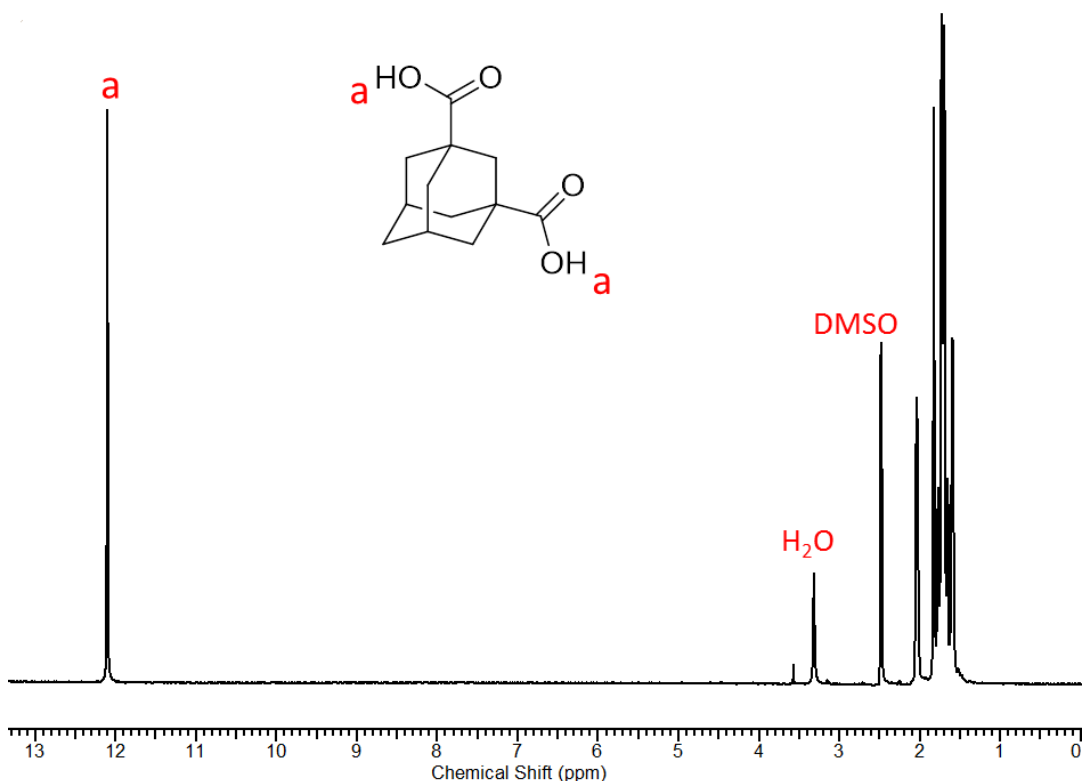
Figure 4.1: ^{1}H-NMR of 1,3-adamantanedicarboxylic acid as received from TCI.

The next step was to investigate the monomer-solvent interaction. To do this a sample of the adamantane monomer and polyphosphoric acid were subjected to the same conditions at which the polymerization occurred. Once again as the temperature reached 80 °C a gas was produced and the solution began to foam indicating that the adamantane monomer was incompatible with the polyphosphoric acid.

While researching this topic it was discovered in the literature that the adamantane containing PBI had been previously synthesized in a bulk polymerization[3]; however, a solution based polymerization of this polymer had not been published. The next topic to investigate was the small molecule analog of this polymer being the adamantane benzimidazole. The first reported method of synthesizing 2-(1-adamantyl)-

benzimidazole was done by Saski et al.[4] In this report, they mention that initial attempts to synthesize the adamantane benzimidazole from 1-adamantanecarboxylic acid and o-pheynlenediamine with hydrochloric acid or polyphosphoric acid were unsuccessful. It is also mentioned that when polyphosphoric acid was used adamantane was recovered. These results explain the phenomenon that was observed while attempting to polymerize the 1,3-adamantanedicarboxylic acid. If adamantane is being formed in the reaction media, then the monomer is decarboxylating and forming carbon dioxide seen as the gas formed and solution foaming. The resulting decarboxylated product is unreactive in the polymerization.

4.4.3 CONCLUSIONS

Based on the results from this set of experiments, it was concluded that 1,3-adamantanedicarboxylic acid is not compatible with the PPA and another synthetic route would need to be devised. Upon further investigation into this topic, this hypothesis was confirmed in the literature.

4.5 POLYMERIZATION OF ADAMANTANE-PBI IN EATON'S REAGENT

Eaton's reagent is a common name for a solution of phosphorous pentoxide and methanesulfonic acid in a 1:10 ratio by weight, which was developed to replace polyphosphoric acid for certain applications. In the article, Eaton describes this solution as having low viscosity compared to PPA, inexpensive starting materials, and a good solvent for many organics.[5] Eaton's reagent could therefore be a good alternative to the polyphosphoric acid with which the adamantane monomer was incompatible. This reagent has also been shown to be an effective condensation media for synthesizing polybenzimidazole polymers.[6]

4.5.1 EXPERIMENTAL

4.5.1.1 PREPARATION OF EATON'S REAGENT

Phosphorus pentoxide (10 g) and 100 mL methanesulfonic acid were measured into a 500 mL flask. The solution was heated to 50 °C and stirred overnight until all phosphorus pentoxide was dissolved.

