8-2024

Exploring the Synthesis of Biobased and Chemically Recyclable Polysulfone Using Imine Chemistry

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Recommended Citation

Jain, Vitasta, "Exploring the Synthesis of Biobased and Chemically Recyclable Polysulfone Using Imine Chemistry" (2024). *All Dissertations*. 3720.
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EXPLORING THE SYNTHESIS OF BIOBASED AND CHEMICALLY RECYCLABLE POLYSULFONE USING IMINE CHEMISTRY

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Material Science and Engineering

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by
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August 2024

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ABSTRACT

Plastic waste poses a major problem because of the chemical stability of these materials, leading to their accumulation in the environment and the leaching of toxic chemicals during their slow decomposition. Additionally, the use of depleting petroleum reserves for synthesis has made for an unsustainable production and risks due to use of chemicals hazardous to the environment and the individuals exposed to it.

To address these concerns, researchers have explored biobased feedstock and incorporating chemical recycling capabilities for a closed loop, sustainable process. One promising feedstock is lignin with its abundant functional groups that can be modified and utilized to obtain high value polymers. Dynamic covalent bonds are good candidates for chemical recycling as they enable design of bonds that on application of external stimuli such as pH, temperature, light, etc. impart the polymer chain the ability to reprocess.

This research focuses on utilizing biobased alternatives, specifically vanillin that can be extracted from lignin, as a substitute for bisphenol A in the production of polysulfones that are biobased and can be chemically recycled. The resulting polymers are then subjected to thermal, chemical, and viscoelastic testing, allowing for a comparison with commercially available counterparts. A life cycle analysis is conducted to determine the viability of the work proposed as a greener alternative.

The principles of green chemistry principles were integrated into this work, aiming for a sustainable future in polymer synthesis. Through this method, the research endeavors to foster a more green and circular polymer synthesis.

ACKNOWLEDGEMENTS

In the development of this dissertation, I extend my sincerest gratitude to Dr. Srikanth Pilla, whose unwavering support and motivation has been indispensable throughout this endeavor. His mentorship, approach to problem solving and, commitment to his work and research have not only influence this work but have also served as a source of inspiration.

I also extend my sincere thanks to my co-advisor Dr. Johnson for his counsel and to the members of my dissertation committee who generously provided their knowledge and expertise: Dr. James Sternberg, Dr. Igor Luzinov and Dr. Olga Kukenok. Their feedback and guidance were instrumental in expanding the scope of my research, motivating me to delve deeper and engage with the subject matter in a more reflective way.

I am also thankful to current and past members of Dr. Pilla's research group - Kavya, Kavan, Dr. James Sternberg, and Olivia. Their theoretical insight and practical assistance have been inestimable. Their support throughout this process has been a resource that made this journey easier.

On a personal note, I am grateful for the continued support and motivation from my parents throughout my educational pursuit and beyond. Their encouragement has been a source of strength. To all who contributed to this journey, I extend my deepest gratitude.

I would also like to acknowledge partial financial support from the Department of Energy, Basic Energy Sciences (Award# DE-SC0021367) and the Advanced Manufacturing fellowship awarded by the Thomas F. Hash Endowed Chair in Sustainable Development.

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CHAPTER ONE:

SYNTHESIS OF BIOBASED AND RECYCLABLE POLYSULFONES

1.1 INTRODUCTION

Petroleum based fuels and chemicals have taken a toll on the environment. Plastics production grew by +18,950% from 1950 to 2015[1]. High-performance polymers account for 1% of plastics production by tonnage and were worth $13.2 billion in 2018[2]. Their high thermal, chemical, and mechanical resistance make them essential in a variety of applications in automotive, electrical, medical etc. Polymers made using dwindling petroleum-based products are unsustainable for the future[3]. Their production may also utilize toxic chemicals like bisphenol A (BPA)[4] a known endocrine disruptor xenoestrogen. This is especially dangerous since these toxic chemicals may end up leaching into the groundwater due to the decomposition of plastic waste in landfills and into oceans. Currently, in the US, about 9% of plastic waste is recycled, 16% is incinerated, yielding fuel as a byproduct, and the remaining is discarded in landfills, oceans[5,6] or is otherwise displaced[1]. The use of non-renewable sources, toxic chemicals, and plastic waste makes the synthesis of polymers that are sourced from renewable sources, utilize non-toxic chemicals, and can be recycled necessary. Figure 1 illustrates the predicted plastic production and its disposal from 1950 to 2050 with methods of plastic waste disposal being discarded, recycled, and incinerated. This discarded waste is the portion that ends up in landfill, oceans and otherwise lost as it becomes a part of the food chain or slowly decomposes leaching harmful chemicals into the water bodies and soil.

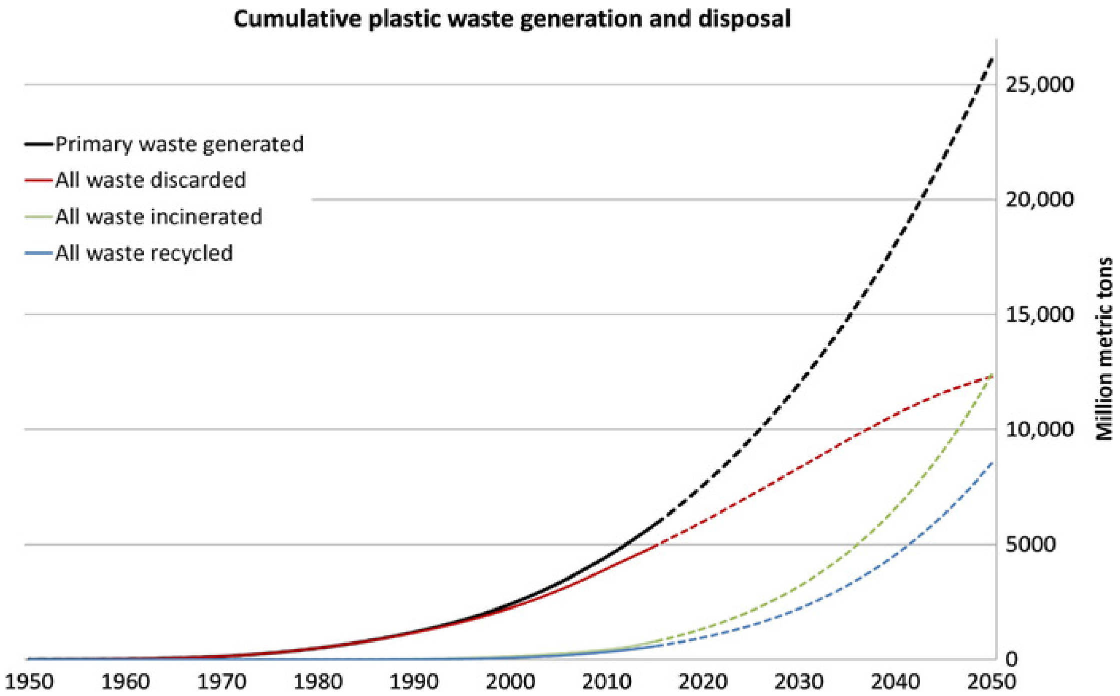


Figure 1: Cumulative plastic waste generation and disposal[1].

Green chemistry is an area of chemistry where chemical products and processes are designed in a way that reduce pollution at source. The principles of green chemistry can be applied to minimize the plastic waste generated and to better deal with the final waste by incorporating recycling capabilities, biodegradability and/ or using benign materials that have low environmental impact. By applying the principles of green chemistry (Table 1) across the life cycle of a product, in its design, manufacturing, use and disposal/recycling phase, materials that are sustainable can be designed. The principles of green chemistry applied in this work are summarized in Table 2.

Table 1: 12 Principles of Green Chemistry from Anastas and Warner 1998.

12 Principles of Green Chemistry	
1. Prevention	7. Use of Renewable Feedstocks
2. Atom Economy	8. Reduce Derivatives
3. Less Hazardous Chemical Syntheses	9. Catalysis
4. Designing Safer Chemicals	10. Design for Degradation
5. Safer Solvents and Auxiliaries	11. Real-time Analysis for Pollution Prevention
6. Design for Energy Efficiency	12. Inherently Safer Chemistry for Accident Prevention

Table 2: Principle of green chemistry applied in this work.

Applied Method	Principles of Green Chemistry
Replacing BPA	3. Less Hazardous Chemical Syntheses 4. Designing Safer Chemicals
Greener solvent	5. Safer Solvents and Auxiliaries
Biobased starting materials	7. Use of Renewable Feedstocks
Chemically recyclable polymer	10. Design for Degradation

Using renewable feedstock such as lignin is one of the principles applied in this work. Lignin comprises 25-30% of lignocellulosic biomass[7,8]. It is one of the byproducts from pulp and paper mills. Its aromatic structure and availability of β-O-4 bonds that allow for further functionalization make it a good candidate for feedstock of polymer synthesis[9–13]. With the biorefinery approach lignins are now considered as a source of aromatic building blocks for various polymers instead of being burned[14].

Depolymerised lignin can produce chemicals like vanillin, syringaldehyde, guaiacol, dimethyl sulfoxide, dimethyl sulfide, etc. Only three products are commercially produced from lignin: vanillin, dimethyl sulfide, and dimethyl sulfoxide (2007). Of which vanillin is the only available molecular phenolic compounds on an industrial scale using biomass[15,16]. In a study in 2004, it was summarized that 15% of the vanillin produced used lignin as a feedstock[17]. It is a popular starting material to make substitutes for bisphenols since the coupling of vanillin can give diols[18–21] which are necessary for polymerization while the additional vanillin moieties ensure that the material passes endocrine activity screening[22]. This is mainly attributed to the methoxy group in vanillin[23]. Material substitution to reduce use of chemicals like BPA is necessary for greener design and vanillin sourced from biomass is a promising substitute to use.

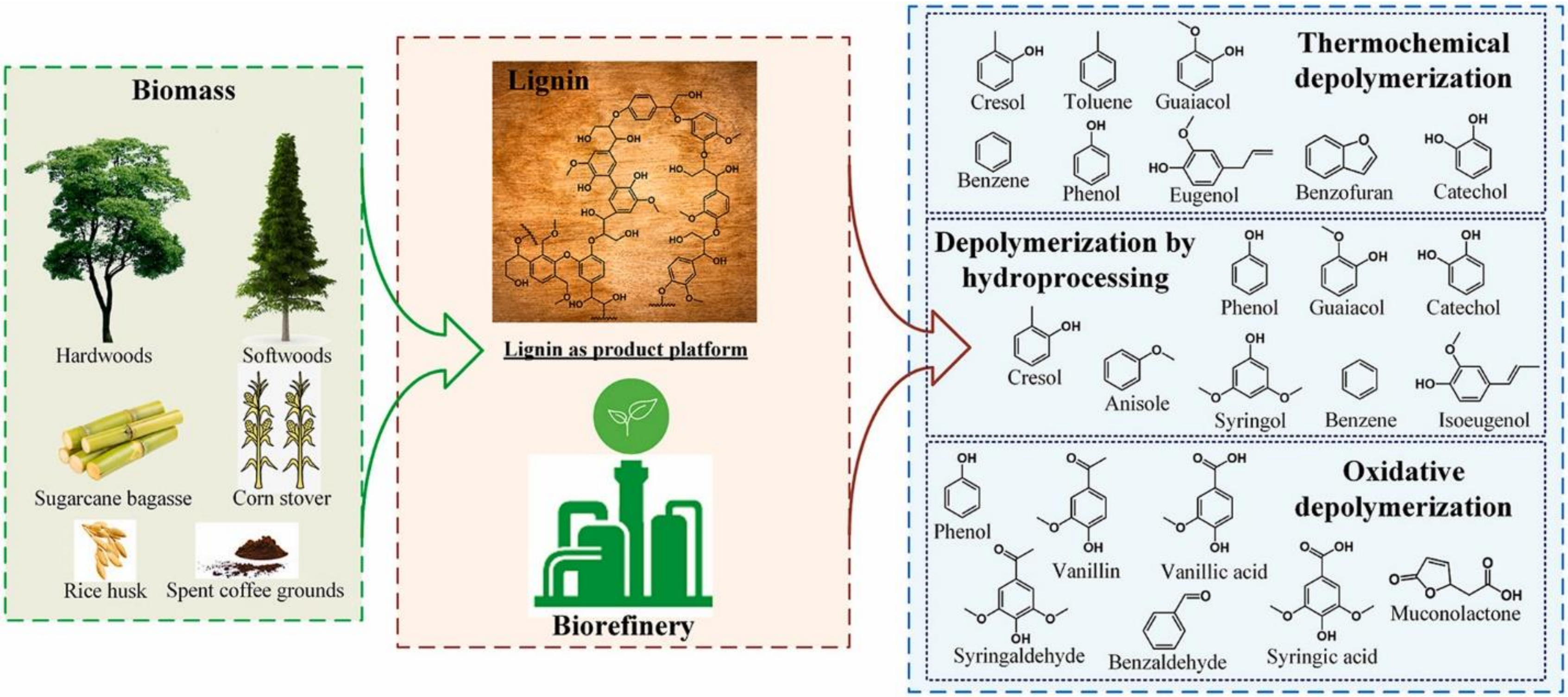


Figure 2: Lignin biorefinery products[151]. Reproduced with permission from Elsevier, license number: 5797071042418.

While thermoplastics can typically be recycled mechanically, degradation in polymer properties can be observed as contaminants become part of the polymer matrix[24–27]. Owing to these limitations, primarily mechanical recycling for high-purity products is limited to industrial scraps with pure polymer streams only[28,29]. Post use polymer streams undergo secondary mechanical recycling and typically have reduced thermomechanical properties. Chemical recycling of waste polymer streams either by design or post processing is categorized as the tertiary method. And finally, a quaternary waste to energy process can be used to deal with plastic waste.

Dynamic covalent chemistry (DCC) has been increasingly explored among available chemical recycling methods in recent years. Reversible covalent reactions are triggered to achieve forward and reverse reactions and utilized to dissociate the polymer into intermediates and back to polymer to achieve chemical recycling under controlled conditions[30–33]. Imine chemistry especially is widely used. The aldehyde group of vanillin make it an easy-to-use biobased monomer for imine synthesis[34,35] as it readily reacts with a primary amine to form the imine bond which can be utilized for recycling. Materials can be recycled with zero to minimal losses in properties and over multiple cycles even from mixed streams. This presents the opportunity to close the loop for a circular economy since, depending on the chemistry, materials can be recycled with zero to minimal losses in properties and over multiple cycles, even from mixed streams. For high performance polymers (HPPs) especially, the high value of the product may justify the costs associated with chemical recycling as the approach enables waste to be upcycled to a high-value polymer. This also makes it more likely to collect waste polymer because of the high-value product. This has the potential to address the problem of plastic waste and presents a sustainable way to use plastics.

The polymers of interest for this work are polysulfones (PSU). PSU were valued at \$1.6 billion in 2020 projected to grow to >\$2.3 billion by 2027[36]. PSU have a variety of applications, including use in water filtration membranes[37], electronics, automotive components[38] and more recently in proton exchange membranes for fuel cell applications[39]. 3D printed PSU have also been explored for use in water-oil separation membranes[37,40].

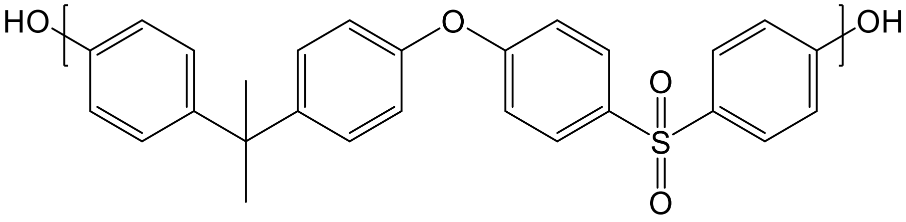


Figure 3: Structure of Polysulfone from BPA

1.2 OVERVIEW OF RESEARCH TASKS

In the work presented here, polysulfones are synthesized using monomers from a biobased feedstock lignin and designed for circularity by introducing covalent bonds that can be employed for chemical recycling.

Research task 1 explores the synthesis of a polysulfone with a biobased alternative to BPA in chapter 3. This alternative monomer is synthesized from vanillin, a compound from lignin biorefinery and has imine bonds to enable polymer recycling. The chemical structure of the polymer is studied using nuclear magnetic resonance spectroscopy (NMR) techniques. Studies were carried out to explore the effect of choice of base catalyst, monomer ratio, reaction time and temperature on polymer properties. The material properties were studied using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and gel permeation chromatography (GPC) to gain insight into the structure property relation of the polymer.

In chapter 4 recycling studies were conducted with varying pH's to design a protocol to enable recycling of the polymer synthesized in the previous study. A model compound study was done to confirm the synthesis of the recycling intermediate for better comparison. The properties of the recycled polymer were compared to the virgin material.

From this study, derivative polysulfones were synthesized in chapter 5. Co-polymers using other lignin derived chemicals such as guaiacol were synthesized and compared. In addition, a protocol was developed to make crosslinked polysulfones in an effort to improve material flexibility while maintaining recyclability and sustainability. This was done by designing a monomer with sites available for crosslinking and curing with a selected biobased diamine.

Finally, in chapter 6 a comparative life cycle analysis was conducted to verify the impact of recycling of this new biobased polysulfone synthetic protocol with the traditional petroleum-based polymer.

The questions this work seeks to answer are:

- How can the imine bond be used to enable recycling effectively for polysulfones and what are the properties of this polymer?
- How does recycling affect the polymer?
- What are the properties of the polymer when copolymerized or crosslinked?
- Is recycling really greener?

The experimental tasks identified to achieve the objective are:

Synthesis of biobased PSU with an imine bond embedded in the polymer backbone to enable recycling:

1. Synthesis of biobased recyclable polysulfones
    a. Replacing BPA, a xenoestrogen[41] with a nontoxic lignin-based monomer.
    b. Introducing a reversible chemical bond in the polymer backbone to enable recycling.
    c. Compare PSU synthesized in this study under various conditions (time, temperature, catalyst)
    d. Performing recycling studies to test recycling conditions and compare virgin and recycled materials.
2. Synthesis of copolymers and crosslinked polysulfone (derivative polymers from 1st task)
    a. Effect of the other biobased monomers on polymer properties
    b. Effect of increased spacing of imine bond on chemical recycling
    c. Effect of crosslinking on polymer properties and recycling
3. Life Cycle Analysis
    a. Determine viability of recycling
    b. Factors that have the most significant impact and methods to mitigate them.

CHAPTER TWO:

LIERATURE REVIEW

2.1 Polymers

In general polymers are large molecules made up of smaller repeating molecules called monomers linked covalently. They are classified as illustrated in Figure 4.

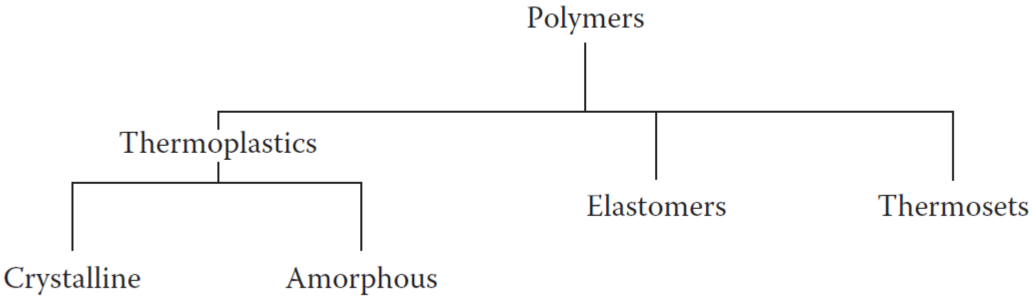


Figure 4: Polymer classification[42].

Polymerization reactions are classified as step growth and chain growth. In step growth the polymer chains grow stepwise as reactions can occur between any two monomers. This results in the doubling of the polymer chain at every step. In chain growth the monomer reacts only with a reactive end-group activated by an initiator, and results in successive addition of the monomers to the chain end. The rate of reaction between the two polymerization reactions greatly differs as illustrated by the trend in molecular weight growth in Figure 5. For step growth polymerization the monomer is rapidly consumed in the earlier reaction steps. To synthesize polymers with high degrees of polymerization a high extent of reaction is needed (≥99%)[42]. This also makes it important to minimize any side reactions from impurities in the reaction vessel, starting chemicals such as solvents and monomers and removal of byproducts from the reaction.

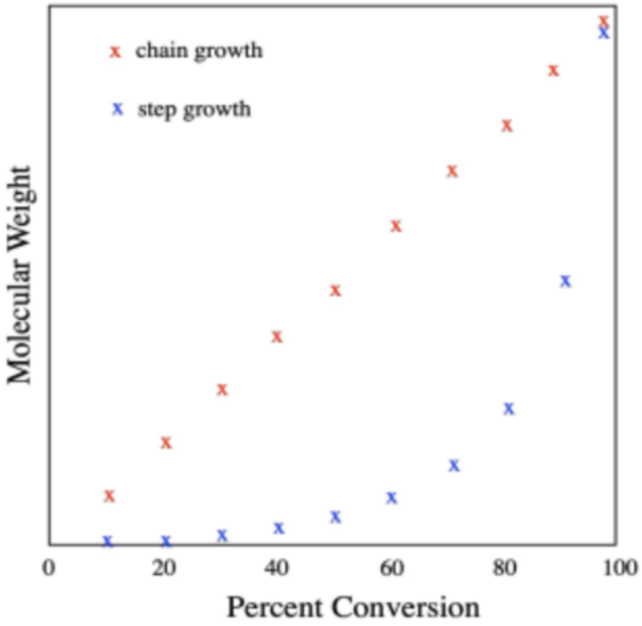


Figure 5: Molecular weight vs percent conversion for chain and step growth[152].

2.1.1 Step Growth Polymers

Step growth polymerizations rely in the reactivity of the functional groups of the monomer[42]. Typically, these functional groups are the end groups. The presence of at least two functional groups is necessary for the reaction. This simple linking reaction is the basis for linear step growth polymerization where difunctional monomers react to form the polymer chain. Trifunctional monomers would lead to branching or network formation. The challenge is the need for extremely high conversions to make high molecular weight polymers with desirable properties. Examples of step growth polymers of commercial relevance are polyesters, polyamides, polyurethanes, and even high-performance polymers like polysulfones (PSU) and polyetheretherketones (PEEK).

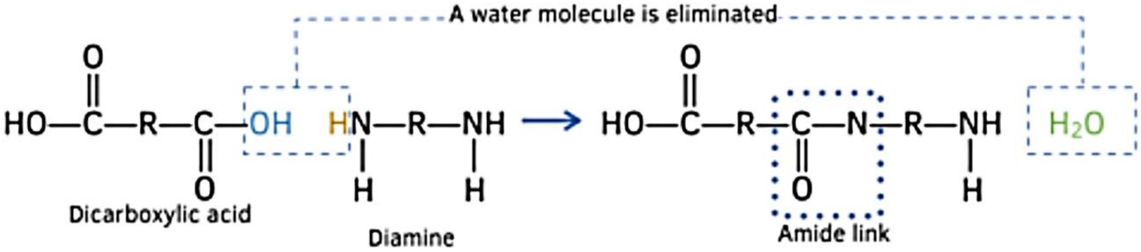


Figure 6: Polyamide reaction with the elimination of a water molecule[153].

Step polymerizations are divided into polycondensation and polyaddition. Polymerizations where a small molecule is eliminated is termed as polycondensation. For example, in the reaction between a dicarboxylic acid and a diamine for the synthesis of a polyamide, a water molecule is eliminated (Figure 6). Examples of polycondensation polymers are polycarbonates, PSU, PEEK, Polyimides, polyphenylene sulfides etc.

Polymerizations where the monomers react without the elimination of another molecule are polyaddition. Examples include epoxy resin and polyurethane.

2.1.2 Glass Transition (T_g) of Amorphous Polymers

Polysulfones are amorphous polymers. Amorphous polymers have randomly orientated molecules, and they typically have good dimensional stability. Solid state amorphous polymers can be thought of as frozen polymer liquids [42]. Glass transition temperature is the temperature at which amorphous polymers go from hard/ glassy state to soft/ rubbery state. For an amorphous polymer, properties can be dramatically different above and below T_g, which might not necessarily be the case for semi crystalline polymers due to only the amorphous portion of such polymers undergoing T_g. Thus, glass transition is an important property in the study of fully amorphous polymers. T_g is a second order thermal transition and can be measure via different methods such as using a differential scanning calorimeter to record the step transition or by using rheology/ dynamical mechanical analysis to obtain the peak of tan δ.

Factors controlling T_g

Different polymers have different T_g affecting polymer properties and their variation with temperature. T_g is affected by the chemical structure, copolymerization, molecular architecture such as molar mass, branching, crosslinking and film thickness. The value of T_g increases as the molar mass of the polymer increases. The following equation can be used to approximate this behavior:

$$T_g = {T_g}^{\infty} - \frac{K}{M_n}$$

Where,

${T_g}^{\infty}$ is the value of T_g for an infinite mass polymer sample,

K is a constant and

M_n is the number average molecular weight.

2.1.3 Non-linear Step Polymerization

Reaction of monomer with functionality greater than two leads to non-linear step polymerization where branched and network polymers are synthesized. The properties of these materials vary greatly. Epoxy resins are an example of a widely used network polymer. They are synthesized by the reaction between epichlorohydrin and bisphenol A, followed by an amine curing.

2.1.4 Copolymerization

Copolymerization reactions are between monomers that results in more than one type of repeat unit. Their properties depend on and can be controlled by the type and proportion of the monomers used. Simultaneously reacting a mixture of monomers is the simplest copolymerization method leading to statistical copolymers. Statistical step copolymerization is of the type ARB+ AR’B. For example, reacting hexamethylene diamine with adipic acid and sebacic acid gives copolyimide with both nylon 6,6 and nylon 6,10 repeat units [42].

The typical composition of a copolymer depends on the compositions of the monomers involved. The properties depend on the composition but also the sequence of the involved monomers. For monomers with similar reactivities, a random copolymer is formed as the probability for the reaction with a specific monomer depends only on the proportion of the monomer in the starting materials. For monomers with different reactivities, the higher reactivity monomer reacts in the initial steps and the less reactive monomer reacts in the later part of the polymerization giving a more block type of repeating unit.

2.1.5 High-Performance Polymers: HPP

HPP are characterized by their ability to withstand harsh chemical and/or thermal environments without change in properties[43],[44]. Some of the criteria for a polymer to be classified as HPP are, a thermal degradation temperature of 450°C at 5% weight loss, durability for 10,000 hours at 177°C, and high glass transition temperature (T_g)[43]. High performance polymers (HPP) account for 1% of plastics production by tonnage and are worth $ 13.2 billion in 2018[45]

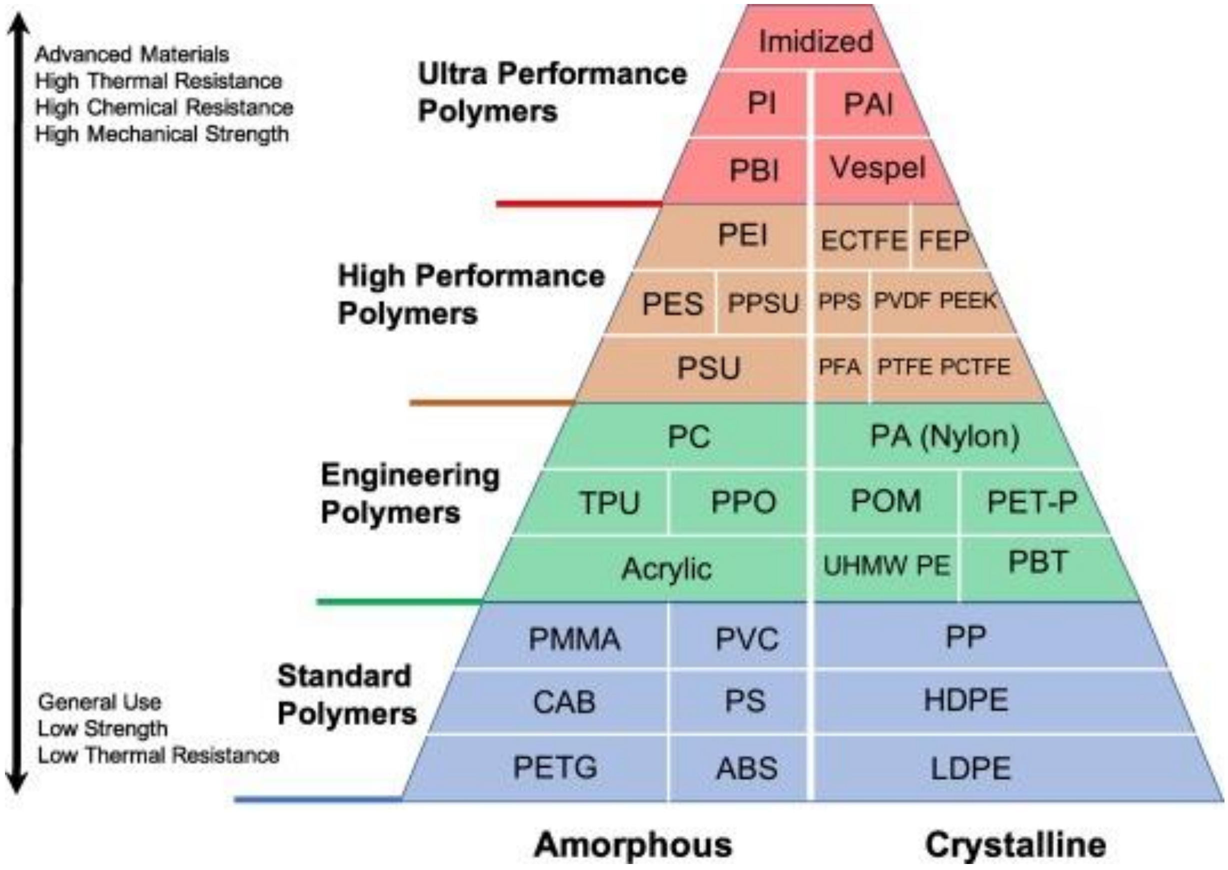


Figure 7: High performance polymer pyramid showing increasing thermal resistance, chemical resistance and higher mechanical strength going up. Examples of HPPs include polysulfones (PSU), polyetheretherketones (PEEK), perfluoroalkoxy (PFA), and other fluorinated polymers [44](Reproduced with permission from Elsevier, license number: 5797070771173)

2.2 Lignin as a biomass

Lignocellulosic biomass is primarily composed of a glucose-based cellulose, a xylose based heteropolymer hemicellulose and lignin [46]. Cellulose and hemicellulose comprise between 30-50% and 20-35% of biomass respectively. Lignin constitutes the remaining 15−30% of biomass and is a complex aromatic network heteropolymer [47]. This section aims to expand on lignin as the biomass of choice for the synthesis of the polymers in this work.

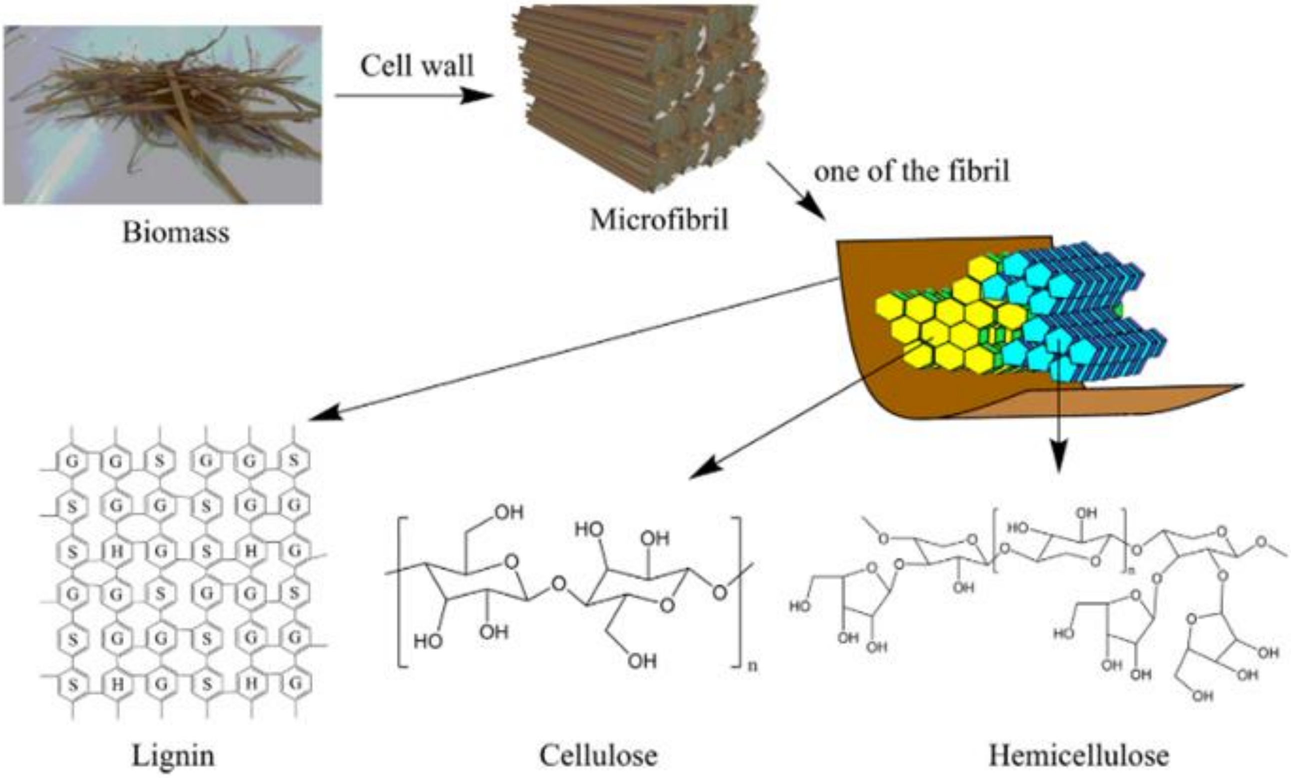


Figure 8: Lignocellulosic complex structure[46]. (Reproduced with permission from Elsevier, license number: 5797340762278).

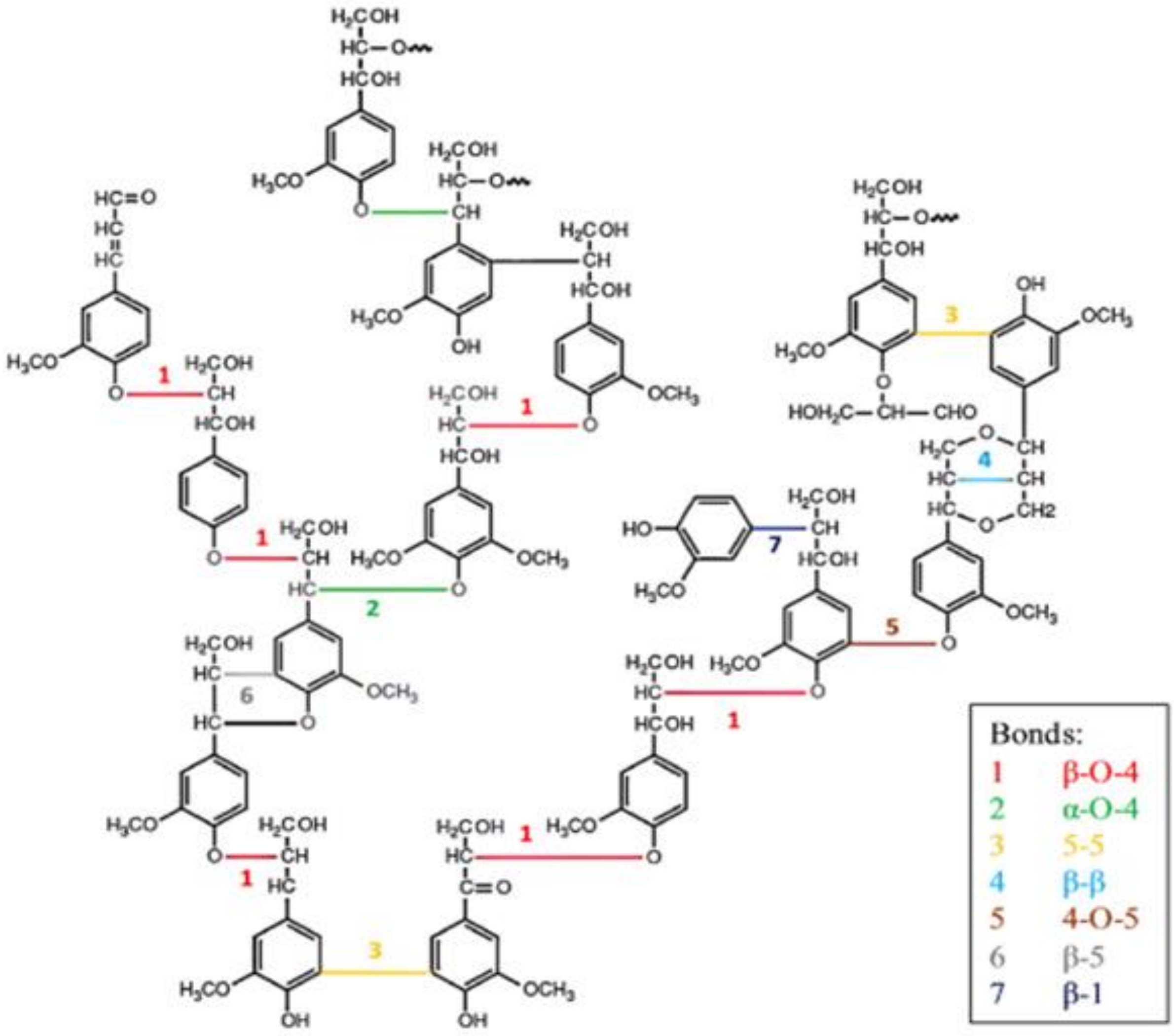


Figure 9: Lignin's chemistry and major bonds. Reproduced with permission from Elsevier, license number 5822751304684[48].

Lignin is the most abundant organic polymer on earth. It is composed of three major hydroxycinnamic alcohols (p-coumaryl, coniferyl, and sinapyl)[49]. These monolignols undergo oxidative coupling to form the structure of lignin. These phenyl propane units within the lignin differ in quantity based on the plant species [47]. These aromatic units are linked by various chemical linkages, with the β-O-4 linkages being the most prevalent and extensively studied in the context of lignin depolymerization[50].

The sulfite and kraft processes to isolate lignin from biomass contains sulfur, while the lignin from the soda and organosolv process does not[51]. Lignins isolated by any of these methods are referred to as technical lignins. While Kraft lignin, the majority of lignin extracted, is typically burned for fuel, increasingly work to investigate methods to depolymerize lignins to commercially viable products is being carried out. This is consistent with the biorefinery approach, where lignins instead of being burned are considered as a source of value-added aromatic building blocks [14].

Hydrogenation and oxidation are the two most common techniques used to degrade lignin. These techniques in addition to other techniques such as acidolysis are used to produce lignin-based chemicals like vanillin, syringaldehyde, guaiacol, dimethyl sulfoxide, dimethyl sulfide, etc. Only three products are commercially produced from lignin: vanillin, dimethyl sulfide, and dimethyl sulfoxide (2007). Dimethyl sulfide is obtained from the reaction of kraft lignin with molten sulfur in alkaline conditions, via the transfer of two methyl groups from lignin to sulfur. Dimethyl sulfide can then be oxidized with nitrogen dioxide to produce dimethyl sulfoxide[52] used widely as a green solvent.

2.2.1 Vanillin

Vanillin (4-hydroxy, 3-methoxy benzaldehyde) is a phenolic aldehyde commonly used as a flavoring agent in food, beverage, and pharmaceutical products. While vanillin can be extracted from vanilla bean, a natural source, more commonly, synthetic vanillin is produced from lignin or guaiacol or via functionalization of petroleum derived phenol. Vanillin from lignin is commercially isolated through the oxidation of lignin in alkaline conditions.

Norwegian company Borregaardthat produces 15% of the overall vanillin production globally from lignosulfonates in Sarpsborg, Norway[53]. The sulfite pulping of wood gives a lignosulfonate-rich sulfite liquor as a byproduct which is further processed as shown in Figure 10. Industrially, only lignin from the sulfite pulping process is used to prepare vanillin, even though it only accounts for less than 10% of the total of lignins extracted[54].

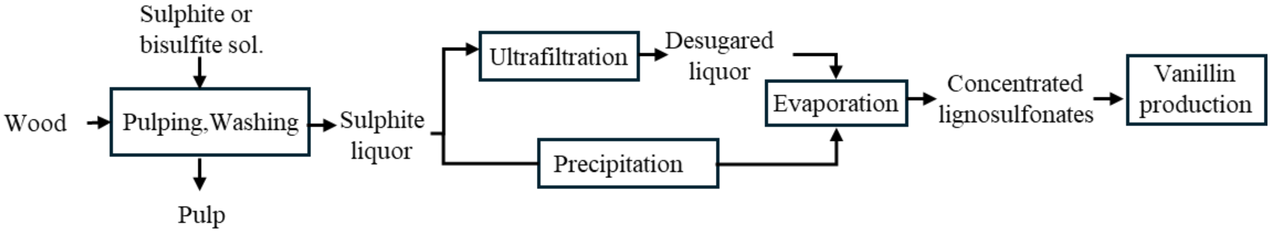


Figure 10: Schematic to produce vanillin from wood[15]. Adapted with permission from {*ACS Sustainable Chem. Eng.* 2016, 4, 1, 35–46} Copyright {2016}. ACS

The parameters that influence alkaline oxidative depolymerization of lignin are summarized in Table 3[55]. A review on the oxidation of lignin to yield aldehyde, namely vanillin and syringaldehyde was done by Rodrigues et.al[56]. Following the bath process parameter review, a continuous process was developed on a pilot scale to produce lignin at 1.8g/L, 85% of the maximum obtained from batch reactors[57]. Isolating vanillin from the oxidized solution is also a challenge. This downstream processing involved precipitation of lignin by acidification by adding CO_2 or a mineral acid. The recovery of vanillin is done by a liquid-liquid extraction with organic solvents like benzene, toluene. This extracted vanillin is a bisulfite complex insoluble in organic solvent and is finally acidified to recover free vanillin[58]. Other methods of extraction have also been proposed such as ion exchange[59,60], membrane filtration[61], supercritical extraction by recovering vanillin dissolved in CO_2[62] through bisulfite treatment[63] to achieve higher purity and further purification can be achieved up to 85-90% by successive crystallization and dissolution in methanol: water mixture[64], vacuum distillation[65], and using charcoal to adsorb the impurities[66] .