4.5.1.2 SYNTHESIS OF ADAMANTANE PBI IN EATON'S REAGENT

Adamantanedicarboxylic acid (1.121 g, 0.005 moles) and 3,3'4,4'-tetraaminobiphenyl (1.071 g, 0.005 moles) were added to a 100 mL resin kettle. 25 mL of Eaton's reagent was poured over the monomers and the resin kettle was fitted with an overhead mechanical stirrer and nitrogen flow. The kettle was placed in a room temperature oil bath and heated to 140 °C for 48 hours. After this time the solution was allowed to cool and poured into 500 mL water. The polymer was neutralized to pH 7 with ammonium hydroxide, filtered off, and dried overnight at 120 °C.

4.5.2 RESULTS

To determine the ideal conditions to polymerize the adamantanedicarboxylic acid monomer in Eaton's reagent, recent literature was reviewed and it was found that a 1 mmol:5 mL ratio of monomer to Eaton's reagent had produced the highest inherent viscosities for other PBI chemistries in Eaton's reagent.[7] Using this same ratio for the adamantane monomer in Eaton's reagent, polymerizations were conducted at this monomer concentration.

During the polymerization in Eaton's reagent, the monomers dissolved completely and the solution turned a dark brown color. When the solution was heated

past 100 °C condensation could be observed on the sides of the reaction kettle indicating reaction of the monomers. After 24 hours at 140 °C the solution viscosity did not increase so the solution was allowed to remain at 140 °C for an additional 24 hours to compensate for the low polymerization temperature. Sometime between 36 and 48 hours the polymer solution increased in viscosity so that the solution no longer flowed and had the consistency of a gel. This rapid increase in viscosity has also been observed with other monomers when polymerizing PBI in Eaton's reagent.[6] At this point, the solution was allowed to cool and was poured into water resulting in the precipitation of a grey-brown polymer.

To characterize this polymer and measure a relative molecular weight, inherent viscosity of the polymer was measured. The standard measurement of inherent viscosity for polybenzimidazole polymers requires that the polymer be dissolved in sulfuric acid at 0.2 g/dL, but after two weeks of shaking, the polymer had not dissolved completely in the sulfuric acid. In previous work adamantane based PBI, Moon et al. reported dissolving the polymer in formic acid to measure inherent viscosity and reported that the polymer was only soluble in some organic solvents.[3] The solvent was then switched from sulfuric acid to formic acid and the polymer was measured to have an inherent viscosity of 1.76 dL/g at a concentration of 0.2 g/dL, indicating a relatively successful polymerization.

Thermogravimetric analysis (TGA) of the polymer (**Figure 4.2**) showed that the polymer retained approximately 15 wt.% moisture content but was stable until 500 °C at which point it rapidly degraded. By comparison, TGA of the adamantane PBI reported by Moon et al. had thermal stability up to 550 °C and a char yield of 55 % at 800 °C.[3] The difference in thermal stability is likely due to incomplete ring closure in the polymer

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backbone as a result of the lower polymerization temperature. Moon et al. used a final polymerization temperature of 310 °C but due to the low decomposition temperature of the Eaton's reagent the solution polymerization in the current study was limited to 140 °C.
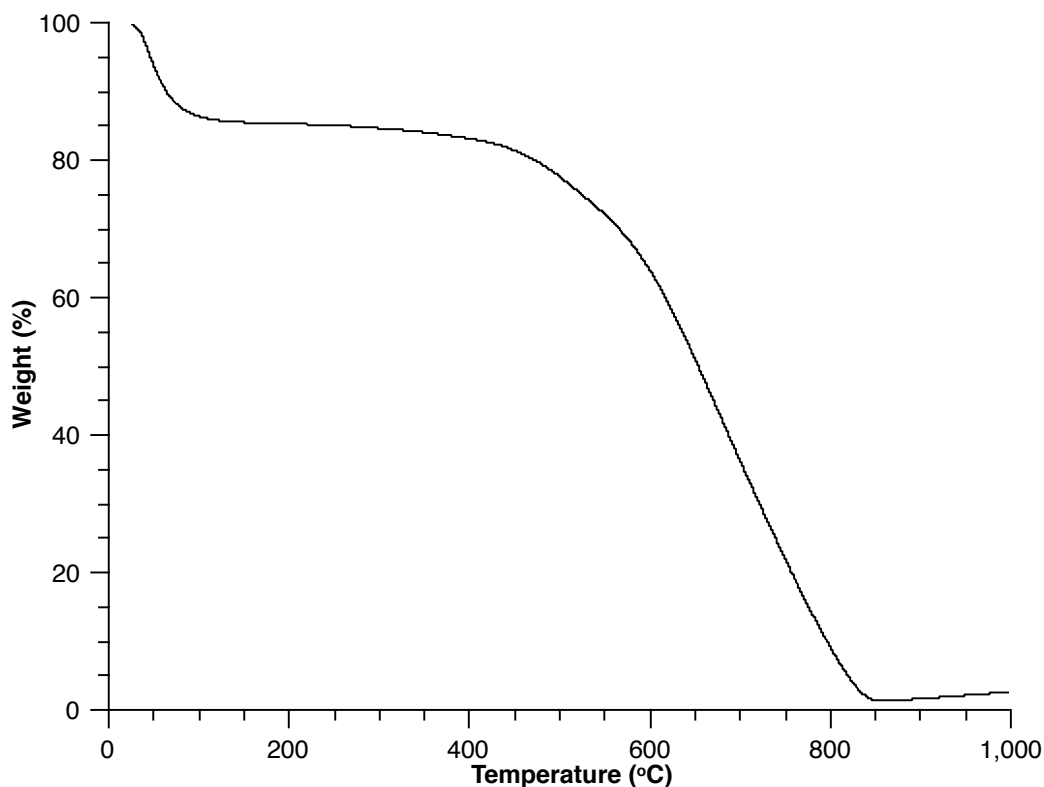
Figure 4.2: TGA in nitrogen of adamantane PBI synthesized in Eaton's reagent.

The IR spectrum of the adamantane polymer (**Figure 4.3**) shows similar absorption peaks to the commercial m-PBI in the 800 to 1700 cm^{-1} region of the spectrum indicating successful polybenzimidazole formation. Additionally, Sasaki published IR data for the 2-(1-adamantyl)-benzimidazole as having peaks at 3040, 1620, 1590, 1530, and 740 cm^{-1} and when compared to the adamantane PBI all of these peaks are present in the adamantane PBI spectrum.[4]
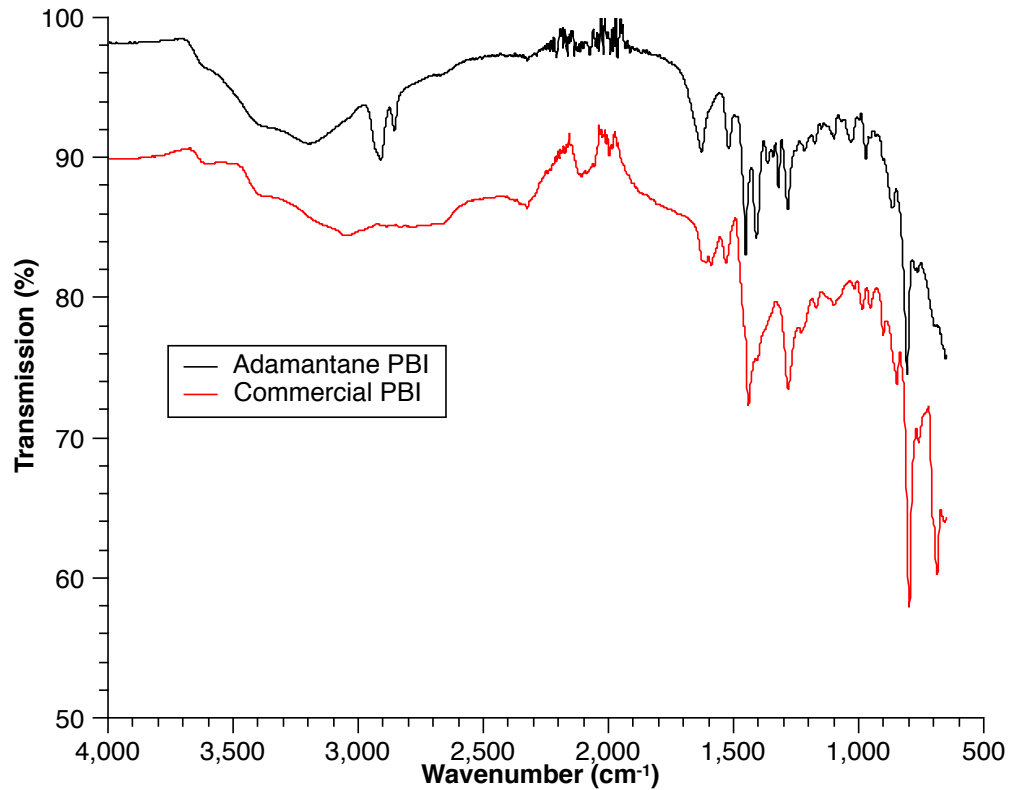
Figure 4.3: IR spectrum of adamantane PBI (top curve) and commercial m-PBI (bottom curve).

4.5.3 CONCLUSIONS

Eaton's reagent proved to be a compatible solvent for the adamantanedicarboxylic acid monomer and an alternative to PPA as the polymerization solvent. The adamantane PBI was successfully synthesized in this reaction medium, which was confirmed by TGA, FTIR, and inherent viscosity measurements. Although benzimidazole ring closure may not be complete, this could be addressed through subsequent thermal treatments or additional reaction in PPA at high temperatures.

4.6 ADAMANTANE PBI FILM FABRICATION

Preparation of a membrane or film made from the new adamantane polybenzimidazole for use in fuel cells or gas separation applications required that a

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method of membrane production be devised. The first method to be investigated would be to modify the PPA Process for creating a phosphoric acid doped membrane to be used in a hydrogen fuel cell. Polymer membranes for use in gas separation devices would require that all solvent be removed so film fabrication from organic solvents was investigated.