Table 3: Parameters that influence the alkaline oxidative depolymerization of lignin[15]. Adapted with permission from {*ACS Sustainable Chem. Eng.* 2016, 4, 1, 35–46} Copyright {2016}. ACS

Lignin	Lignin origin
	Prior processing
	MW, PDI
Reaction conditions	Lignin concentration in feed
	Reaction conditions (temperature, pressure, time)
	Nature and concentration of base, catalyst, and oxidant

More recent work has focused on finding effective catalysts[67] to solve the problem of avoiding over oxidation. Metal catalysts and ionic liquids were screened in a study by Stark et al. to ensure optimal oxygen solvation and prevent over oxidation. They found Mn(NO3)2 (2% catalyst loading) in 1-ethyl-3-methylimidazolium-trifluoromethansulfonate ([EMIM][CF3SO3]) gives the highest conversion (63%) to monomeric products such as vanillin, syringaldehyde, syringol, and 2,6-dimethyoxylbenzoquinone[68]. Original methods such as using molecular imprinting polymer technique to create a 3D crosslinked polymer with binding sites capable of recognizing vanillin with high selectivity for purification[69] have also been discovered.

Vanillin and its derivatives are of interest in the synthesis of a variety of polymers[70] such as polyester[20], epoxy resins[71,72], polycarbonate[73,74], unsaturated polyolefins[75,76] and schiff base polymers[77,78]. In strongly oxidizing conditions, vanillin may be oxidized to vanillic acid or to methoxyhydroquinone via decarboxylation[52] and in strongly reducing conditions, vanillin can be reduced to vanillyl alcohol[15,75].These monomers with their different functional moieties can serve as a platform to synthesize a variety of biobased aromatic polymers including polysulfones.

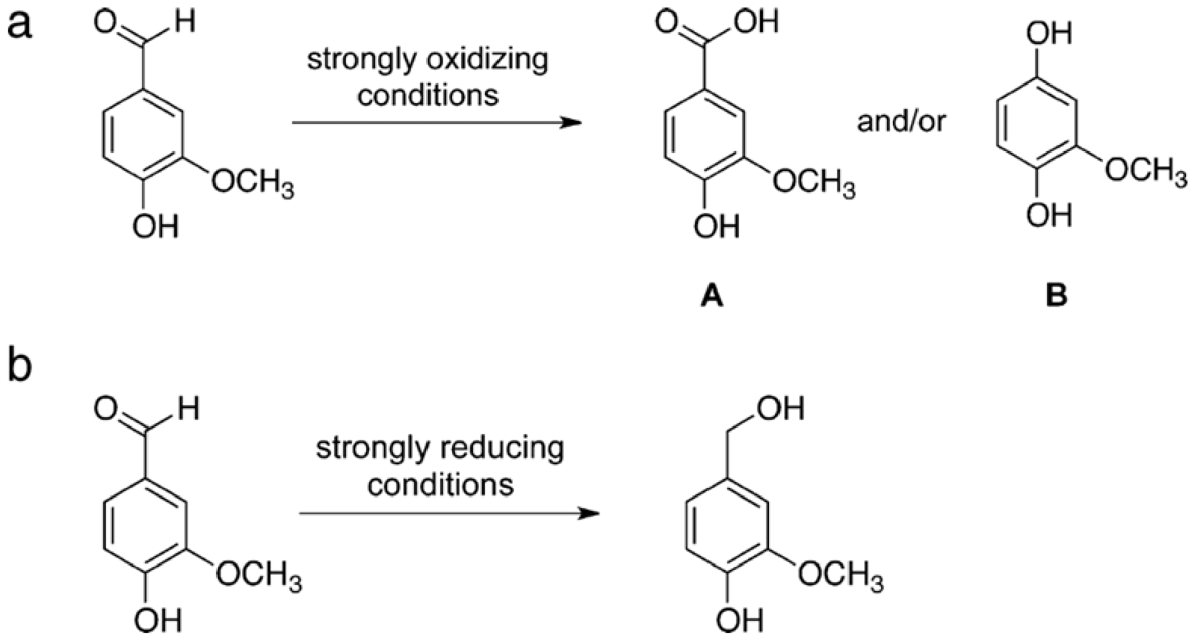


Figure 11: a) Formation of vanillic acid (A) and/ or methoxyhydroquinone (B) under strongly oxidizing conditions. B) Formation of vanillic alcohol under srongly reducing conditions[47]. Adapted with permission from {Chem. Rev. 2016, 116, 4, 2275–2306}. Copyright {2016} American Chemical Society.

2.3 Polysulfones:

PSU are amorphous HPPs containing aryl -SO_2- groups in their backbone. These lend the polymers higher glass transition temperatures (T_g), greater solubility, and thermo-oxidative stability[79]. PSU have high T_g 185°C, retain mechanical properties in a wide temperature range, are resistant to mineral acids, alkalis, oxidizing agents, electrolytes and are hydrolytically stable. These properties allow the use of PSU in medical applications[80,81], wastewater recovery[82], food processing, automotive[38], as insulating material in electronics, and oil and gas[44]. Sulfonated PSU have been explored for use as proton exchange membranes for fuel cell applications[39]. 3D printed

PSU have also been explored for use in water-oil separation membranes[37,40]. Polysulfone (PSU) were valued at $1.6 billion in 2020 with projected growth to >$2.3 billion by 2027[83].

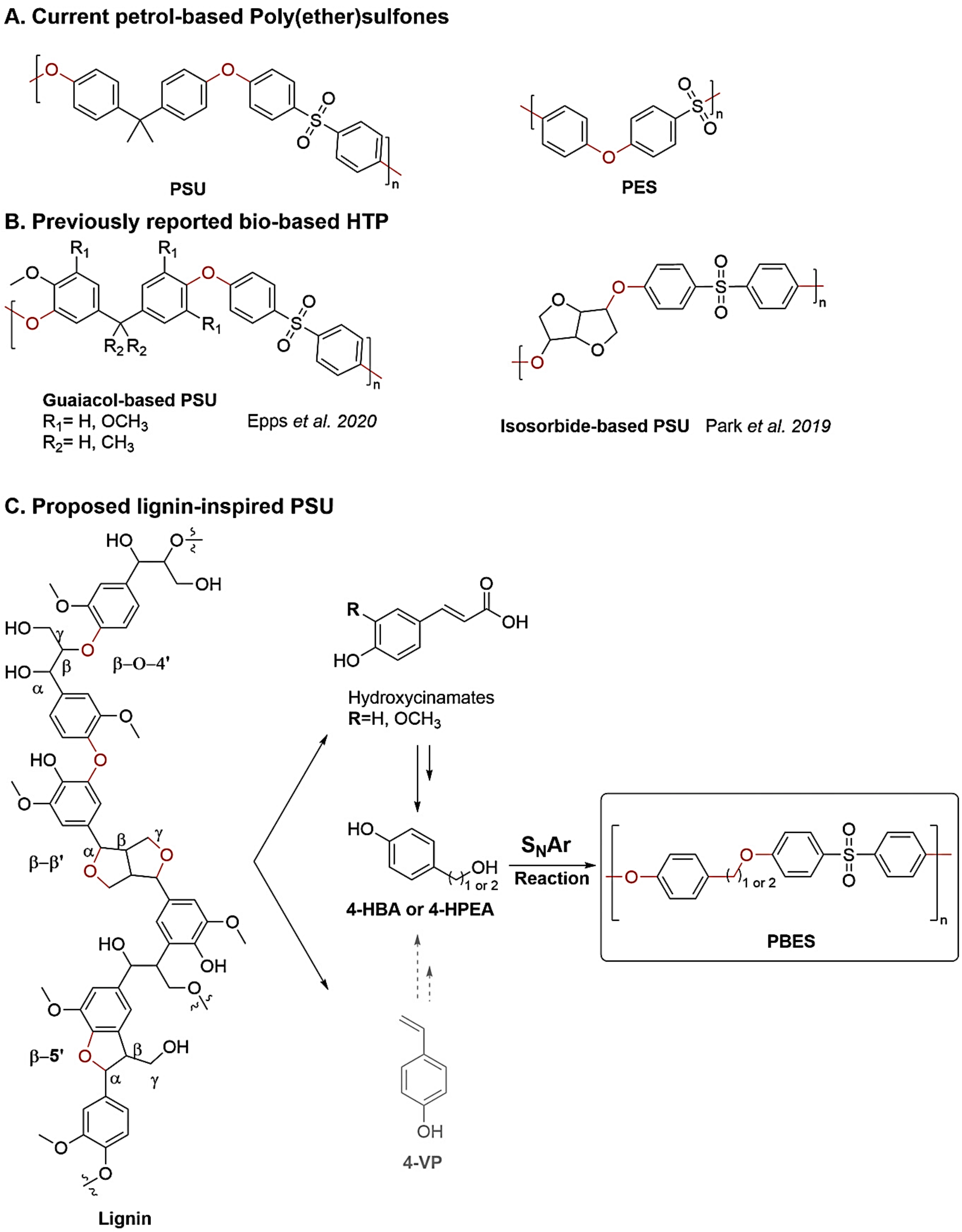
In general, polysulfones are obtained via polycondensation between di-halogen containing disulfone group (DXDPS) with a diphenol in the presence of a base catalyst[84],[85]. Typical polysulfone synthesis uses BPA as the diol. However, BPA has been recognized as a multifunctional endocrine disruptor. It is structurally similar to thyroid hormones (THs) and could act as a TH antagonist causing disruption of the thyroid system[22,86]. It is also linked to aquatic toxicity and is increasingly being considered a potential concern for the ecosystem.

Hazard Statement	
H317	May cause an allergic skin reaction.
H318	Causes serious eye damage
H335	May cause respiratory irritation.
H360	May damage fertility or the unborn child.
H411	Toxic to aquatic life with long lasting effects.

Figure 12: Hazards associated with BPA recreated from Safety Data Sheet Sigma Aldrich (9 July 2024)[154].

Due to the concerns for the effects of BPA on the human body and the environment, research has been done on making polysulfones by replacing BPA with biobased and nontoxic alternatives such as lignin. By methylating the excess hydroxyl groups to reduce crosslinking and branching, functionalized Kraft lignin was used to synthesize thermoplastic PSU and the properties controlled by careful depolymerization and methylation of the lignin biomass, albeit with modest MW (~900 Da)[87]. Studies on using derivatives of lignin in PSU synthesis have also been performed by using bisguaiacol as an alternative diol to BPA[88], and model compounds from lignin[89] and isosorbide[90]. Recycling was demonstrated for a lignin-based PSU via bromination and acid cleavage[89]. Another study employed depolymerized lignin to produce a wholly biobased bisphenol featuring pendant-furyl groups. These furyl moieties facilitate Diels-alder based crosslinking, enabling recycling of the resulting thermoset PSU. The properties of the crosslinked copolymers were found to be higher than the parent copolymer and properties post recycling were comparable to those of the virgin copolymer[91].

Yu et al. concluded that due to the mixing of impurities and degradation of the molecular structure during mechanical recycling, the long-term stability of virgin PSU are better than recycled PSU [92]. This points to the need for the chemical recycling of thermoplastics.



A. Current petrol-based Poly(ether)sulfones

B. Previously reported bio-based HTP

C. Proposed lignin-inspired PSU

Figure 13: PSU Synthesis from A) petroleum, B) literature, C) lignin derived model compounds[89].

2.4 Recycling Strategies:

Most recycling studies have targeted commodity polymers due to the enormous waste volume generated. Increasingly research has moved towards recycling by design owing to the limitations in other methods. Landfilling is limited and has the potential to contaminate groundwater and soil[93–95]. Primary mechanical recycling is limited to industrial scraps[28]. Secondary mechanical recycling needs expensive pretreatment, and any contamination can degrade the polymer matrix and result in diminished material properties[27,96]. Tertiary chemical recycling techniques like solvolysis, glycolysis, pyrolysis, hydrogenation, and gasification[97,98] have all been extensively researched. The major drawback is that such techniques are limited in what types of materials they can handle[99], which implies that the waste must be reasonably free from other materials to prevent unwanted byproducts. Pyrolysis is advantageous in terms of volume reduction and energy recovery[100] however tends to generate dioxins in the case of halogen-containing plastics[101]. The quaternary technique of incineration[102] shares the same problem as pyrolysis.

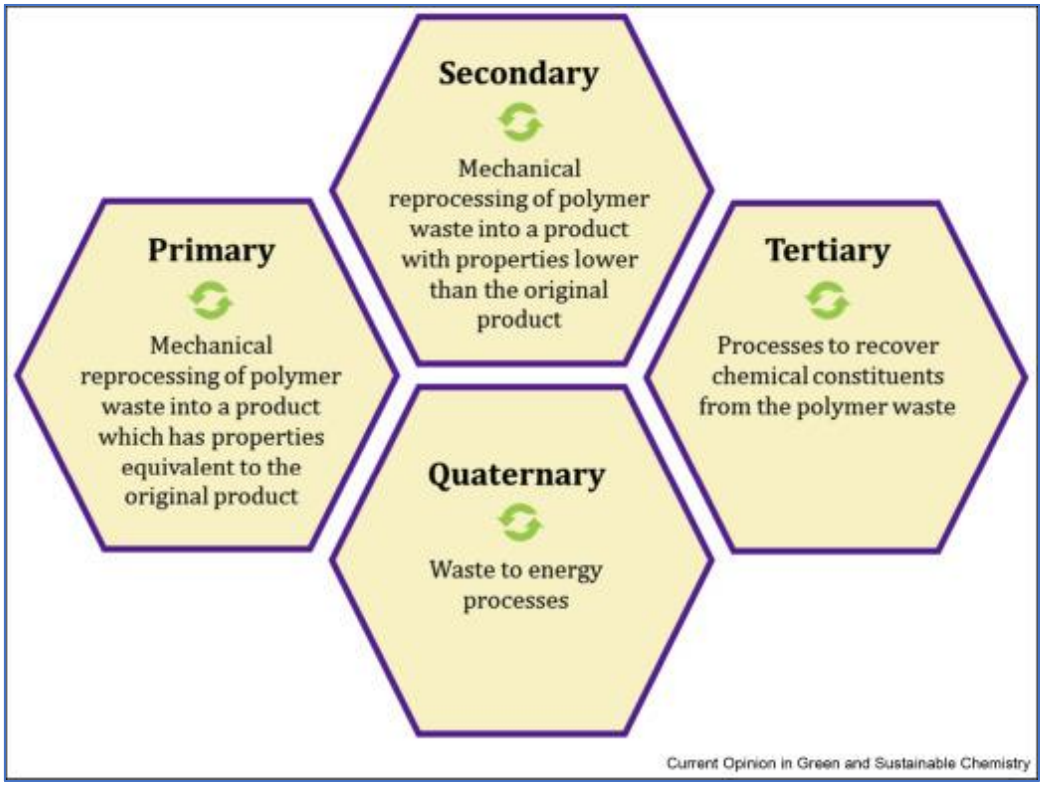


Figure 14: Recycling methods to deal with plastic waste[103]. Adapted with permission from Elsevier, license number: 5797320826215.

Incorporating reversible covalent bonds is a recycling-by-design strategy referred to as DCC (Dynamic Covalent Chemistry)[104]. These bonds can bring thermosetting materials closer to thermoplastic by increasing their processability and recycling and can additionally lead to an increase in thermal and mechanical properties. The drawback of this strategy is that it does not contribute to the existing waste stream and can only help going forward. The principle of DCC is the equilibrium between various species with desirable properties, and their intermediates. These species can be selectively favored by shifting the equilibrium by modifying the conditions to recover the now stable product. Recycling is accomplished by switching between intermediates and products by manipulating the equilibrium shifts. DCC [33,105,106] has been applied to synthesize a variety of smart, recyclable, and self-healable materials. This chemistry is characterized by[32] a thermodynamically stable product to overcome the entropic cost of assembly, covalent linkages between building blocks, and reversible intermediates. Equilibrium processes are typically slower; thus, this leads to use of catalysts to equilibrate to the thermodynamically stable product in a reasonable time frame[107]. The advantage to that is that without external stimuli such as a catalyst, these covalent bonds do not undergo rupture and the product formed is stable, while also enabling recycling simply by catalyzing the rupture allowing for recycling. Examples include Diels-Alder[108], imine chemistry[78], disulfide[109], disulfide-thiol, ketoenamine[110] etc.

2.4.1 Imine Chemistry:

Imine chemistry has been a widely utilized DCC. Imine formation via condensation of an aldehyde or ketone with a primary amine is well known[35]. Figure 15 shows a free energy diagram of a simplified imine reaction including the formation of the intermediate tetrahedral hemiaminal[111]. The overall imine formation is exothermic even though the intermediate formation is endothermic. This endotherm is the low energy barrier towards imine formation that can typically be overcome at mild temperatures and the final imine product is thermodynamically stable making it ideal for a use as a dynamic covalent bond.

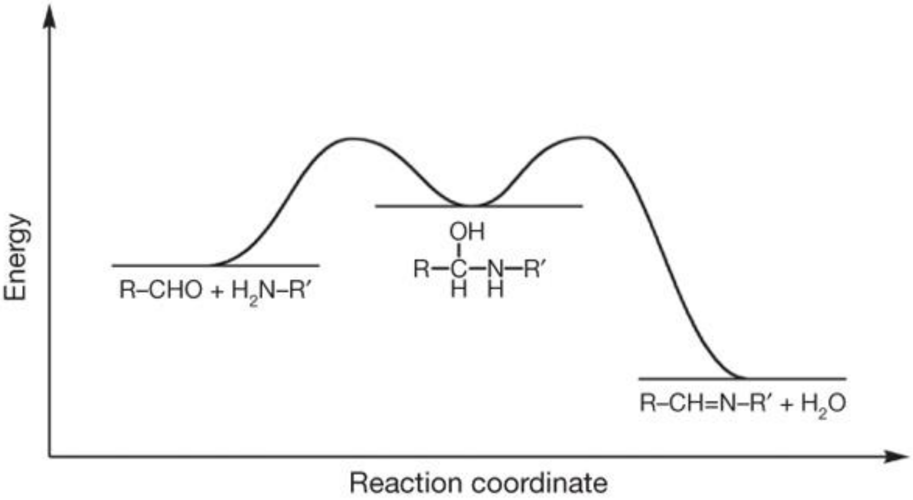


Figure 15: Simplified imine free energy diagram with its intermediate.[111] Reproduced with permission, license number 5822761123282.

Figure 16 illustrates the major imine reaction types. Imine association reaction in simple the condensation reaction between an aldehyde and an amine. Hydrolysis or dissociation can be achieved by dissociation in acidic media to enable recycling. The other associative pathways include transamination and imine metathesis.

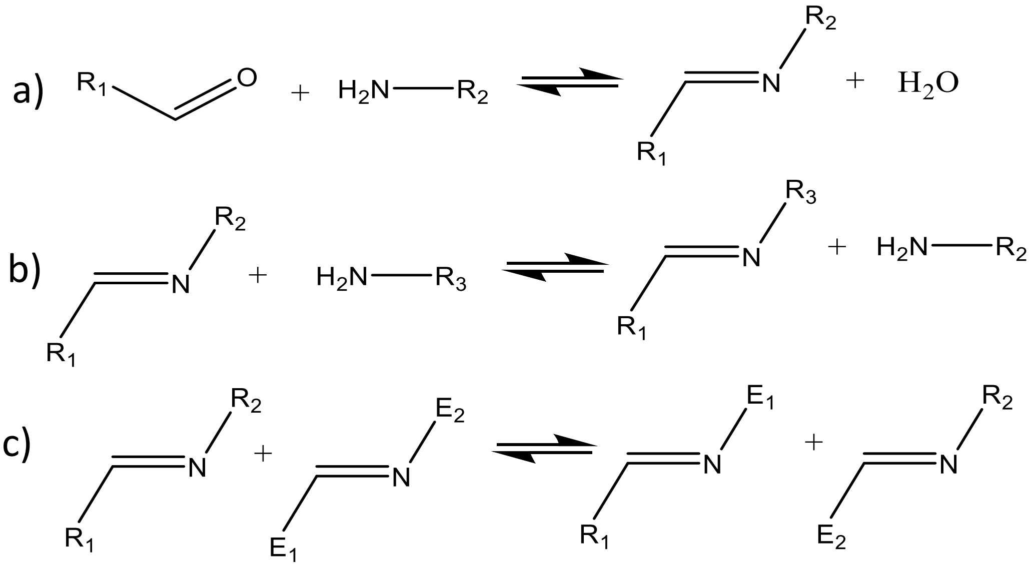


Figure 16: Imine association and dissociation pathways: a) hydrolysis, b) transamination, c) imine metathesis.

The contributing factors to high thermal properties for polymers using imine are resonance stabilization, secondary bonds like hydrogen bonding, Vander Waals forces, etc., high molecular weight, and narrow molecular weight distributions[43]. Imine chemistry is favorable because of the high bond energy of the C=N bond (166 kJ/mol)[112] and its metathesis could help synthesize polymers of narrow molecular weight distributions. Imine chemistry has been utilized in the synthesis of self-healing polyurethanes[78], malleable thermosets with flame retardancy properties [113] reprocessable vanillin based vitrimers[77] that could be utilized as adhesives, etc. The drawback is in the hydrolytic instability of imine bonds. However, that can be exploited for biodegradability[114], property tuning[34], or overcome by shielding the bonds from water.

This study aims to make thermoplastic PSU, herein referred to as PIS (polyiminesulfone) that are non-toxic, sourced from bio-based feedstock and are chemically recyclable via dynamic covalent imine bonds. In chapter 3 “Synthesis of Biobased and Chemically Recyclable Polysulfone” a vanillin-based monomer with an imine bond is used to synthesize PIS as an alternative to the traditional polysulfone. PIS is then studied under various conditions to draw conclusions about the impact of imine bonds on polymer synthesis conditions and the properties. The work then moves on to study the chemical recycling of PIS in chapter 4 “Chemical Recycling of Polyimine Sulfones via Imine Chemistry”. This chapter focuses on exploring the conditions required for recycling and minimizing any side reactions. The properties of the recycled PIS were then compared to the virgin material. From this, the work goes on to study derivative polysulfones in chapter 5 “Biobased and Chemically Recyclable Derivative Polyimine Sulfones”. Co-polymers and network PIS were synthesized using other lignin derived chemicals and compared. Finally, in chapter 6 “Life Cycle Analysis” the feasibility and impact of chemical recycling of this new PIS was compared with PSU.

CHAPTER THREE:

SYNTHESIS OF BIOBASED AND CHEMICALLY RECYCLABLE POLYIMINE SULFONE

3.1 INTRODUCTION

Globally the production of plastics has grown from 2Mt to 380 Mt between 1950 and 2015 at a compound annual growth rate of 8.4% [1]. The use of petroleum resources in the synthesis of such materials adds to the environmental footprint of plastic production, prompting a shift towards more renewable feedstock such as lignin, agricultural byproducts, or organic waste feedstocks for valorization. For example, synthesis of polymers such as polymethacrylates from lignin[115,116], polyurethanes[117] and epoxies[118] from lignin derivatives, epoxide blends from soybean oil[119], biobased polyamides[120] from vegetable oils, biobased composites[121] etc. The choice of feedstock is important since biobased sources may not necessarily be sustainable. Environmental damage caused by deforestation for increasing agricultural material acquisition must be avoided. This also has social implications for the possibility of taking away from the food sources for human consumption. With these considerations, lignin was selected as the feedstock in lieu of agricultural products like glucose, vegetable oils etc. Lignin is a byproduct of the paper and pulp industry and is typically burned for fuel consumption. Use of lignin in polymer production as opposed to quaternary fuel use is upcycling by the value addition of the final product.

This shift in renewable material source also presents an opportunity for the replacement of toxic chemicals in the use of plastic production. Bisphenol A[86] which is widely used has been linked to adverse health effects, and its replacements Bisphenol F and S[122] have also been suspected of having comparable risks to BPA rendering their purpose as safer substitutes moot.

BPA free biobased materials have been synthesized in making polymers such as polycarbonates[74], furanic diols[22], epoxies[21] etc.

The polymer of interest in this study is polysulfone (PSU). PSUs are amorphous HPPs with high T_g 185°C. They are chemically and mechanically resistant and have good thermal stability. In general, polysulfones are obtained via polycondensation between di-halogen containing disulfone group (DXDPS) with a diphenol in the presence of a base catalyst[84],[85]. The diol used is typically BPA. Work has been done to replace BPA with biobased and nontoxic alternatives such as lignin[87] and its derivatives[88]. Recycling was demonstrated for a lignin-based PSU via bromination and acid cleavage[89] though no mention of the properties of the recycled material was made.

Much work has been done to solve the plastic problem. From using renewable feedstock, to replacing toxic chemicals and designing for recyclability in a bid for greener material synthesis. In accordance with green chemistry principles, this study was designed to synthesize polysulfones that are partly sourced from renewable sources derived from lignin, does not utilize the toxic BPA, and have the capability for chemical recycling.

3.2 EXPERIMENTAL SECTION

3.2.1 Materials

Vanillin (≥ 99%), 4amino-phenol (≥ 98%), bis (4-florophenyl) sulfone (DFDPS) (≥ 99%), bisphenol A (BPA), potassium hydroxide (KOH) (≥90%), toluene (≥ 99.5%), and dimethyl sulfoxide (DMSO) (≥99.9% ACS grade) were sourced from sigma Aldrich. The chemicals were used as received with no further purification.

3.2.2 Synthesis of monomer: BPA alt

In a beaker 40 mmol (6.08 g) of vanillin and 40 mmol (4.36 g) of 4-aminophenol were added to 125 mL DI water and stirred for 4 hours at room temperature[34,123]. The resulting yellow mixture was filtered by centrifuging, washed with DI water, and left to dry overnight. The final product was a pale-yellow powder. The formation of this di-phenol was confirmed via H-NMR and C-NMR, where an imine peak was observed at 8.4 ppm in H-NMR and an ether peak in C-NMR was observed at 152 ppm.

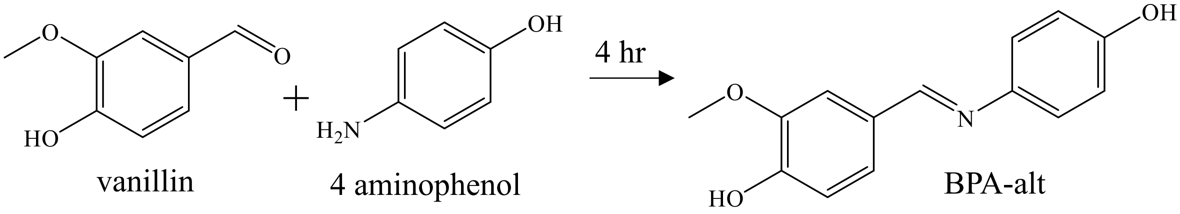


Figure 17: Synthesis of BPA-alt from vanillin and 4 aminophenol in DI water for 4 hours.

3.2.3 Synthesis of polymer: Polyiminesulfone

The next step of the process is a base SNAR-driven nucleophilic substitution. 5 mmol of BPA-alt (1.21 g), 10 mmol of KOH (0.56 g) and 20 mL of DMSO were added to a round bottom flask and reacted at 55 °C for 2.5 hours. This led to the formation of an insitu phenoxide intermediate using a strong base, KOH that deprotonates the BPA-alt shown in reaction scheme Figure 17. This step increases the reactivity of the BPA-alt as the anion is more reactive than the hydroxyl group. Additionally, it eliminates the formation of HF as a byproduct which would lead to imine dissociation. The selection of DMSO as a solvent is based on its polar, non-protic characteristics, non-toxicity, and its inability to solvate the nucleophile, ensuring reaction integrity. Previous experiments that successfully used DMSO instead of NMP for PSU synthesis contribute to this selection[84,87].

The formation of the phenolic base intermediate produces water which hinders further polymerization. It was removed using a low boiling azeotrope of water and toluene via a dean stark trap under nitrogen. Dry toluene washes were done to ensure removal of water.

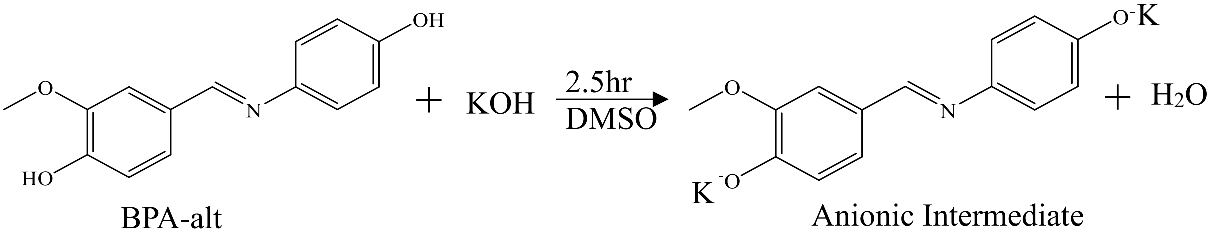


Figure 18: Synthesis of anionic intermediate after 2.5 hours or reaction with base in DMSO as a solvent.

The polymerization was then done by adding DFDPS (5 mmol, 1.27 g) to the flask for 4 hours at 120°C, reaction scheme Figure 19. DFDPS reacts with the intermediate forming a resonance stabilized Meisenheimer complex where the fluorine acts as a leaving group, to yield an ether bond. The polymer was recovered by utilizing water as a non-solvent. It is then centrifuged, washed, and dried. The polymer structure was confirmed via H-NMR where an imine peak is observed at 8.6 ppm and a C-NMR where an ether peak is confirmed at 153 ppm.

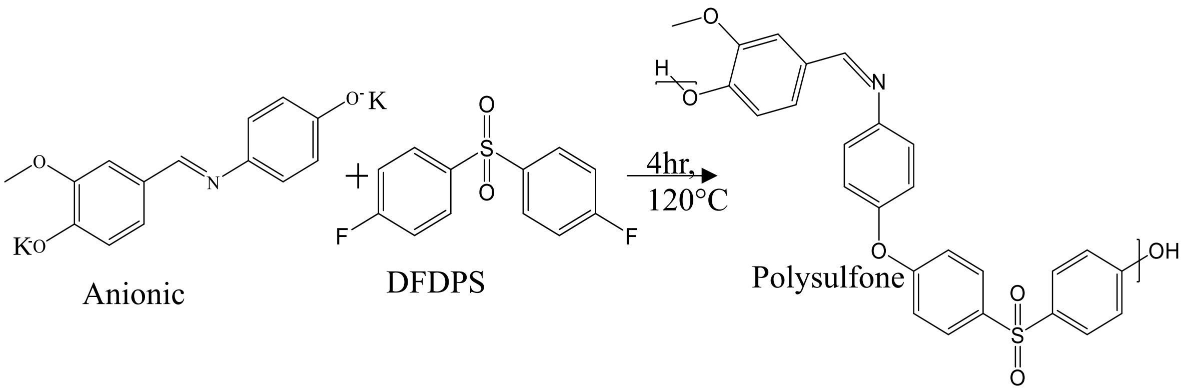


Figure 19: Synthesis of polyiminesulfone PIS via polycondensation of anionic intermediate and DFDPS (4,4 difloro-diphenyl sulfone)

3.2.4 Characterization

Chemical

Attenuated Total Reflectance Infrared (ATR-IR) Spectroscopy - Spectra were collected by a Thermo 6700 spectrometer from 500–4500 cm^{-1} using 16 scans. Nuclear Magnetic Resonance (NMR) spectroscopy - NMR spectra were collected on Bruker Neo 300 MHz spectrometer and Bruker Neo 500 MHz spectrometer. The solvent used was d-DMSO. Topspin 4.2 software was used for data analysis and integration. Trioxane was used as an internal standard.

Gel Permeation Chromatography

The molecular weight of polymer samples was measured using GPC (Alliance GPCV2000) with a Waters Styragel HT5 followed by Agilent PolarGelL column. The polyiminesulfone was dissolved in N, N dimethylformamide at a concentration of 1 mg/ml. 0.2 um nylon filters were used for the mobile phase. PEG calibration standards were used with a Waters differential refractometer and 2487 UV-Vis detector. A multi angle light scattering detector (MALS) was also used for molecular weight distribution determination.

Thermal Analysis

A Differential Scanning Calorimetry (DSC) 2500 TA instruments was used to study T_g of samples with a heat-cool-heat cycle at 10 ℃/min under nitrogen atmosphere. Degradation was studied by a Thermogravimetric Analysis instrument (TGA) 5500 TA instruments with a ramp rate of 20 ℃/min from 30 ℃ to 700 ℃.

3.3 RESULTS AND DISCUSSION

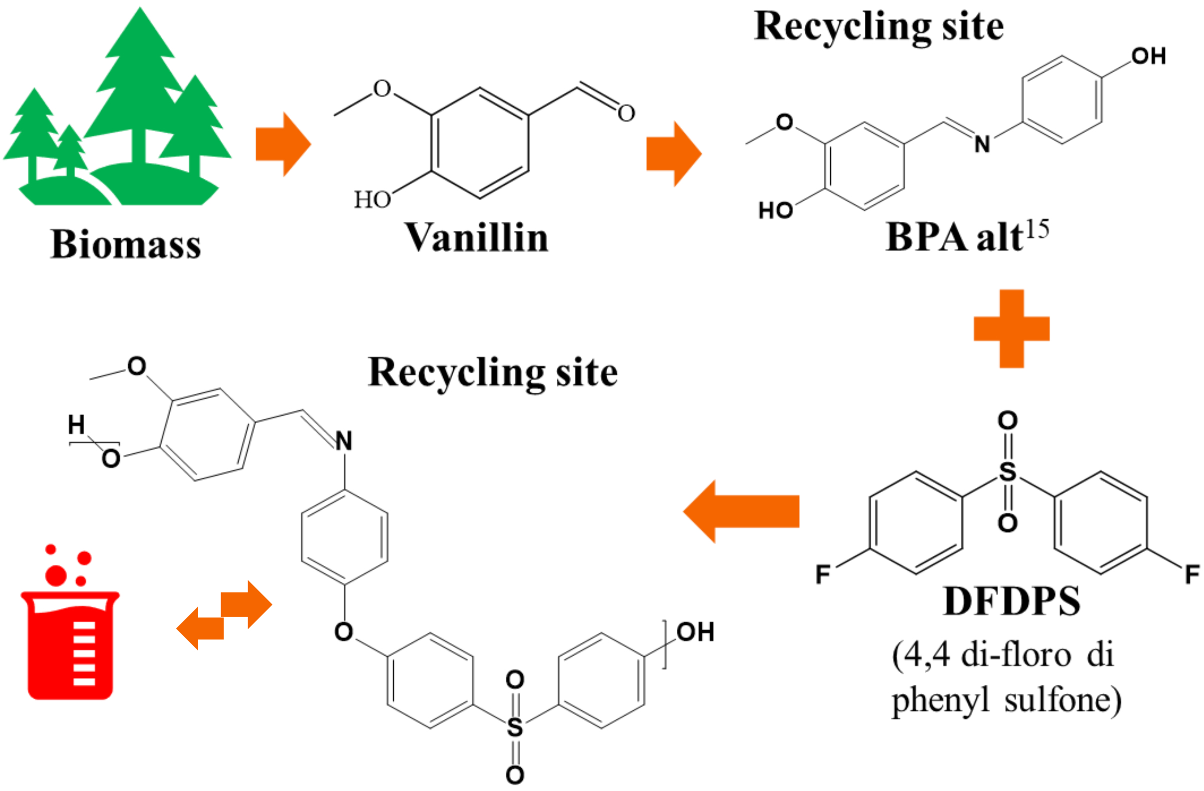


Figure 20: Overall Reaction Schematic

3.3.1 Structural Characterization

The reaction scheme in Figure 20 shows the chemical structure of the monomer (BPA- alt) formed via reaction between aldehyde and amine to an imine bond. From the H-NMR analysis (Figure 21), the presence of the peak at 8.4 ppm corresponding to imine is used to determine successful monomer synthesis[123]. The 5 doublets in the ~7.5 to ~6.7 ppm region correspond to the aromatic peaks of BPA-alt. The peak at ~3.8 ppm is assigned to the vanillin methoxy group. Trioxane was used as an internal standard (~5.1 ppm) as a check for peak shifts. From the spectroscopy results the reaction between vanillin and 4-aminphenol was successful and the expected peaks were accounted for.

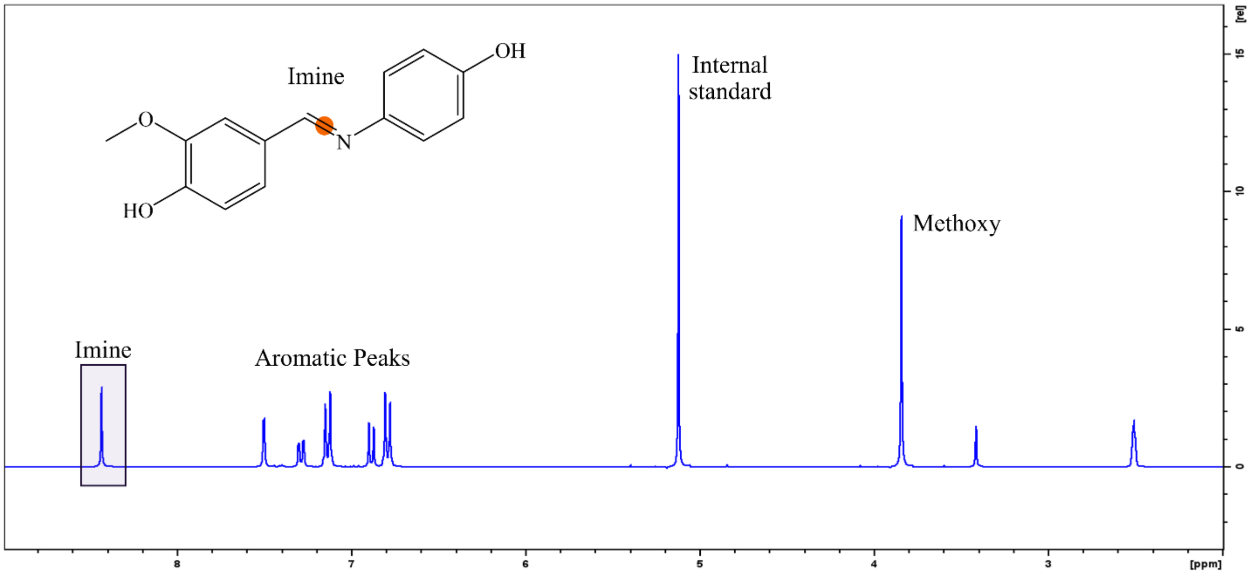


Figure 21: H-NMR of BPA alt with imine peak highlighted.

Next, the biobased bisphenol was used to create the chemically recyclable polysulfones using the procedure in the experimental section. The polymer structure is shown in Figure 22. The carbon adjacent to the ether bond of interest between the phenolic salt of BPA and the leaving -F group of the DFDPS monomer is highlighted in orange along with the carbons next to imine and sulfones. A C-NMR shown in Figure 22 is done to confirm the polymerization by identifying the ether peak at 155.6 ppm. H-NMR analysis shows peaks corresponding to imine at ~8.6 ppm, aromatic BPA-alt doublets at ~7.3 to ~ 6.3 ppm. It also has aromatic peaks from the DFDPS monomer at ~7.5 and 7.1 ppm. The methoxy group from vanillin in at 3.8 and trioxane as an internal standard at 5.1 ppm. In Figure 23 a stacked H-NMR spectra of the monomer and polymer is shown to show peak broadening of all aromatic peaks and peak shifts. Specifically, the imine peaks from BPA-alt shifts from 8.4 to 8.6 ppm and the aromatics from 7.5-6.7 to 7.3 to 6.3. These can be used as indicators to further confirm polymer formation.

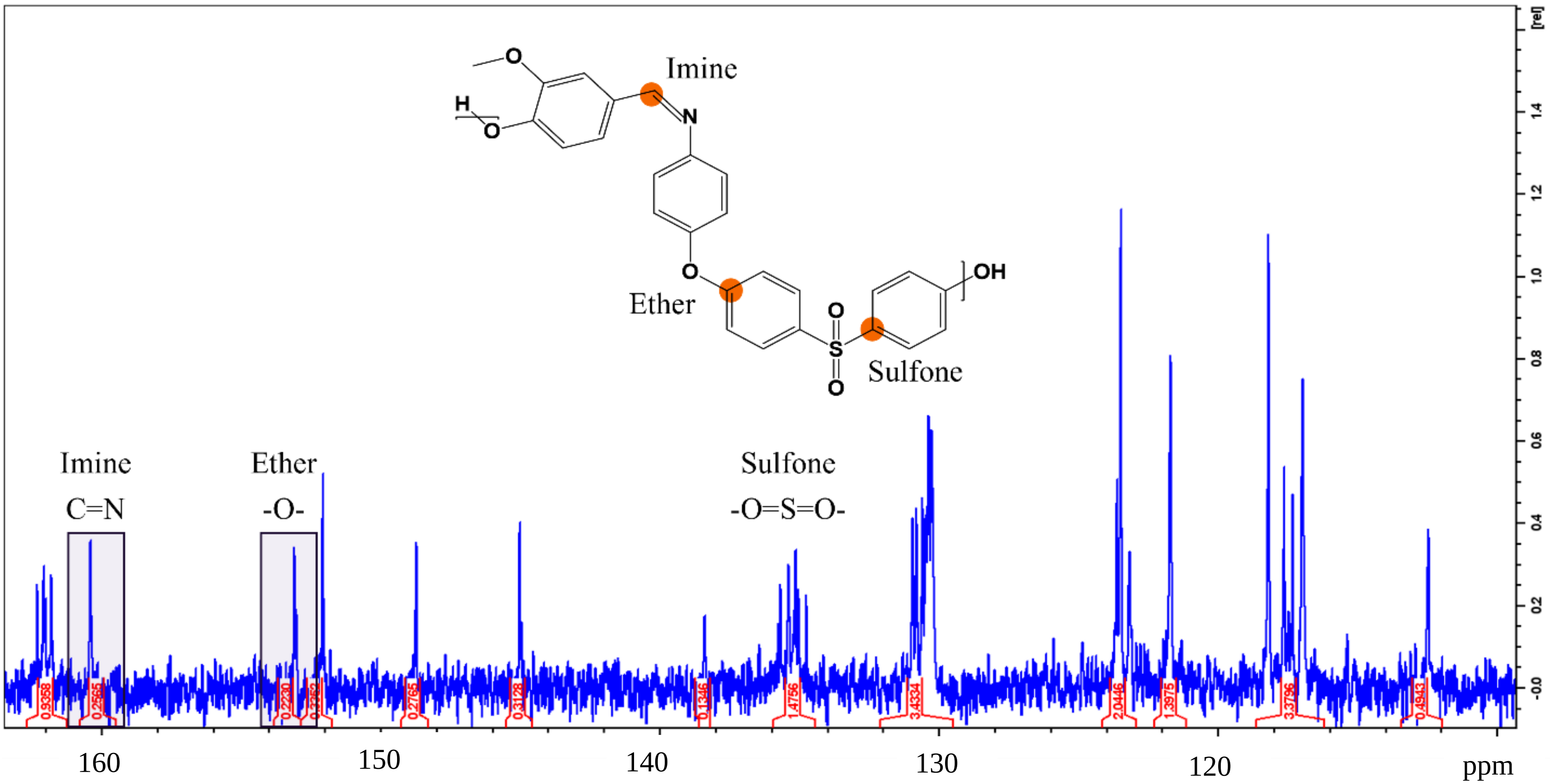


Figure 22: C-NMR of PIS with key peaks highlighted.