4.6.1 Experimental

4.6.1.1 Preparation of Phosphoric Acid Doped Adamantane PBI Membrane from Polymer Powder

Adamantane PBI (1.5 g) was added to a 100 mL resin kettle. 50 g PPA was poured over the polymer powder and the resin kettle was fitted with an overhead mechanical stirrer and nitrogen flow. The mixture was stirred and heated to 200 °C for 24 hours. After this time, the solution was cast onto glass plates and placed in a 55 % relative humidity chamber.

4.6.1.2 Preparation of Phosphoric Acid Doped Adamantane PBI Membrane from Eaton's Reagent Solution

Following the same method described in section 4.5.1, the adamantane PBI was synthesized in Eaton's reagent. After the 48 hours, 96 g PPA was poured into the resin kettle over the polymer solution. The resin kettle was reassembled with the overhead mechanical stirrer and nitrogen flow and heated to 200 °C overnight. The solution was then cast onto glass plates and placed in a 55 % relative humidity chamber.

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4.6.1.3   PREPARATION OF ADAMANTANE PBI FILM FROM ORGANIC SOLVENTS

Adamantane PBI powder (0.50 g) was measured into a 100 mL round bottom flask. Dimethylacetamide (50 mL) was poured over the polymer powder and the mixture was heated to reflux for 24 hours. The solution was poured into a petri dish and placed on a hot plate set to 40 °C in a nitrogen environment. Once all solvent had evaporated the polymer film was removed from the petri dish.

4.6.2   RESULTS

Dissolving the adamantane PBI powder in PPA and casting a film proved to be difficult. At 3 weight percent polymer content the solution appeared homogeneous but after casting and hydrolysis of the PPA a solid membrane was not formed. Increasing the polymer content was attempted, however, the polymer did not completely dissolve and the resulting membranes were not homogeneous. Lowering the polymer content did not form solid membranes either.

In order to achieve higher polymer content, the next approach was to add PPA at the end of a polymerization in Eaton's reagent. Attempting this procedure did provide a means for increasing the polymer concentration to 5 weight percent but when the solution was cast, the polymer did not form a homogeneous membrane after hydrolysis of the PPA. Since neither method of producing a phosphoric acid doped adamantane PBI membrane was successful, the focus was shifted to using organic solvents to create a film.

To begin these trials, DMAc was used to dissolve the polymer and it was found that the adamantane PBI was only soluble up to 1 weight percent. Attempts to produce a film from this solution were unsuccessful as the polymer film that remained after

evaporation of the solvent was very brittle and could not withstand removal from the glass. The next step was to add lithium chloride as a solution stabilizer to increase the solubility of the polymer and increase the casting concentration. Using DMAc with 2 % lithium chloride did allow for a marginal increase in solubility to 2 % polymer content. The films from this solution were also brittle and did not withstand removal from the glass.

Switching solvents to N-methylpyrrolidone (NMP) gave better solubility compared to the neat DMAc but still only 2 % polymer content was achievable. Much like the films made from DMAc, using NMP did not affect the final film durability. The final solvent was DMSO, which showed similar solubility to DMAc, and only 1 wt.% polymer solutions were obtained. Again, the films were brittle and broke apart when removed from the glass.

4.6.3   CONCLUSIONS

A series of solvents were studied in an attempt to create an adamantane PBI film. The trials using PPA to generate a phosphoric acid doped membrane proved unsuccessful. Additionally, all attempts to use organic solvents to create a film failed as well. The low solubility of this polymer did not provide enough polymer chains to entangle and form a film that would hold up to external stresses. A method to increase the polymer solubility in organic solvents would be the next area of research.

4.7   ADAMANTANE MONOMER MODIFICATION

In order to increase the solubility of the adamantane PBI and stabilize the monomer in PPA, a modification to the adamantane monomer was proposed that would install benzimidazole moieties onto the adamantane prior to polymerization. The

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proposed method of modification (**Scheme 4.2**) would first utilize the Eaton's reagent to condense methyl-3,4-diaminobenzoate with the adamantane monomer to form the bisbenzimidazole. The methyl ester could then be hydrolyzed to the carboxylic acid for use in the polymerization. This modification would stabilize the adamantane monomer in PPA since the carboxylic acid would not be as easily removed in the acidic conditions. Also, slightly decreasing the adamantane content would allow for better solubility in organic solvents without sacrificing the desired effects of the adamantane in the backbone.
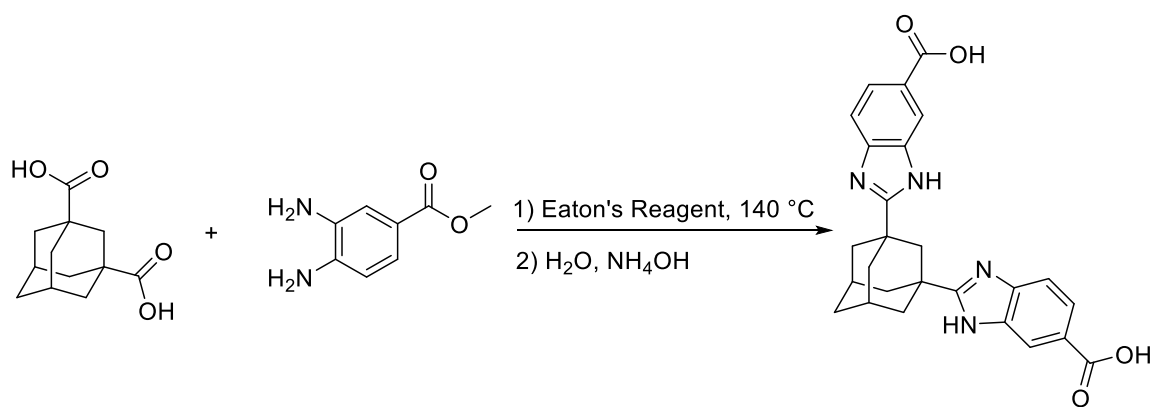
Scheme 4.2: Proposed synthesis of adamantane monomer modification.