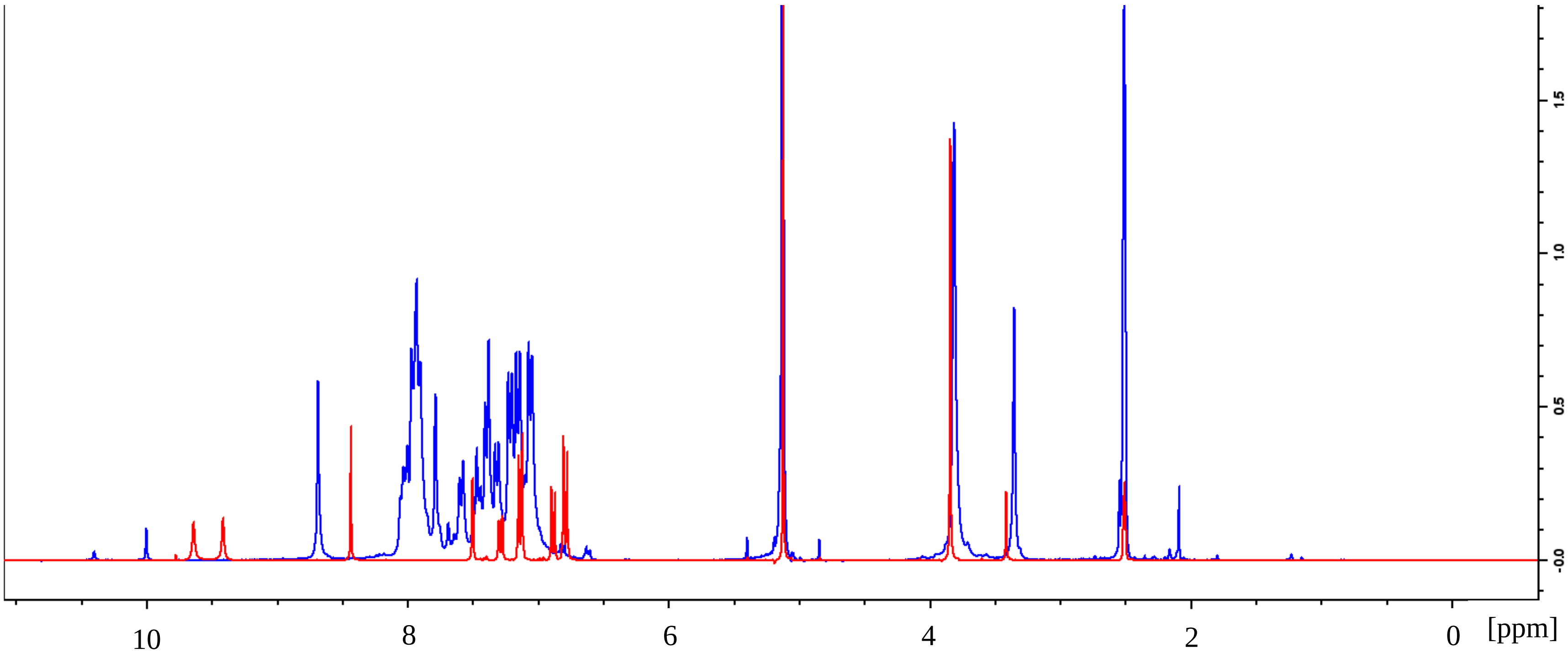


Figure 23: Stacked H NMR spectra of BPA alt (red) and PIS (blue) to show peak shift and broadening.

During the polymerization, it is important to monitor the imine peak to track any possible degradation and was studied in next few studies to determine the effect of reaction conditions on the imine bond.

3.3.2 Control Study

The imine bond is liable to undergo dissociation when hydrolyzed. While this process is accelerated in acidic environment, water and higher temperature conditions can still cause the imine to dissociate. Since the in situ intermediate reaction of the phenolic salt generates water, a control study was conducted to investigate the effect of solvent, base, and temperature on the imine bond in the monomer. Aliquots of the reaction were taken out at different times to monitor the concentration of imine bonds based on an internal standard. Figure 24 summarizes the results of the study. Pre-distillation refers to reaction before toluene was added for azeotropic distillation. Post-distillation refers to sample after the toluene-water azeotrope was removed via distillation. The time of 1-24 hours was used for the reaction without DFDPS. The percent dissociation of the imine is calculated by comparing the expected amount of imine in the sample and the actual imine peak integration from the H-NMR via quantitative analysis by utilizing trioxane as an internal standard. Trioxane is chosen as an internal standard since it has a single sharp peak corresponding to 6-H atoms at ~5.1 ppm in a region where no other sample peaks are expected. The calculation method is as given in Equation 1:

Sample calculation: $\%\, mine\ dissociation = mol\ imine\, \frac{theoretical - actual}{theoretical} * 100$

$$mol\ imine = mol\ trioxane\ \left(\frac{mass\ in\ nmr\ sample}{MW\ of\ trioxane}\right) * 6 * \frac{peak\ integration\ of\ imine}{peak\ integration\ of\ trioxane}$$

Equation 1: Formula used to calculate the % imine dissociation.

Table 4: Summary of the imine stability control study

Time	**% Imine Dissociation**
Pre-distillation	10.9
Post-distillation	36.4
1	10.9
2	28.2
3	80.8
4	73.3
5	85.5
24	99.9

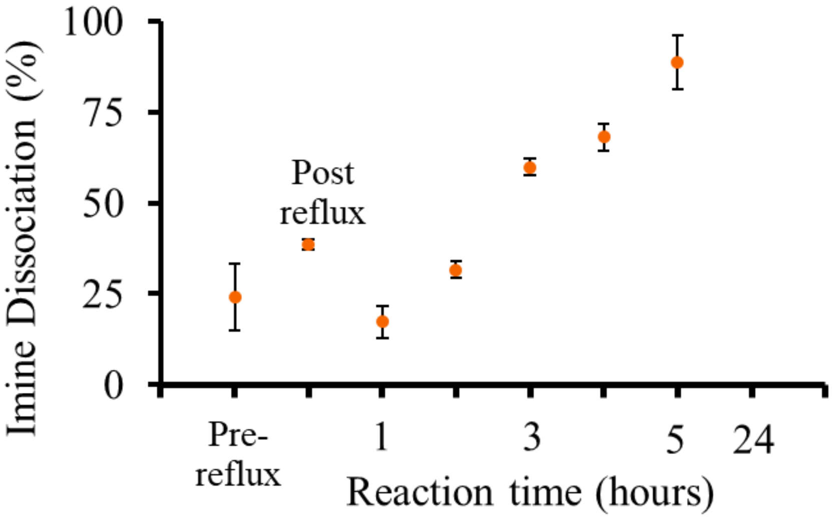


Figure 24: Imine control study showing an increase in dissociation.

The decrease in imine bond is proof of dissociation of the bond during the reaction. The recovery of imine bonds followed by post-distillation and is attributed to the removal of the water causing a decrease from 36.4% to the initial levels of dissociation at 10.9%. The imine dissociation continued to increase, reaching 99.9% at 24 hours. Molecular sieves were also added to ensure the removal of water. The dissociation is attributed to both the reaction conditions, where the addition of heat promotes entropy-driven dissociation, and the nature of DMSO and water forming a non-ideal mixture, rendering complete separation of water challenging without specialized techniques.

Despite this, polymerization studies were conducted since it was hypothesized that during the actual polymerization of the BPA alt and DFDPS, the increasing chain length would give imine stability due to an increase in the degree of conjugation.

3.3.3 Base Variation Study

This study was to test the effect of different bases to determine the effect of base catalyst on the final polymer. Table 5 shows the bases in increasing pKa values. In the case of no base, the expected intermediate formed is hydrofluoric acid (HF) which causes the imine bonds to break due to the low pH and hinders any polymerization. In the case of potassium carbonate (K_2CO_3), a weak mineral base it was determined that it is not strong enough to deprotonate the monomer entirely indicated by the low yield of the polymer recovered. KOH a strong inorganic base was chosen to deprotonate both −OH groups of the diol monomers and has the highest yield with a high T_g. It is likely due to higher anion conversion that increases the reactivity of the BPA-alt, ease of filtration of final polymer and salt (KF) that does not hinder polymerization due to bulky side groups.

A strong organic base tetrabutylammonium bromide (TBAB) was used since it has a low boiling point of 100 C. Inorganic bases have poor solubility in DMSO and TBAB was used determine if an ionic liquid base catalyst would promote the rate of the reaction. The results from using TBAB are a surprisingly high T_g polymer with an unexpectedly low yield. This can only be attributed to the difficulty in polymer purification in a reaction media using TBAB leading to a low yield. Another strong organic base 1,8- diazobicyclo (5.4.0_ undec-7-ene (DBU) was used to test the effect of a bulky organic base to eliminate the possibility of the potassium ion, or the corresponding salt causing side reactions. It also had a high T_g, lower than KOH, and an overall low yield 57%. It is hypothesized that the bulky DBU hindered the reaction leading to slower reaction and the reaction might not have reached completion. However, due to the imine dissociation any advantage of eliminating possible interference from potassium ions is outweighed by the increase in dissociation. And lastly a strong non- nucleophilic strong organic base like potassium trimethylsilanolate (KOTMS) was selected[89] as well to eliminate the possibility of a nucleophilic attack interfering with imine stability. However, likely due to the bulky salt interfering with polymerization higher T_g polymer could not be synthesized.

Table 5: Base variation study

Base	**pKa** [124]	**Polymer T_g (°C)**	**Yield (%)**
No base	-	-	-
K_2CO_3	10.25	107.3	16
DBU	12.8	151.6	57
KOTMS	13	135.7	73
TBAB	13.2	167.7	30
KOH	15.7	162.6	72

3.3.4 Monomer Ratio Study

This study was to test the effect of different monomer ratios. In the case of excess DFDPS, it was found that the T_g values and yield were very low. This was attributed to termination due to capping because of excess DFDPS. In the case of excess BPA-alt, the ideal monomer ratio was found to be 1.3:1 mol% of BPA-alt to DFDPS. This was attributed to the excess BPA-alt leading to continuation of the reaction beyond the equimolar case owing to the reassociation as the terminal aldehydes and amines reacted with the dissociated monomer to continue polymerization.

A typical step growth polymerization has a 1:1 monomer ratio for the highest degree of polymerization. However, due to the imine dissociation observed (about 30% by the 4-hour mark), the addition of extra BPA-alt monomer acts like a catalyst allowing the reaction to continue despite partial imine dissociation. A higher ratio of BPA alt was used, and it was determined that the yield decreased drastically likely due to the capping of reactive functional groups with imine halting the reaction. Table 6 summarizes the results with the corresponding TGA and DSC graphs in Figure 25 and 26.

Table 6: Monomer ratio study summary

Monomer Ratio **DFDPS: BPA-alt**	**$T_{d5\%}$** **°C**	**T_g** **°C**
1.2:1	289.05	130.80
1:1	260.9	117.8
1:1.1	206.15	116.48
1:1.3	255.12	181.23
1:1.7	333.28	183.50

Note: This study was done at 140 °C for 3 hours at various monomer ratios. The best monomer ratio was selected to be 1:1.3 with excess BPA-alt due to a high T_g value. This was because despite having slightly better thermal properties at 1:1.7 monomer ratio, a much lower yield (~30%) in comparison to the yield of 1:1.3 run (~65%).

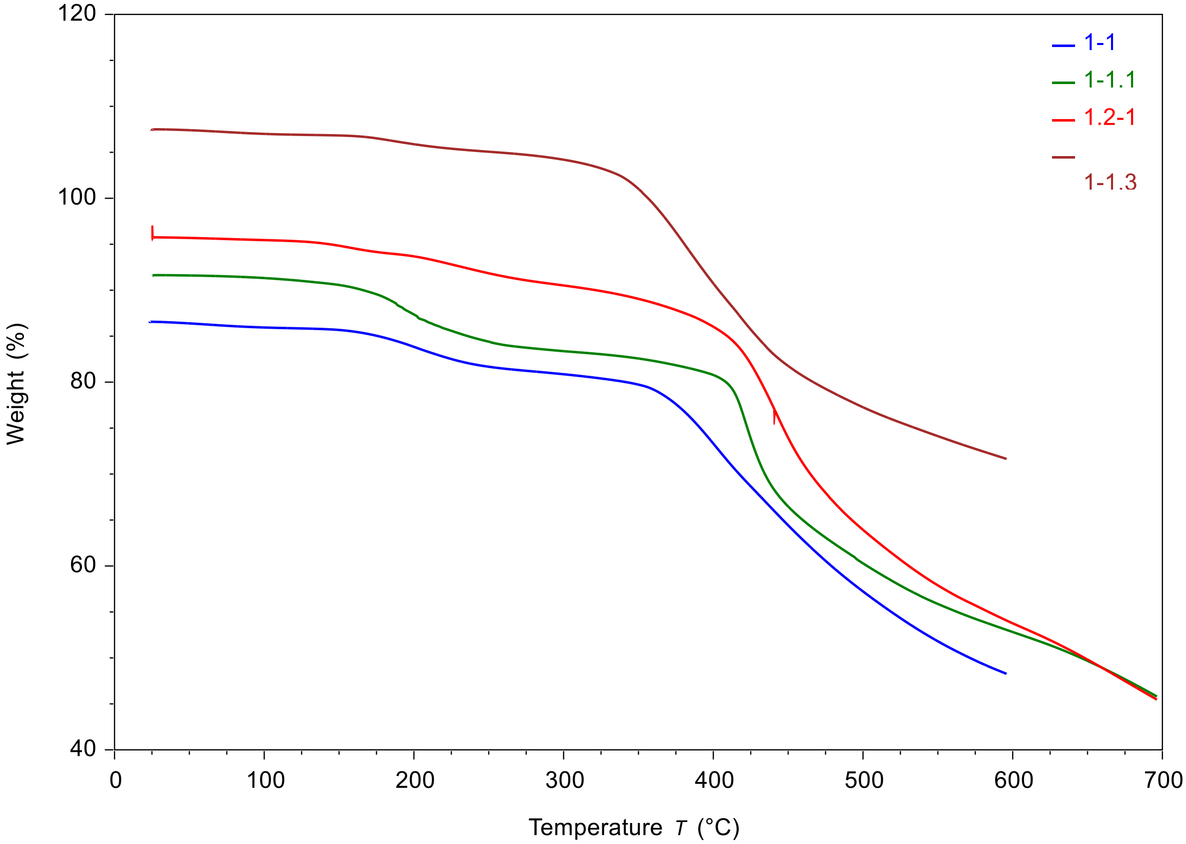


Figure 25: TGA curves for monomer ratio study.

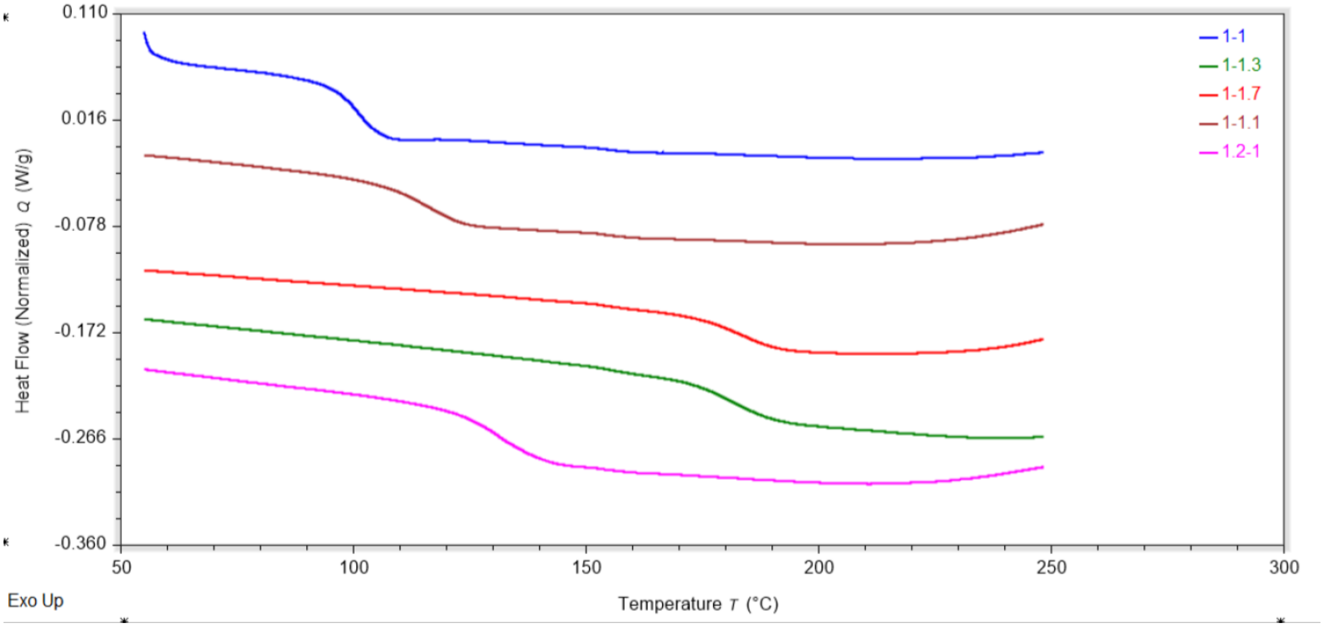


Figure 26: DSC curves for various monomer ratios.

3.3.5. Reaction Time Study

This study was done to find the effects of reaction time on the final polymer and the imine dissociation. At the 1-hour mark, though the imine levels were optimal, it was concluded that it was an insufficient amount of time for the polymerization reaction to reach completion. From literature, it was found that typically DFDPS requires about 4 hours to reach ~100% conversion[85] and the results of this study were comparable due to the highest MW polymers synthesis at this reaction time (Table 8). The decreases in percent dissociation of the imine bond from the control study to the reaction time study (Table 7) shows that the imine bonds are indeed stabilized by further polymerization. However, dissociation dominates after the DFDPS reaction reaches completion at the 4 hours marked by a decline in MW. The increase in MW at 20 hours but low polymer yield was attributed to imine metathesis reactions where the imine exchange leads to a high MW polymer but also an increasing percentage of low MW oligomers that get filtered from the final sample.

The T_g of the PIS does not follow the same trend as the MW. This is attributed to the fact that unlike a typical step growth, imine dissociation adds to the variability of the final product. As the reaction time increases so does imine dissociation. So instead of a correlated T_g vs Mn, imine dissociation leads to the formation of smaller oligomers that can act as plasticizer. Additionally, the chemical structure of the material does change slightly during the imine dissociations as more aldehyde and amine end groups contribute to the properties and interact. The imine bonds also add to the increased conjugation stability likely leading to additional effects such as pi stacking, hydrogen bonding and electrostatic interactions.

At the 2-hour mark while the T_g value is high, the MW value is low and that is due to the lower conversion of the DFDPS. The high T_g is likely due the minimal dissociation observed at 2 hours from the equilibrium shift after the water removal in the reflux step. This leads to a polymer of narrow MW distribution with minimal imine dissociation effects. As the reaction proceeds at 3 hours while more of the DFDPS has reacted, imine dissociation gave rise to larger oligomers that act like a plasticizer lowering the T_g and this effect becomes more pronounced at the 4-hour mark where despite having the highest MW, a larger PDI and a lower T_g are observed. At the 5-hour mark, the imine reaction effect dominates as the DFDPS has finished reacting. A lower PDI is observed, and a higher T_g due to the narrower MW distribution likely from imine exchange. At 16 hours, minimal change is observed and the sharp rise in MW at 20 hours is partly attributed to the imine metathesis (imine exchange) leading to slightly higher T_g and MW.

Table 7: Summary of the reaction time study

Time	**% Imine Dissociation**
1	39.6
2	23.5
3	36.3
4	43.4
5	22.3
16	32.6
20	26.5

Note: This set of experiments was repeated twice, and the results shown are averaged. The percent dissociation of the imine is calculated like control study, by comparing the expected amount of imine in the sample and the actual imine peak integration from the H-NMR via quantitative analysis by utilizing trioxane as an internal standard.