4.7.1   EXPERIMENTAL

4.7.1.1   SYNTHESIS OF METHYL-3,4-DIAMINOBENZOATE

3,4-Diaminobenzoic acid (9.998 g, 0.065 moles), methanol (200 mL), and concentrated sulfuric acid (9.0 mL) were added to a 500 mL round bottom flask. The solution was stirred and refluxed for 24 hours. The methanol was removed by vacuum distillation followed by neutralization of the sulfuric acid with saturated aqueous sodium bicarbonate solution. The product was extracted with diethyl ether (10x50 mL) and the ether extracts were dried over magnesium sulfate. The ether was removed by vacuum

distillation leaving 7.52 g of product (69 % yield), m.p. 105 °C (lit. m.p. 105-110). ^{1}H-NMR (DMSO-d$_6$), ppm: 3.70 (3H, s, CH$_3$), 4.65 (2H, s, NH$_2$), 5.27 (2H, s, NH$_2$), 6.51-7.14 (3H, m, ArH).

4.7.1.2 SYNTHESIS OF 1,3-(2,2'-BISBENZIMIDAZOLE-6-METHYL ESTER)-ADAMANTANE IN EATON'S REAGENT

Adamantanedicarboxylic acid (1.121 g, 0.005 moles), methyl-3,4-diaminobenzoate (1.6618 g, 0.010 moles), and 25 mL of Eaton's reagent were added to a 100 mL round bottom flask. The solution was stirred and heated to 140 °C for 48 hours under a nitrogen atmosphere. After allowing the solution to cool, it was poured into 500 mL water forming a grey precipitate. The aqueous mixture was neutralized with ammonium hydroxide and the product was filtered off. The product was recrystallized from DMF leaving 1.017 g of product (42 % yield). Elemental analysis: C, 62.70; H, 5.75; N, 12.39 (calc. C, 69.41; H, 5.82; N, 11.56).

4.7.1.3 SYNTHESIS OF POLYPHOSPHORIC ESTER (PPE)

Phosphorus pentoxide (10 g), 10 mL chloroform, and 20 mL of diethyl ether were added to a 50 mL round bottom flask. The solution was stirred and refluxed until the solution became clear (18 hours). The chloroform and excess diethyl ether were removed by vacuum distillation, leaving a pale yellow viscous liquid.

4.7.1.4 SYNTHESIS OF 1,3-ADAMANTANEDIACID CHLORIDE

1,3-Adamantanedicarboxylic acid (1.0 g, 0.0044 moles) was added to a 50 mL round bottom flask and 15 mL of thionyl chloride was poured on top. The solution was stirred and heated to 55 °C for 2 hours. Excess thionyl chloride was removed by vacuum

distillation and the product was dried under vacuum overnight. 0.89 g recovered (0.0034 moles, 77 % yield). ^{1}H-NMR (DMSO-d$_6$), ppm: 1.5-1.9 (12H, m), 2.05 (2H, s).

### 4.7.1.5 TWO-STEP SYNTHESIS OF 1,3-(2,2'-BISBENZIMIDAZOLE-6-METHYL ESTER)-ADAMANTANE

1,3-Admantanediacid chloride (0.965 g, 0.0036 moles), methyl-3,4-daminobenzoate (1.196 g, 0.0072 moles), triethylamine (0.728 g, 0.0072 moles), and 50 mL of diethyl ether were added to a 100 mL round bottom flask. The solution was stirred overnight at room temperature. Precipitate was filtered off, washed with water, and dried overnight under vacuum.

The product (0.200 g) from the previous step, 5 drops of polyphosphate ester, and 20 mL of chloroform were refluxed for 24 hours. The solution was poured into water and the organic layer was washed with aqueous sodium bicarbonate. The organic layer was collected and dried over magnesium sulfate. The solution was filtered and chloroform removed by vacuum distillation. 0.115 g (6 % yield) of material was recovered. ^{1}H-NMR (DMSO-d$_6$), ppm: 1.61-2.06 (14H, m, Ad-H), 3.70 (6H, s, CH$_3$), 5.28 (2H, s, NH$_2$), 6.48-7.14 (6H, m, Ar-H).