Table 8: Thermal properties and MW of reaction time study:

Time	**$T_{d5\%}$ (°C)**	**T_g (°C)**	**Yield (%)**	**MW (kDa)**	**PDI**
2	405.21	181.94	36.70	5.97	1.76
3	368.03	154.25	70.21	10.39	1.64
4	399.09	162.56	70.50	11.13	2.56
5	401.68	176.33	64.20	8.28	1.71
16	408.04	177.78	62.78	8.08	1.57
20	408.27	179.39	30.59	10.52	1.69

Note: This table summarizes the thermal properties of the various reaction times tried for this set of experiments. The yield is calculated by:

$$Yield\ (\%) = \frac{Theoretical\ yield - Actual\ yield}{Theoretical\ yield} * 100$$

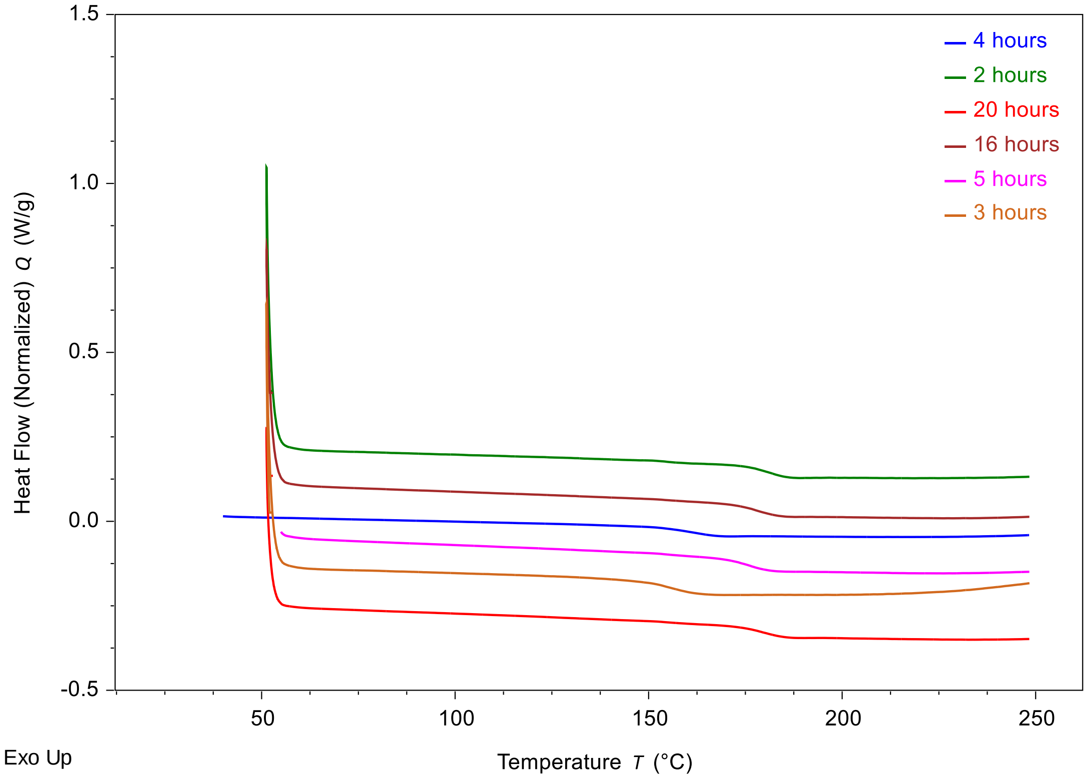


Figure 27: DSC Reaction time study.

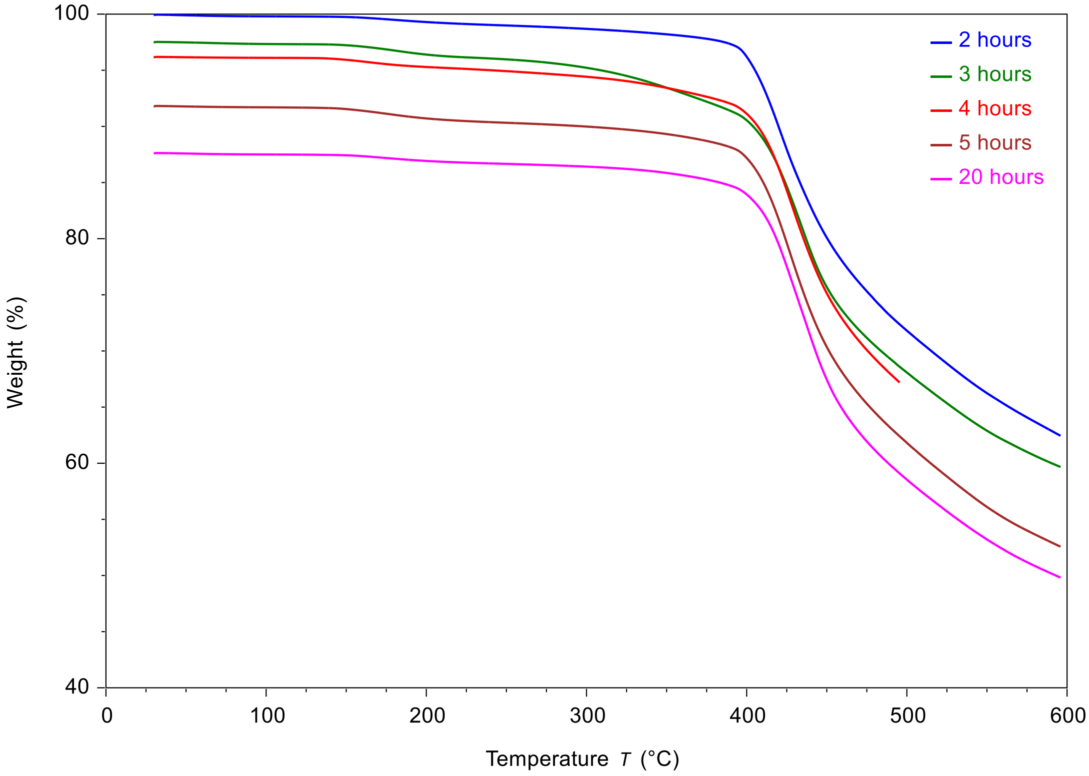


Figure 28: TGA Reaction time study.

3.3.6 Temperature Study

Typical PSU reactions are done at 140-160 °C. However, after the control study it was determined that a low temperature would likely lead to lower imine dissociation. With the high reactivity of DFDPS, lower temperatures still led to a high yield of the final polymer (Table 9). Depending on application a polymer with a T_g of 180°C can be synthesized in lower yields at 140°, 3-hour reaction time. The $T_{d5\%}$ for this sample is lower and that is attributed to greater imine dissociation owing to the higher temperature. That is also likely the reason for the low yield of the polymer. For the dataset at 120°C, 2 hours, it is concluded that the low yield and MW for this sample is indicative of the reaction not having reached completion yet.

From a study by yang et al it was concluded that at about 4 hours DFDPS reaches full conversion. That is consistent with the high yields observed at 4 hours[125] at 100 and 120 °C temperature. The 70% yield at 2 hours is consistent with close to full conversion observed at 4 hours for conventional PSU synthesis. However, due to imine dissociation being more rapid at higher temperatures, additional reaction time leads to lower yield as the imine breaks down.

Table 9: Temperature Study

Temperature (°C)	**Time (hr)**	**$T_{d5\%}$ (°C)**	**T_g (°C)**	**Yield (%)**
100	2	180.85	125	43.18
	3	232.50	143	51.02
	4	329.90	153	70.94
120	2	405.21	181	36.70
	3	368.03	154	70.21
	4	399.09	162	70.50
140	2	266.37	163	71.50
	3	232.55	188	42.80
	4	233.33	127	65.61

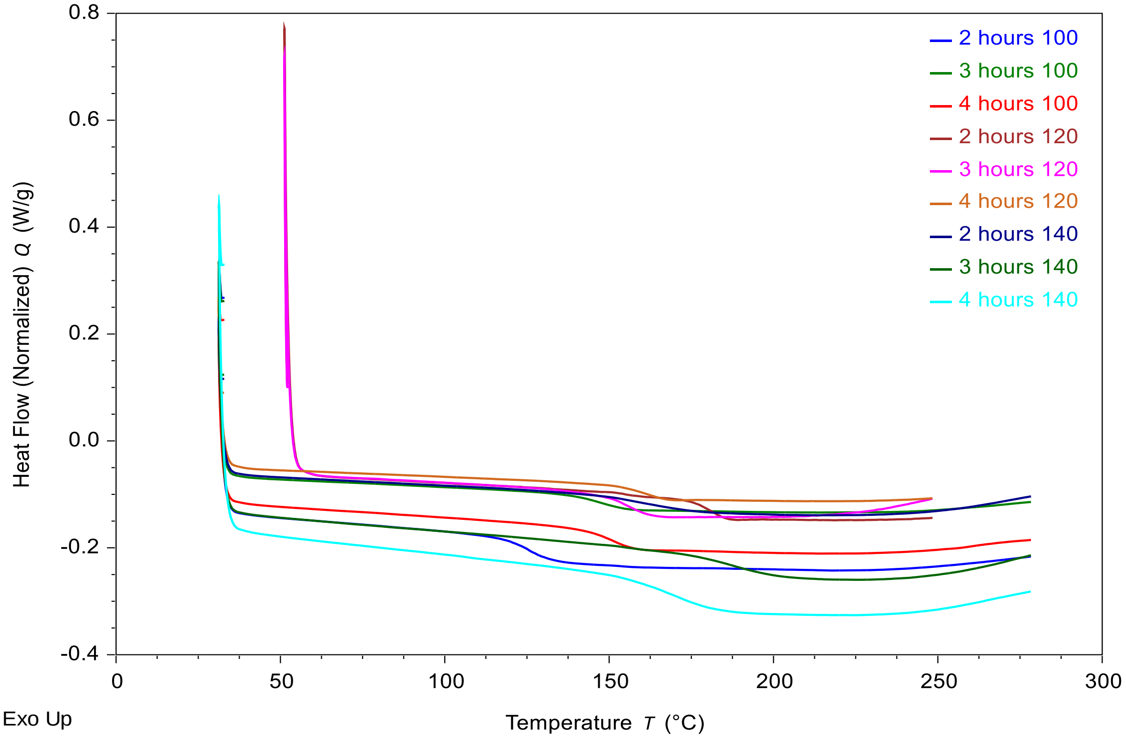


Figure 29: DSC Temperature study.

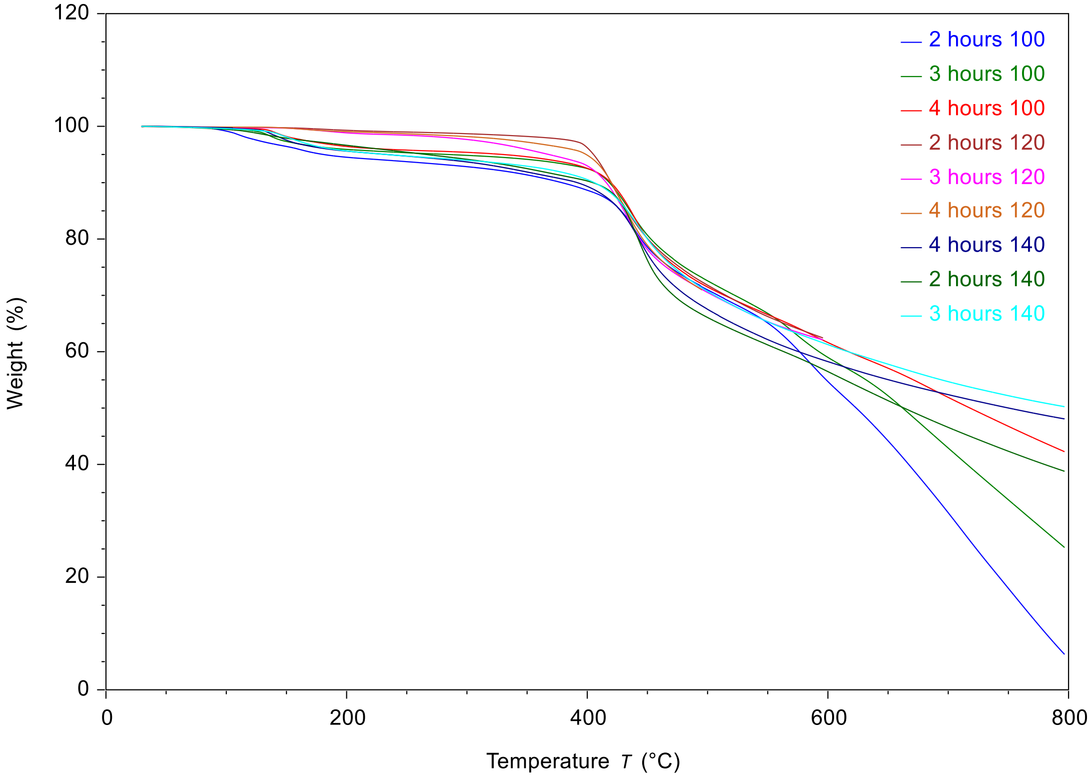


Figure 30: TGA Temperature study.

From these various studies the highest MW achieved was 11 kDa. Tables 10 and 11 summarize the parameters studied and a comparison of the properties of the polymer in this study PIS with a commercial polymer sample. It was concluded that the molecular weight (MW) of the sample in this study is lower than the minimum needed for commercial application while the thermal properties of glass transitions temperature (T_g) and 5% decomposition temperature ($T_{d5\%}$) are comparable.

Table 10: Summary of range of parameters studied and the experimentally determined conditions for the polymerization of PIS using BPA-alt with highest MW.

Property (unit)	Range Considered	Optimal conditions
Temperature (°C)	100-140	120
Time (hr)	1-24	4
Monomer Ratio (BPA-alt: DFDPS)	1.7:1-1:1.2	1.3:1

Table 11: Highest MW PIS vs PSU Sample Ultrason S2010 35k

Sample	T_g (°C)	$T_{d5\%}$ (°C)	MW (kDa)	Yield (%)
Highest MW PIS	162.6	399.1	11.13	70
PSU (Ultrason S2010)	185[126]	460[127]	35	-

3.3.7. Chemical Stability

The polymer was also studied for chemical resistance since PSU are known for the stability in harsh chemical environments. The polymer was immersed in a 1.1 pH solution of 38% HCl and a 14-pH solution of KOH in water for 48 hours. No deformation, dissolution or other changes to properties were noted. It was concluded that the polymer is stable in a pH range of 1-14. For pH lower than 1 as is for 98% sulfuric acid (~pH 0.2), the polymer dissolves and the solution changes to a red color indicating dissociation of imine bond. Imine bond can be hydrolyzed back to an aldehyde and an amine under certain conditions as seen from the control study in section 3.3.2 and is studied further in the next chapter. Water was concluded to affect the imine dissociation, however, after polymerization, water is insufficient to cause the imine bond to dissociation even at high temperature due to the added stability due to increased conjugation range and due to imine sites being less accessible due to the amorphous polymer structure, shielding the bond from degradation. For the polymers synthesized in this study, using just water could not cause any significant amount of dissociation.

3.4 CONCLUSIONS

In this study, we proposed a thermoplastic biobased and recyclable polyiminesulfone as a potential alternative to the conventional polysulfone made from BPA. PIS was successfully synthesized using vanillin and the incorporation of a dynamic covalent imine bond to replace BPA for a more sustainable polymer. The dissociation of imine was analyzed in a control study, indicating that the longer the bond was subjected to the high-temperature reaction conditions, the more dissociation of the bond takes place. The final polymer end-product was found to be more stable and less sensitive to pH and temperature largely due to the increase in conjugation length on polymerization. Monomer ratio, reaction time and temperature were varied to synthesis polymers and discover the behavior of imine bonds under these conditions and the impact on final polymer properties. From the studies it is observed that the imine dissociation causes the synthesis of PIS to diverge from expected trends leading to a 1.3:1 monomer ration with the highest thermal properties. Further study into the specifics of the imine kinetics, its interactions with the DFDPS can be undertaken to better characterize the reaction. This study concludes that the synthesis of a chemically recyclable PSU capable of participating in a circular lifecycle is feasible. The limitations of the imine bond can be addressed by exploring different chemistry or using this monomer in conjunction with other monomers to minimize dissociation while still have recycling capabilities.

CHAPTER FOUR:

CHEMICAL RECYLING OF POLYIMINE SULFONES VIA IMINE CHEMISTRY

4.1 INTRODUCTION

Plastic production is increasing as it is becoming integral to our society. It has found use in a variety of applications from end consumer products, equipment, infrastructure etc. The unique properties of plastics make it irreplaceable and contribute to the growing plastic waste problem. The stability if these long chain molecules make their subsequent disposal difficult. Plastic waste is responsible for widespread pollution in land, water and air. From the leaching of toxic chemicals to becoming a part of the food chain due to consumption by fish and animals, plastic waste has been problematic. For greater circularity, recycling of plastics has emerged as an area of interest as these materials are harder to replace.

There are four main ways of plastics recycling: primary (mechanical), secondary (mechanical), tertiary (chemical) and quaternary (incineration for energy recovery) [102]. Primary recycling is the most widely used and is typically limited to industrial scraps which are simply remelted in a close loop production. Secondary mechanical recycling for commercial plastics is done. This however leads to a degradation in properties (downcycling) and is generally limited in the number of times it is viable[27,128]. Chemical recycling has received much attention in recent years and many polymers have been designed for chemical recycling[129]. For e.g. recycling of polyurethane[130], polyamides via hydrolysis[131], poly-p-phenylene terephthamide via amide cleavage[132]etc. Finally quaternary method of incineration can lead some energy recovery however can also lead to release of toxic gases such as NOX, acids to the atmosphere and contribute to GHG in the process as these materials are burned[29,133].

The advantage of chemical recycling lies in the fact that it can be done over multiple cycles and from mixed media depending on the specific conditions for recycling. Using dynamic covalent chemistry to design chemically recyclable materials has been increasingly explored in recent years. Reversible covalent bonds with stable end products, low activation energy and controllable rupture via stimuli such as temperature, pH, light have been embedded into the polymer structure and used for recycling. Reversible covalent reactions are triggered to achieve forward and reverse reactions to dissociate the polymer into intermediates and back to polymer to achieve chemical recycling [30–33]. There are a variety of DCC's such as Diels Alder, ester exchange, imine bonds, disulfide bonds that can be used.

Imine chemistry especially is widely used due to its thermodynamically stable product that does not undergo rupture without the use of a catalyst under normal conditions. The aldehyde groups in the vanillin-based monomer makes imine an easy-to-use chemistry[34,35] as it readily reacts with a primary amine to form the site for chemical recycling, i.e. the imine bond. A variety of imine-based materials have been synthesized according to literature but not all of them were studied for their recycling potential. Some examples of polymers that utilize imine bonds for recycling are polyamides[134], polyesters with both ester and imine-based recycling/ degradation[114] and thermosets that were synthesized with imine networks [34,35] .

In this section the recycling of the PIS synthesized in the previous study was explored. The imine bonds were used to depolymerize the polymer and repolymerize it by varying the pH of the polymer solution.

4.2 EXPERIMENTAL SECTION

4.2.1 Materials

Vanillin (≥ 99%), 4amino-phenol (≥ 98%), bis (4-florophenyl) sulfone (DFDPS) (≥ 99%), potassium hydroxide (KOH) (≥90%), hydrochloric acid (HCl) (≥ 99.5% ACS reagent grade), and ethanol (EtOH) (≥99.5% ACS reagent, absolute), were sourced from sigma Aldrich and VWR. The chemicals were used as received with no further purification. Polyimine sulfone (PIS) from previous study was also used.

4.2.2 Recycling of PIS

The PIS sample (0.2 g) was dissolved in 10 ml of DMSO in a beaker and heated to 60°C. Upon reaching temperature, 0.5 µL of HCl was added, resulting in a rapid color change to red, indicative of intermediate formation. Excess HCl was added to isolate the intermediate, and the solution was left to evaporate overnight to remove the solvent/ acid mixture, and lastly dried in an oven. The intermediate formation is confirmed via H-NMR.

To recover the polymer, KOH was introduced to neutralize the acid, adjusting the pH to an optimal 5 for efficient imine association. Stirring for 4 hours allowed sufficient time for imine reassociation and polymer recovery. The polymer was then recovered by filtration and subsequent washing with water and acetone. This protocol serves as a representative procedure, with parameters adjusted as needed for specific experimental conditions and further investigations.

4.2.3 Model Compound Synthesis

Williamson ether synthesis is used to make model compounds of the recycling intermediates. It is a base SNAR-driven nucleophilic substitution. 10 mmol of vanillin (1.52 g), 10 mmol of KOH (0.56 g) and 20 mL of ethanol were added to a round bottom flask. This leads to the formation of an insitu phenoxide intermediate. This step increases the reactivity of the phenolic group of vanillin as the anion is more reactive. DFDPS (5 mmol, 1.27 g) was then added to the flask and reacted for 8 hours at 120°C. DFDPS reacts with the intermediate forming a resonance stabilized Meisenheimer complex where the fluorine acts as a leaving group, to yield an ether bond. The formation of the phenolic base intermediate produces water which hinders ether formation but was difficult to remove due to reaction condition and solvent system. The ether compound is recovered by using rotary evaporation to remove the solvent. It is then washed to remove residual base and the salt formed during the reaction. This procedure is repeated using 4 aminophenol to make the other model compound.

4.2.4 Characterization

Chemical

Attenuated Total Reflectance Infrared (ATR-IR) Spectroscopy - Spectra were collected by a Thermo 6700 spectrometer from 500–4500 cm^{-1} using 16 scans. Nuclear Magnetic Resonance (NMR) spectroscopy - NMR spectra were collected on Bruker Neo 300 MHz spectrometer and Bruker Neo 500 MHz spectrometer. The solvent used was d-DMSO. Topspin 4.2 software was used for data analysis and integration. Trioxane was used as an internal standard.

Thermal Analysis

A Differential Scanning Calorimetry (DSC) 2500 TA instruments was used to study T_g of samples with a heat-cool-heat cycle at 10 °C/min under nitrogen atmosphere. Degradation was studied by a Thermogravimetric Analysis instrument (TGA) 5500 TA instruments with a ramp rate of 20 °C/min from 30 °C to 700 °C.

4.3 RESULTS AND DISCUSSION

4.3.1 Preliminary Recycling of PIS

To recycle the PIS samples, the dynamic dissociation - reassociation of imine is utilized. The dissociation of imine is achieved by the hydrolysis of the imine bond leading to the formation of the starting carbonyl, aldehyde, and an amine due to the protonation of the imine bond by an acid, which in this case is HCl. To induce dissociation the polymer is first dissolved in DMSO and heated to 110°C. HCl was then added till a red intermediate formed and the pH of the solution was 2. This intermediate was isolated by adding excess acid and allowing the evaporation of the solvent and acid to yield the red intermediate as a dry powder. This was confirmed via H-NMR by the absence of imine peak and the prominent aldehyde peak in Figure 31.

After the addition of a neutralizing base to the intermediate according to the procedure in the experimental section, the recovery of the polymer did not proceed as anticipated as the recovered polymer had no imine peaks, but still displayed a reduction in the aldehyde peak to virgin polymer levels (Figure 31).

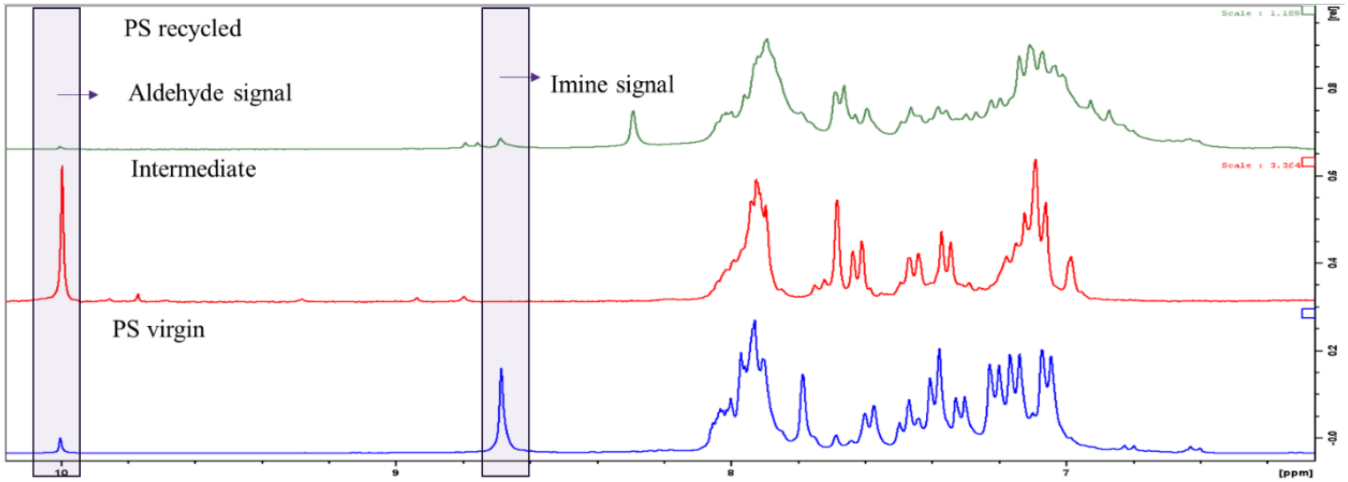


Figure 31: H-NMR of PSU recycled, intermediate and virgin sample.

4.3.2 Model Compound Study

Further study of the recycling intermediate via the synthesis of model compounds using the Williamson-ether synthesis reaction was done. However, only the vanillin-based ether was considered for further study due to the side reaction that occurs with amine and halogen leaving group in the presence of a base.

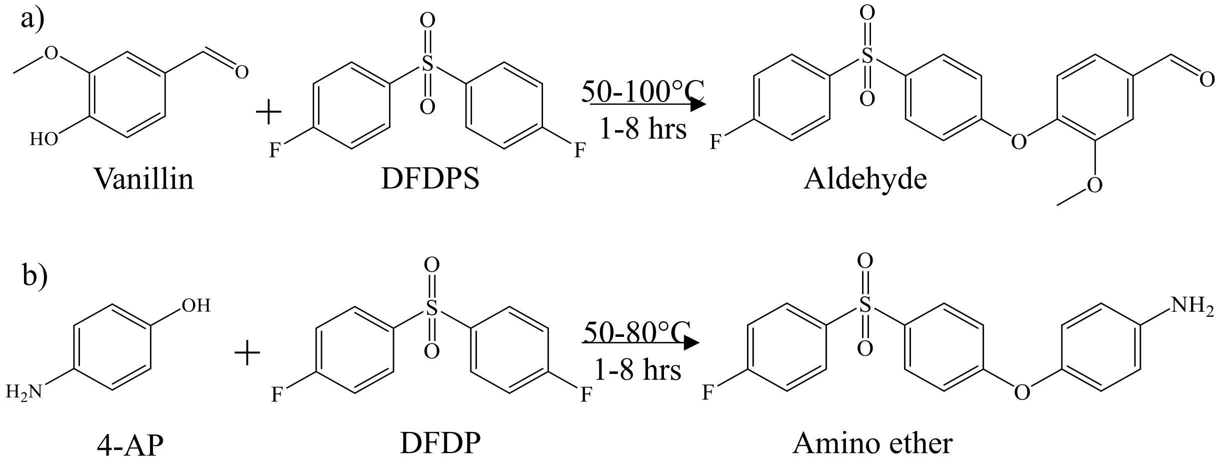


Figure 32: Recycling study model compounds reaction scheme a) vanillin, b) 4 aminophenol.

The vanillin-based ether spectra were compared to the intermediate spectra to confirm the peak identification and peak shifts. A C-NMR was also done to confirm the ether formation, indicating successful Williamson synthesis. From this vanillin- based ether compared with the C-NMR of a recycled sample, it was concluded that the cleavage of ether bonds during the recycling of PIS led to the low recovery of the polymer. This was due to the high temperature and the presence of excess Lewis acid [135] which led to the unexpected spectra of the recycled polymer. The excess acid reacted with the ether bonds after the imine bonds were hydrolyzed. The C-NMR of the recycled sample in Figure 34 shows no ether peaks in the expected region. This is further corroborated by the imine peak shift upfield, as it was noted in chapter 3 (Figure 23) that polymerization causes the imine signal to shift downfield and broaden. The material was closer to the monomer than a polymer due to the ether cleavage.

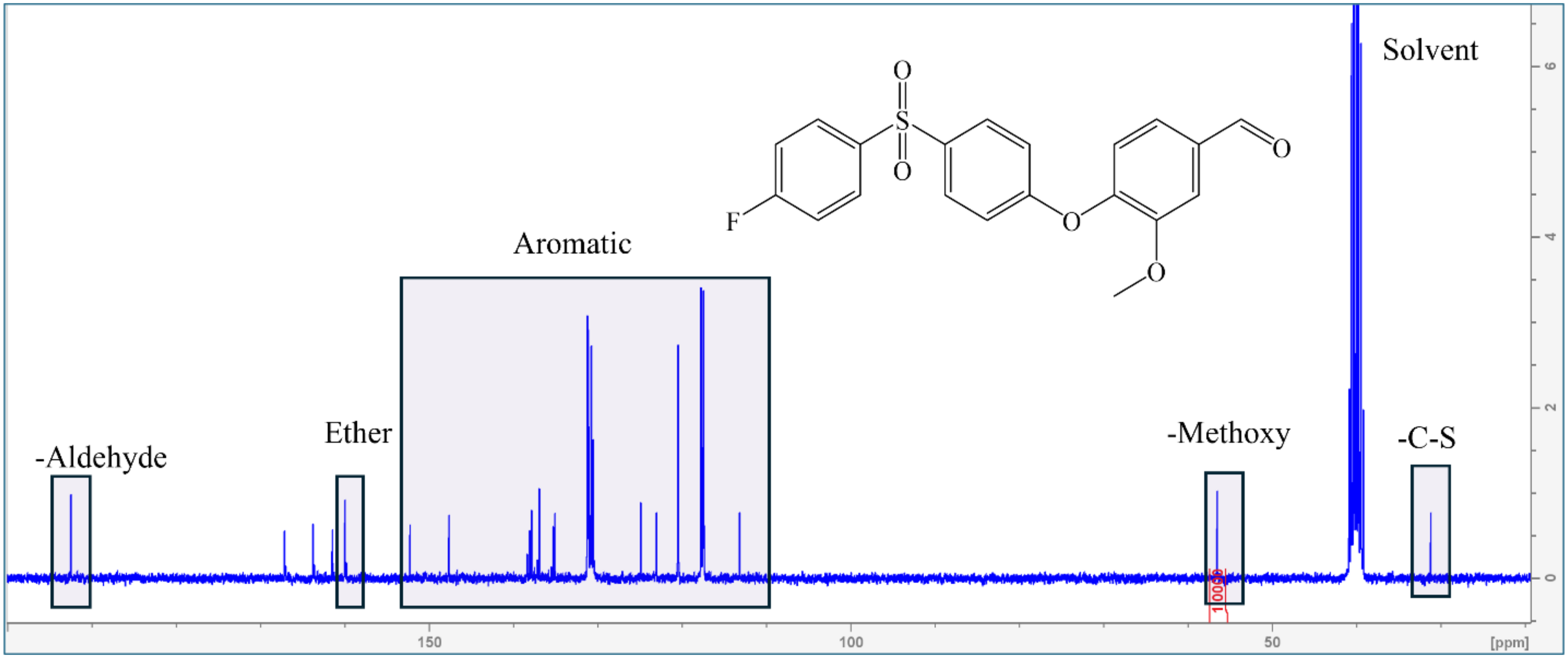


Figure 33: C-NMR of the model compound DFDPS-Vanillin ether synthesis.

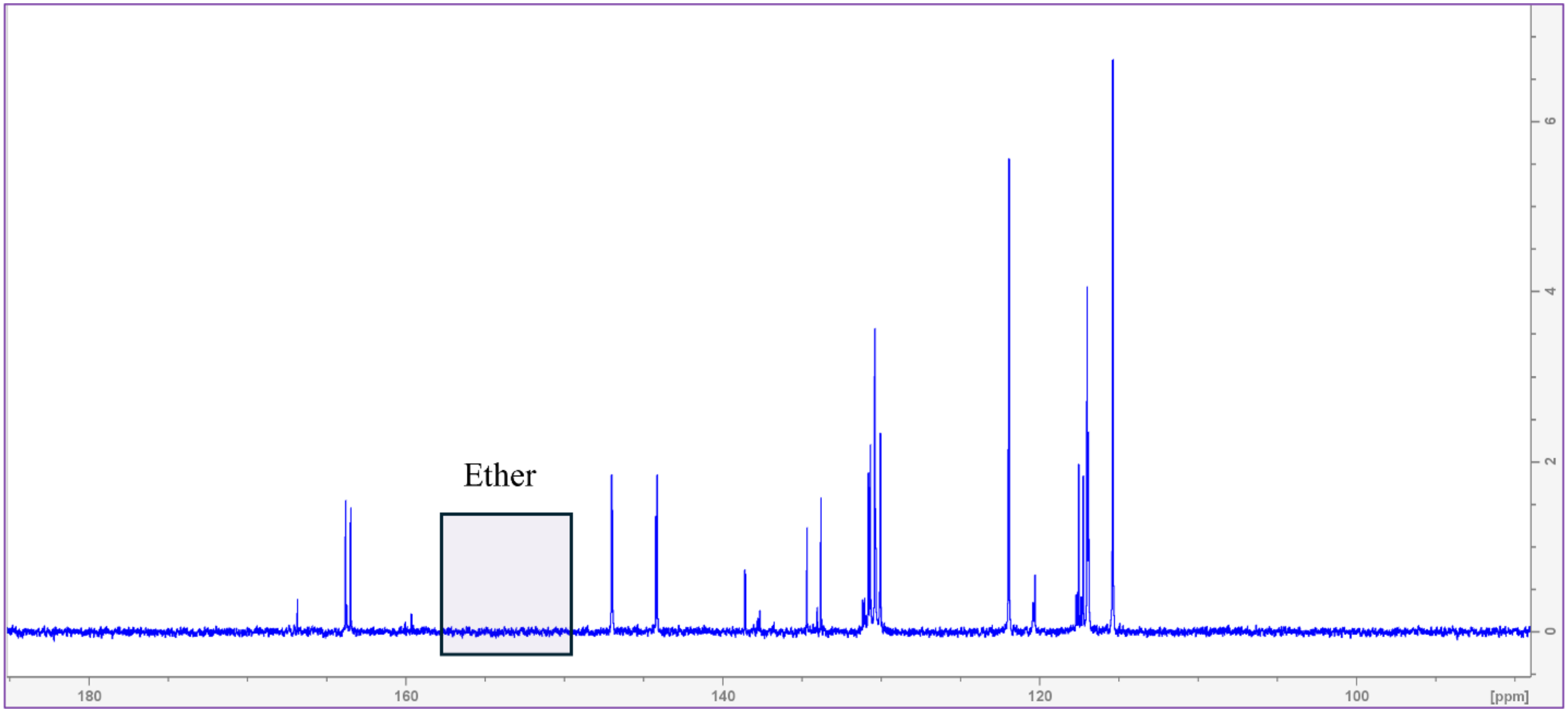


Figure 34: C-NMR of material after preliminary recycling with marked region with no ether observed.

4.3.3 Recycling Study PIS

Figure 35 shows the typical dissociation and reassociation mechanism of the imine bond. In general, acidic conditions were used to shift the equilibrium towards imine dissociation breaking the long polymer chains into monomers and oligomers. When the conditions turn neutral or basic, the equilibrium shifts towards imine bond formation and resynthesis of the polymer.

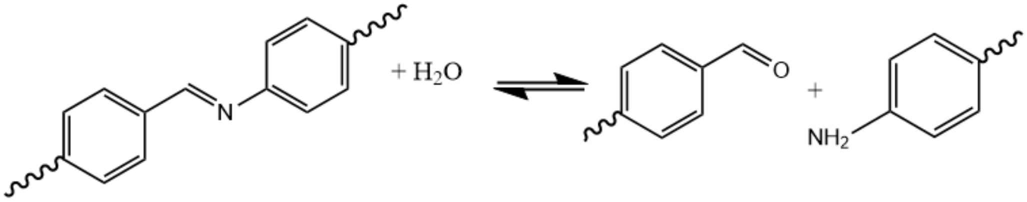


Figure 35: Mechanism of imine hydrolysis and chemical recycling.

Various pH levels for dissociation and reassociation were tested (Figure 35). It was found that during dissociation the low pH of 2 led to side reactions and ether cleavage, dissociation by using base (pH 8-10) led to no polymer recovery at all and the optimal conditions for imine recycling were lowering the pH to just below 5, at 4.8 for imine dissociation and the addition of KOH to bring the pH to 5 for rapid association leading to polymer with high yield and no unexpected side reactions (right most region in Figure 36) . The synthesis of recycled polymer was confirmed via H-NMR showing the expected imine peak at 8.6 ppm and no aldehyde peak at 10 ppm (Figure 37). The FTIR also shows no carbonyl peaks corresponding to aldehyde bonds and an imine peak in the 1687 cm^{-1} (Figure 38). The temperature was lowered to 60 °C to test effect of milder conditions and it was observed that the polymer yield increased to 98%.

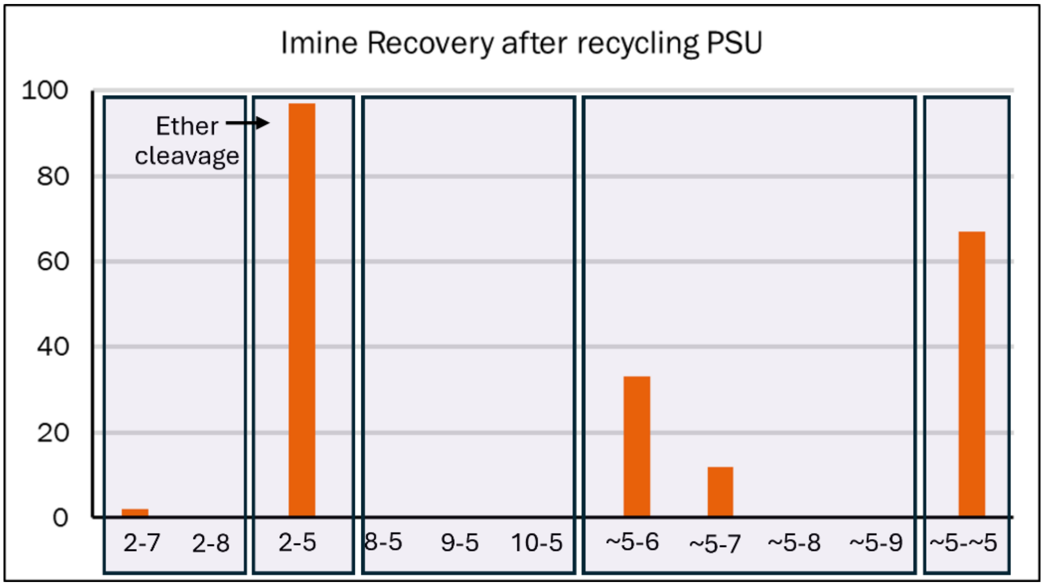


Figure 36: Imine Recovery for various pH levels

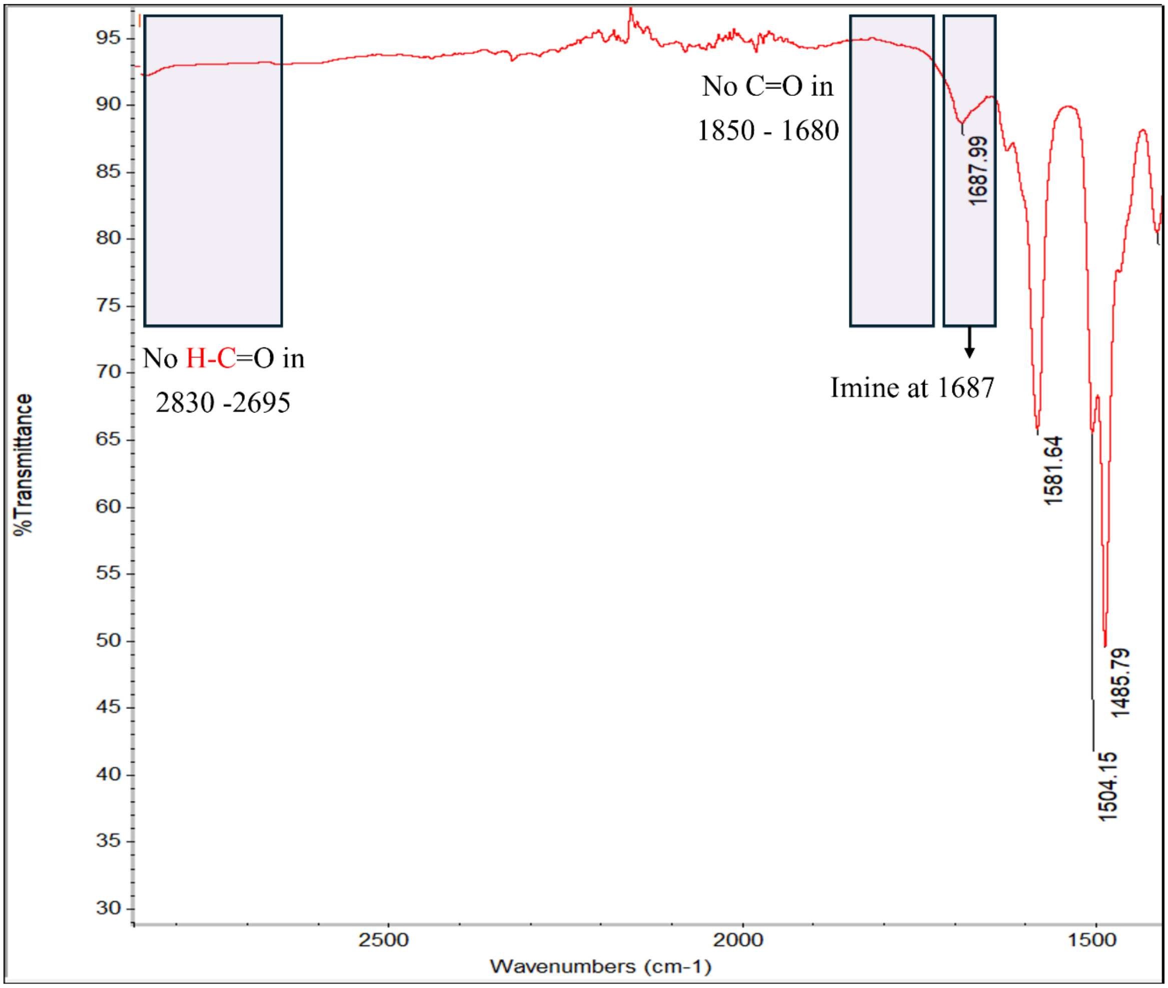


Figure 37: a) FTIR of recycled PIS highlighting the imine peak and absence of aldehyde peaks.