4.7.2 RESULTS

Since Eaton's reagent had proved to be an effective condensing agent for the synthesis of the adamantane-PBI polymer, it was the first solvent system to be attempted for the adamantane bisbenzimidazole synthesis. Very quickly the solution turned a dark brown color and remained this color for the entire duration of the synthesis. After heating the solution for 24 hours, excess water was used to precipitate the product followed by neutralization of the Eaton's reagent. ^{1}H-NMR of the recrystallized product (**Figure 4**)

shows the product of the synthesis in blue the adamantanedicarboxylic acid (green) and methyl-3,4-diaminobenzoate (red). Analyzing the peaks in the product and starting materials, the product shows all of the same peaks from the starting materials except for the carboxylic acid proton peak at 12 ppm. The aromatic peaks are shifted downfield from 6.5-7.5 ppm in the diaminobenzoate to 7.5-8.5 ppm in the product as well as the amine protons from 4.5-5.5 ppm to 5.5-6 ppm. These results indicate that the amide was formed. The presence of amine peaks and the absence of a benzimidazole N-H peak around 13-14 ppm in the product NMR indicates ring closure did not occur and the benzimidazole was not formed.
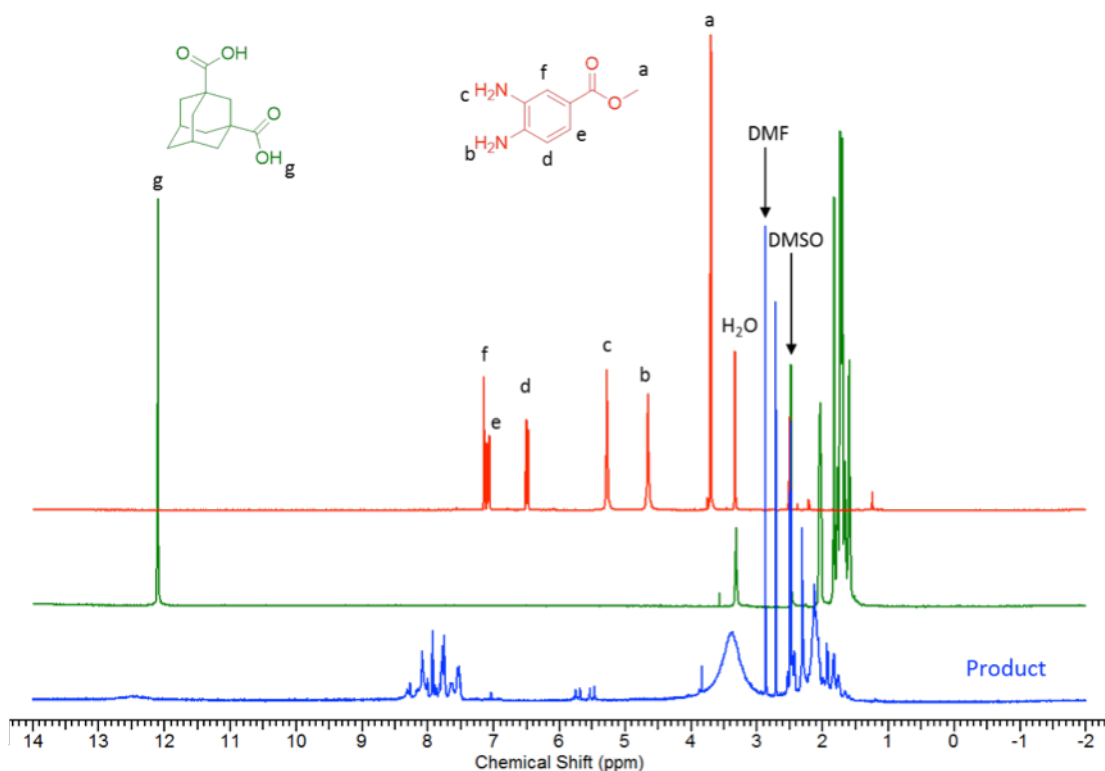

Figure 4.4: ^{1}H-NMR of product formed in Eaton's (bottom curve) reagent and the starting materials (middle curve, 1,3-adamantanedicarboxylic acid; top curve, methyl-3,4-diaminobenzoate).

These results ultimately led to the investigation of another synthetic route to install the benzimidazole moiety onto the adamantane prior to polymerization. Reviewing

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the literature produced few synthetic options. The only technique to use the carboxylic acid form of the adamantane to synthesize a benzimidazole derivative involved using 8.0 kbar of pressure for which the equipment to do this was not available.[8] Another route involved first using the acid chloride derivative of adamantane to first generate the amide product. The benzimidazole would then be formed in a second step.[4]

Synthesizing the 1,3-adamantanediacid chloride was a fast and efficient process with thionyl chloride. **Figure 5** shows ^{1}H-NMR of the carboxylic acid derivative of adamantane (red) and the adamantanediacid chloride (blue). The carboxylic acid presents a peak at 12 ppm and after the reaction with thionyl chloride this peak completely disappears. This product was used for the next step of synthesis without further purification.
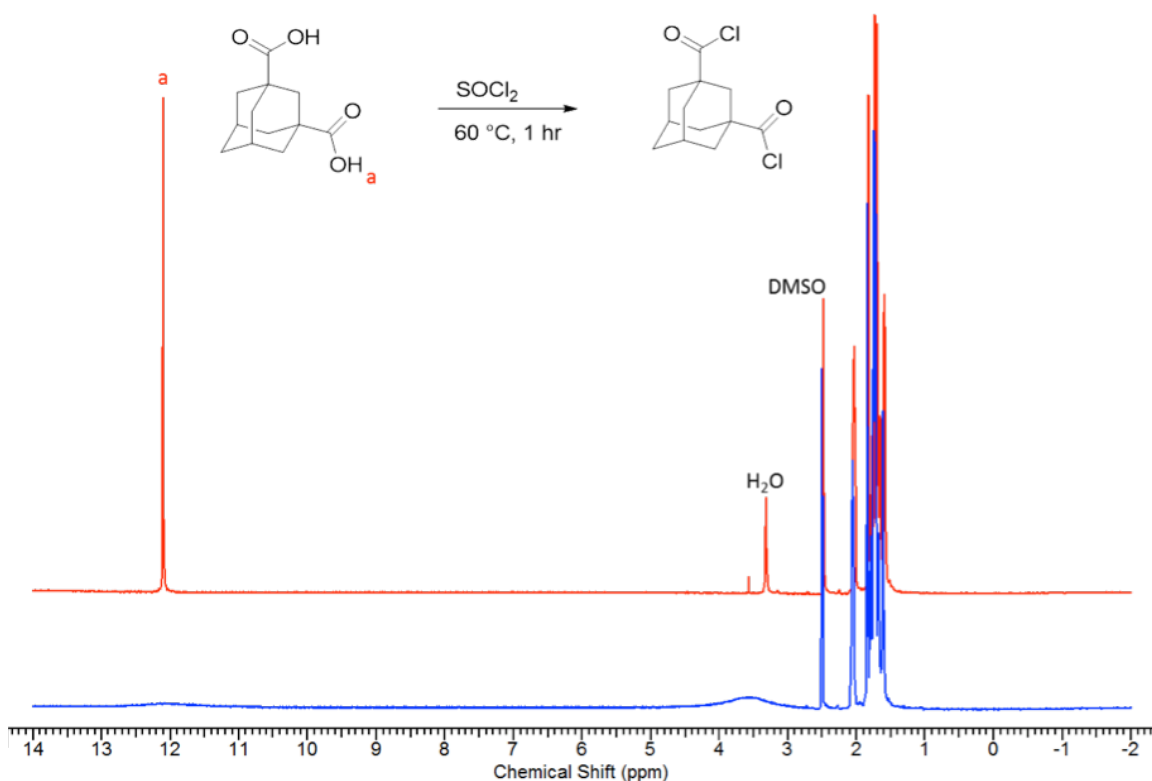
Figure 4.5: ^{1}H-NMR of 1,3-adamantanedicarboxylic acid (top curve) and 1,3-adamantanediacid chloride (bottom curve).

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The next step in the synthesis was to form the amide from the adamantanediacid chloride and the methyl-3,4-diaminobenzoate. This reaction also proved to be easy and efficient. After stirring the solution overnight the product precipitated and was able to be filtered and dried. The ^{1}H-NMR (**Figure 6**) of the product shows a single peak at 5.3 ppm from the remaining amine as well as the aromatic proton peaks at 6.5-7 and a methyl ester peak at 3.7 ppm.
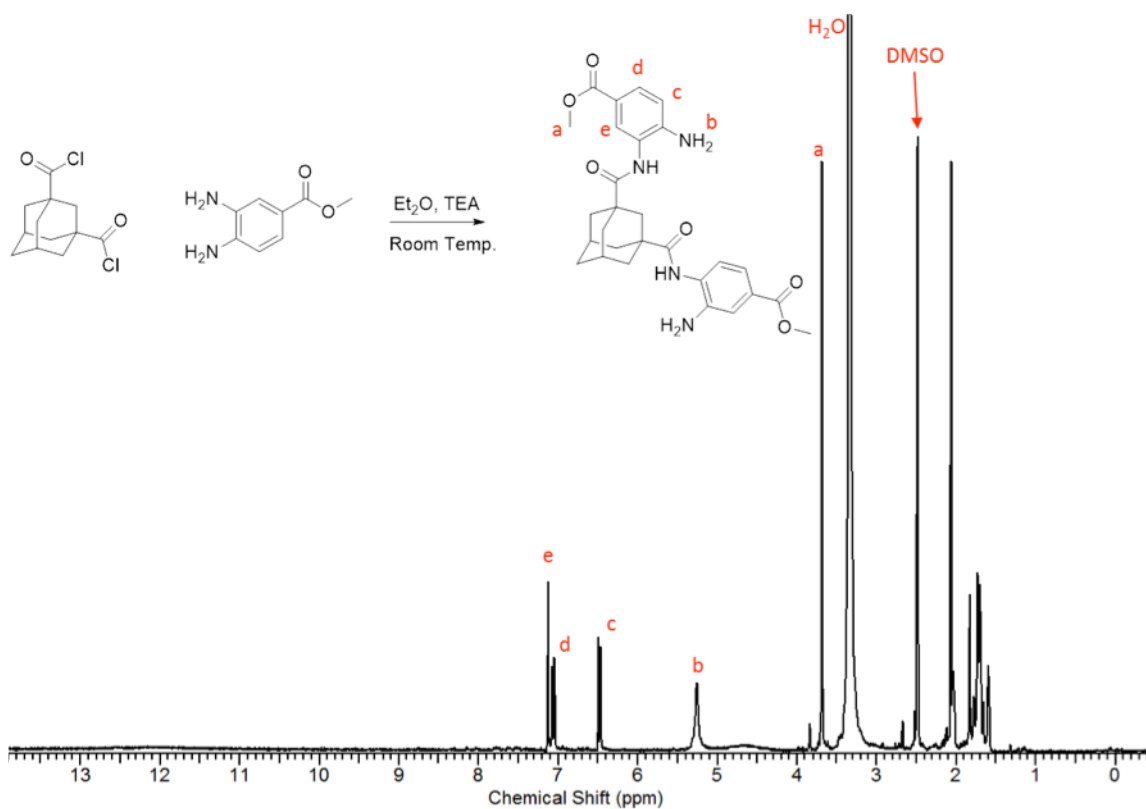
Figure 4.6: ^{1}H-NMR of adamantane amide product.

After the amide synthesis was completed the final step was to perform the ring closure. Following the synthesis previously reported,[4] the amide was refluxed in chloroform with a few drops of PPE; however, the desired product was not obtained and the starting materials were recovered. One point of concern is that the PPE, which was reported in Sasaki's experimental section, was not described. The use for such material

can only be speculated as a condensing agent to remove any water byproduct and push the reaction. Additionally, the low boiling point of chloroform likely does not provide enough energy to form the benzimidazole ring.

4.7.3 CONCLUSIONS

The synthesis of the bisbenzimidazole derivative of adamantane was attempted by two methods. In the first method, Eaton's reagent was used to try to form the desired product but only the amide was formed. The second method utilized a two-step synthesis but again only the amide could be synthesized. Ring closure of the amino-amide likely requires very high temperature (>200 °C) as is case in polymerizations in PPA and solid-state. Alternatively, a more reactive functional group on the adamantane could allow for the benzimidazole to be formed at lower temperature but more research is required to determine the optimal chemistry to make this monomer modification.

4.8 PROJECT CONCLUSIONS AND FUTURE DIRECTIONS

In this work, the synthetic methods for incorporating the adamantane moiety into the backbone of PBI was studied. Using the PPA process, which has shown in recent years to be a convenient method for synthesizing various PBI chemistries,[1-2] the adamantane monomer proved to be incompatible with PPA and decarboxylated. Eaton's reagent was then found to be an alternative solvent for polymerization, which would not cause decarboxylation at elevated temperatures and still act as a condensing agent. The adamantane PBI synthesized from Eaton's reagent had an inherent viscosity of 1.76 dL/g as measured in formic acid and showed thermal stability up to 500 °C. Attempts to use this polymer to form a phosphoric acid doped membrane for use in a fuel cell or a film from organic solvents were all unsuccessful. Monomer modifications were performed in

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order to gain solubility in organic solvents; however, the desired monomer could not be synthesized.

Alternative methods of producing a PBI film with the adamantane in the backbone could be achieved by exploring alternative functional groups on the adamantane monomer or even copolymer systems using monomers that are more soluble than the adamantanedicarboxylic acid. The aldehyde functionality has shown to be a convenient route to forming PBI in solution by way of a bisulfite adduct. Additionally, copolymers of the adamantane PBI and meta-PBI could provide the solubility necessary to form a film while still enhancing the gas separation performance over the meta-PBI homopolymer.

4.9 REFERENCES

1.   Xiao, L.; Zhang, H.; Scanlon, E.; Ramanathan…, L., High-temperature polybenzimidazole fuel cell membranes via a sol-gel process. *Chemistry of Materials* **2005**.

2.   Xiao, L.; Zhang, H.; Jana, T.; Scanlon, E.; Chen, R.; Choe, E. W.; Ramanathan, L. S.; Yu, S.; Benicewicz, B. C., Synthesis and Characterization of Pyridine-Based Polybenzimidazoles for High Temperature Polymer Electrolyte Membrane Fuel Cell Applications. *Fuel Cells* **2005,** *5*.

3.   Moon, S.; Schwartz, A. L.; Hecht, J. K., Polybenzimidazole Containing Adamantane Units. *Journal of Polymer Science, Part A-1: Polymer Chemistry* **1970,** *8* (12), 3665-6.

4.   Sasaki, T.; Eguchi, S.; Toru, T., Synthesis of Adamantane Derivatives. III. Synthesis of Adamantane Heterocycles. *Bulletin of the Chemical Society of Japan* **1969,** *42*, 1617-1621.

5.   Eaton, P. E.; Carlson, G. R.; Lee, J. T., Phosphorus pentoxide-methanesulfonic acid. Convenient alternative to polyphosphoric acid. *The Journal of Organic Chemistry* **1973,** *38*.

6.   Leykin, A. Y.; Fomenkov, A. I.; Galpern, E. G.; Stankevich, I. V.; Rusanov, A. L., Some aspects of polybenzimidazoles' synthesis in P2O5 containing condensation media. *Polymer* **2010,** *51*.

7.   Qian, G.; Smith, D. W.; Benicewicz, B. C., Synthesis and characterization of high molecular weight perfluorocyclobutyl-containing polybenzimidazoles (PFCB–

PBI) for high temperature polymer electrolyte membrane fuel cells. *Polymer* **2009,** *50.*

8.   George, H.; John, J. E.; Max, L., Formation of benzimidazoles at high pressure. *Journal of the Chemical Society, Perkin Transactions 1* **1977**.