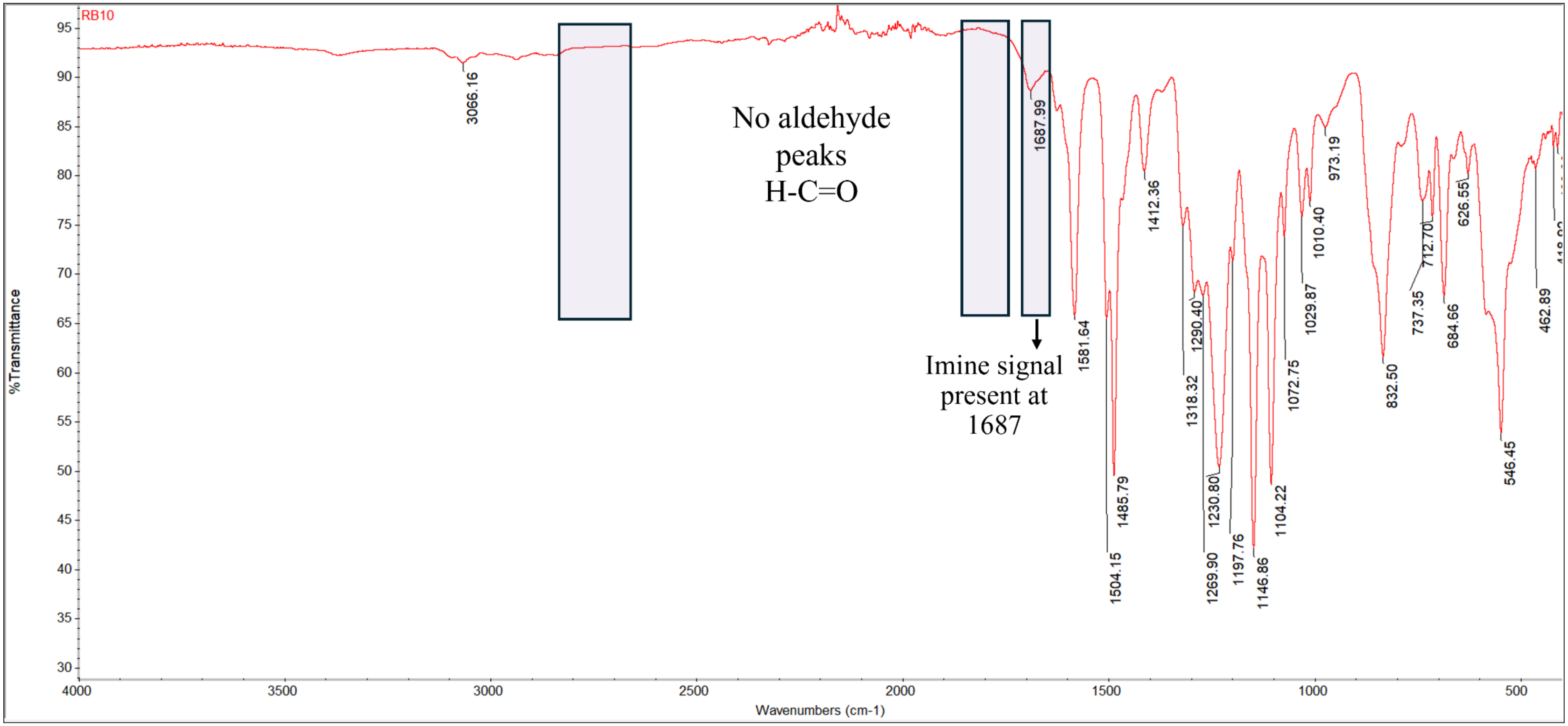


Figure 37: b) Full FTIR of recycled PIS.

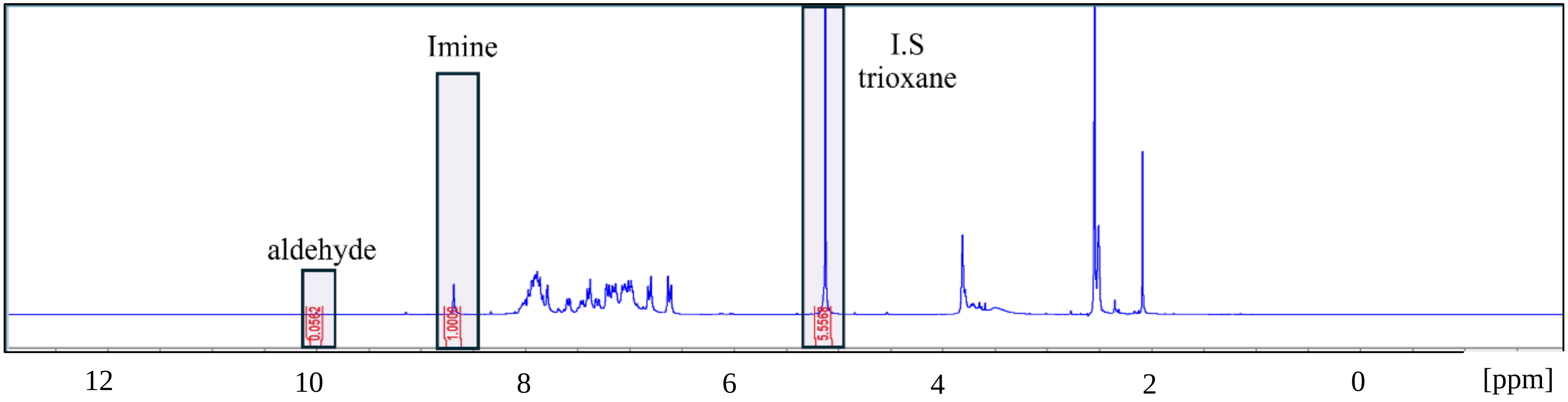


Figure 36: H-NMR of recycled PIS with marked imine peak and minimal aldehyde peak.

4.3.4 Thermal Analysis of Recycled PIS

The recycled sample was compared to virgin PIS with $T_{d5\%}$ of 401 °C and T_g of 162 °C. Table 12 summarizes the results.

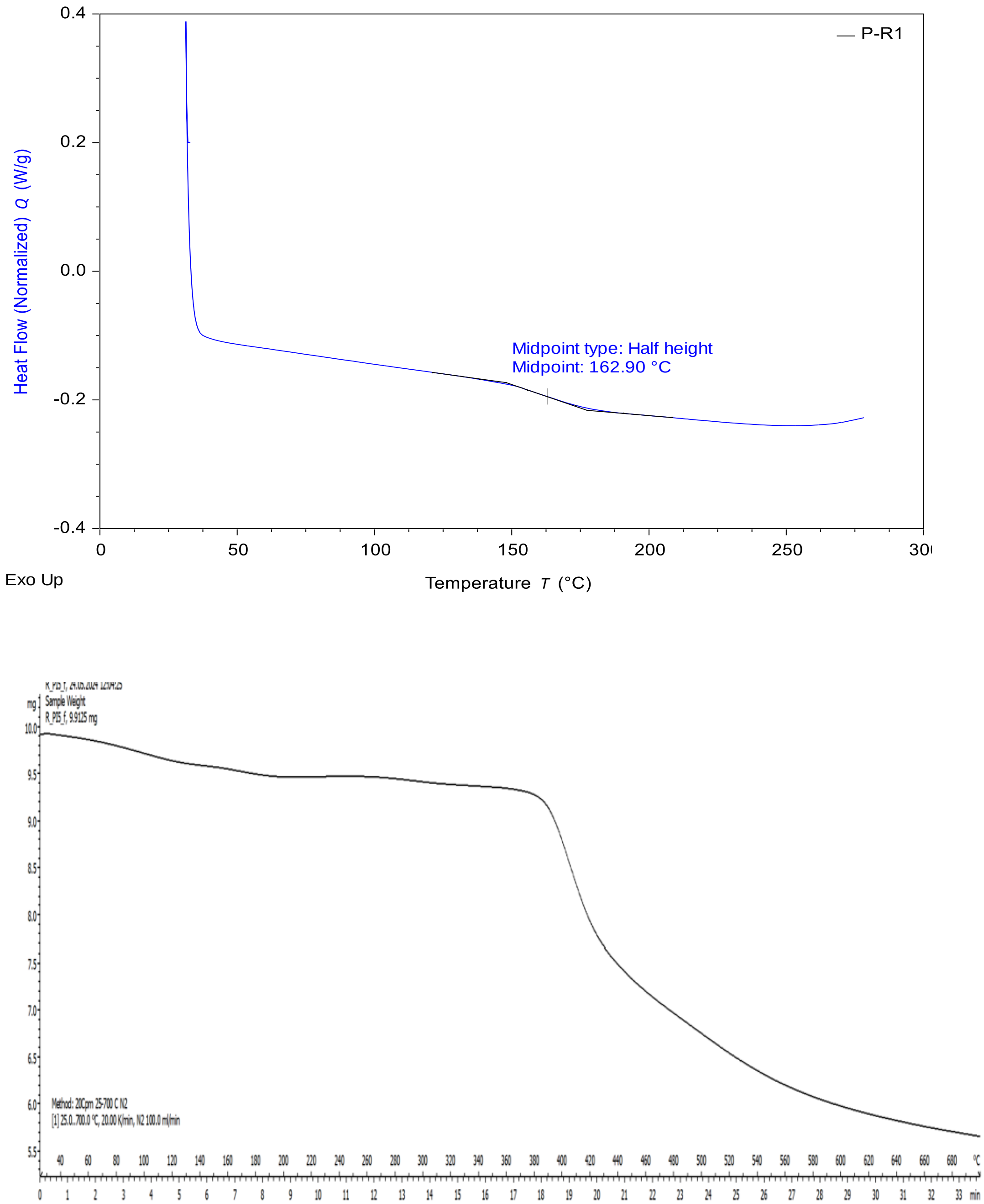


Figure 37: DSC (top) and TGA (bottom) of recycled PIS.

Table 12: Comparison of highest PIS vs recycled PIS.

Sample	T_g (°C)	$T_{d5\%}$ (°C)	MW (kDa)	Yield (%)
Highest MW PIS	162.6	399.1	11.13	70
Recycled PIS	162.9	401.7	-	98

4.4 CONCLUSION

The recycling study showed that the majority of the polymer material (98%) could be reliably recovered under fairly mild conditions of 60 °C and a pH of 4.8. The initial recycling trials at a high temperature led to ether cleavage which was confirmed by comparison with a model recycling intermediate. Various pH's were tested to find the conditions for imine dissociation without any side reactions and imine association at the fastest rate with the highest yield. It was found that imine association was the best at ~5 pH. Thermal comparison of the recycled and virgin polymer showed that there was minimal change in polymer properties indicating that recycling could be done over multiple cycles. This study concludes that the synthesis of a chemically recycling strategy employed here enables a new PIS capable of participating in a circular lifecycle.

CHAPTER FIVE:

BIOBASED AND CHEMICALLY RECYCLABLE DERIVATIVE POLYIMINE SULFONE

5.1 INTRODUCTION

Apart from linear step growth polycondensation reactions for the synthesis of polymers, copolymerization and network polymerization can be done to obtain polymers with different properties for a variety of applications. After noticing imine dissociation and the subsequent modifications needed to synthesize PIS, the next step was to synthesize derivatives o PIS that had different properties that could be controllable, were still biobased without using the toxic BPA and retained their recyclability. From the recycling study it was determined that the recycling reaction was successful and that it was possible to achieve recyclability even with possibly longer imine spacing, or in a network at appropriate levels of imine inclusion in these derivatives.

By introducing an appropriate biobased repeating unit to the existing polymerization in different ratios, the polymer properties can be modified and form copolymers. The most used copolymerization method for this type of reaction is simply reacting with the monomers in suitable ratios and proceed with the reaction. A study was done to observe the effects of various isomers and their properties on a copolymer in different ratios. In this work random copolymers of polycarbonate were synthesized using a mixture of bisguaiacol isomers[23].

Imine based network polymers have been synthesized with a largely epoxy pre-polymers[34]. Work has also been reported on polyamides[134] and polyesters with imine-based networks[114]. These studies have utilized the properties of imine bond to make recyclable thermosets.

In this section copolymers using other biobased diols were synthesized in conjunction with the BPA-alt monomer. This was done in various ratios to study the properties and to compare the structure property relations of the copolymers using the different monomers. Polymers with 100% of the non-BPA-alt monomer were also synthesized as baseline tests. The network-based PIS was also synthesized by making a PSU prepolymer with a new biobased monomer from guaiacol with an aldehyde group for further crosslinking.

5.2 EXPERIMENTAL SECTION

5.2.1 Materials

Vanillin (≥ 99%), vanillyl alcohol (≥ 98%), guaiacol, 2 hydroxy-benzaldehyde (salicylaldehyde) (≥ 98%), bis (4-florophenyl) sulfone (DFDPS) (≥ 99%), acetic acid (glacial ACS grade ≥ 99.7%), sulfuric acid (H_2SO_4)(ACS grade, 95-98%), hydrochloric acid (HCl) (≥ 99.5% ACS reagent grade), potassium hydroxide (KOH) (≥90%), hydrogen peroxide (H_2O_2) (30% in water), horseradish peroxide (Type I, essentially salt free, ≥50 units/mg solid), ethanol (≥99.5% ACS reagent, absolute), dichloromethane (DCM) (≥ 99.8%, anhydrous), toluene (≥ 99.5%), dimethyl sulfoxide (DMSO) (≥99.9% ACS grade), priamine 1074 (by Croda dimer diamine manufactured from natural fatty acids with an amine value of 209 mg KOH/g), p-phenylene diamine were sourced from sigma Aldrich. The chemicals were used as received with no further purification.

5.2.2 Synthesis of bisguaiacol (BGF)

A 250 mL round bottom flask equipped with a magnetic stirrer and a reflux condenser were charged with vanillyl alcohol (1 mol, 1.52 g) and guaiacol (1 mol, 1.24 g). To the mixture, 100 mL of ethanol was added with 5 mL H_2SO_4 (0.5N). The mixture was refluxed at 80°C and stirred for 24 hours. Ethanol is removed using a rotary evaporator leaving behind a viscous reddish-brown liquid. The synthesis of bisguaiacol BGF from hereon was then confirmed via NMR.

5.2.3 Synthesis of divanillin (DV) via enzymatic route[18]

In a 150 mL beaker, vanillin (1.0 g, 6.6 mmol) was added to 100 mL of deionized water and dissolved. Acetic acid (0.010 M in water, 0.022mmol) was added to lower the pH to 4. This was followed by addition of horseradish peroxidase (Type I, 1000 units of activity) and hydrogen peroxide (3% in water, 7.5 mL, 6.6 mmol) to the solution while stirring. The reaction was stirred for 5 min and the tan precipitate was then recovered by using a Buchner funnel and the solids were rinsed with DI water. This was left to dry overnight in the hood and analyzed via NMR.

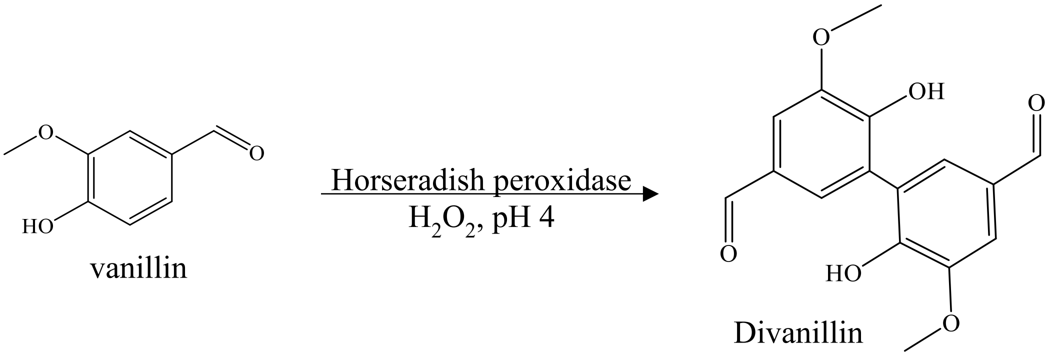


Figure 38: Reaction scheme for divanillin synthesis.

5.2.4 Synthesis of bisguaiacol derivative (BGD)

A 250 mL round bottom flask equipped with a magnetic stirrer and a reflux condenser were charged with vanillyl alcohol (1 mol, 1.52 g) and salicylaldehyde (1 mol, 1.22 g). To the mixture, 100 mL of ethanol was added with 5 mL H2SO4 (0.5N). The mixture was refluxed at 80°C and stirred for 24 hours. Ethanol is removed using a rotary evaporator leaving behind a viscous reddish-brown liquid which is recovered using DCM and dried overnight on a hot plate. The synthesis of this bisguaiacol derivative BGD from hereon was then confirmed via NMR.

5.2.5 Synthesis of Polysulfones

5 mmol of divanillin (1.51 g), 10 mmol of KOH (0.56 g) and 20 mL of DMSO are added to a round bottom flask and reacted at 55 °C for 2.5 hours. The formation of the phenolic base intermediate from this step produces water which hinders further polymerization. Nitrogen assisted azeotropic distillation using nitrogen and a dean stark trap is carried out to separate the water from the reaction mixture. Finally for polymerization, DFDPS is then added (5 mmol, 1.27 g) to the flask and reacted for 4 hours at 140°C. DFDPS reactions typically reach full conversion in 4 hours compared to DCDPS reactions which can take up to 48 hours[125]. The polymer is then filtered via phase inversion using water as a nonsolvent and dried overnight in an oven at 110 °C. This is a representative protocol. Parameters were varied accordingly during experimentation to conduct further studies.

5.2.6 Curing of polymer

The polysulfones made using BGD (BGD-PSU) were pre-cured with priamine and small amounts of solvent (DMSO) to ensure even mixing at 80 °C for 30 min. The exothermic peak of a DSC was used to determine curing temperature and BGD polymers were cured at 167 °C for 5 hours followed by 2 hours at 120 °C for post curing and further testing.

5.2.7 Recycling of cured Polysulfones

The cured polysulfone sample was added to a beaker with DMSO (5 ml). HCl (2 mL) was added, and the mixture heated to allow for the acid to catalyze imine dissociation. The sample was observed to have dissolved. The solvent and acid were then evaporated to recover the initial polymer.

5.2.8 Characterization

Chemical

Attenuated Total Reflectance Infrared (ATR-IR) Spectroscopy - Spectra were collected by a Thermo 6700 spectrometer from 500–4500 cm^{-1} using 16 scans. Nuclear Magnetic Resonance (NMR) spectroscopy - NMR spectra were collected on Bruker Neo 300 MHz spectrometer and Bruker Neo 500 MHz spectrometer. The solvent used was d-DMSO. Topspin 4.2 software was used for data analysis and integration. Trioxane was used as an internal standard.

Thermal Analysis

A Differential Scanning Calorimetry (DSC) 2500 TA instruments was used to study T_g of samples with a heat-cool-heat cycle at 10 °C/min under nitrogen atmosphere. Degradation was studied by a Thermogravimetric Analysis instrument (TGA) 5500 TA instruments at a ramp rate of 20 °C/min from 30-700 °C.

5.3 RESULTS AND DISCUSSION

5.3.1 Copolymer Overall Schematic

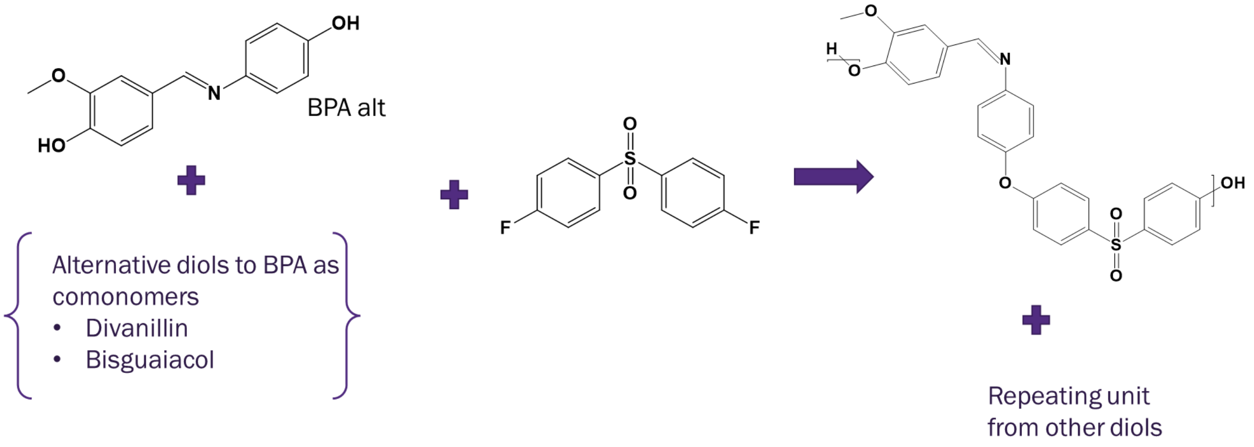


Figure 39: Copolymer overall reaction schematic using divanillin and bisguaiacol.

5.3.2 Copolysulfone BGF

Synthesis of the BGF monomer was confirmed via H-NMR with the singlet at 3.7 ppm assigned to $-OCH_3$ and the singlet at 3.8 ppm assigned to $-CH_2$ the methylene bridge. The peaks at 3.6 were assigned to the -OH groups and the doublets in the 6.5 ppm region to the aromatic benzene ring (Figure 42 a). BGF was used with BPA alt in various ratios to synthesize co-polyiminesulfones. The H-NMR had the key peas from the BGF monomer, the methylene bridge $-CH_2$ at 3.8 ppm and the imine peak at 8.6 ppm. The peak at 10 ppm was assigned to the trace amounts of aldehyde in the polymer due to imine dissociation (Figure 42 b).

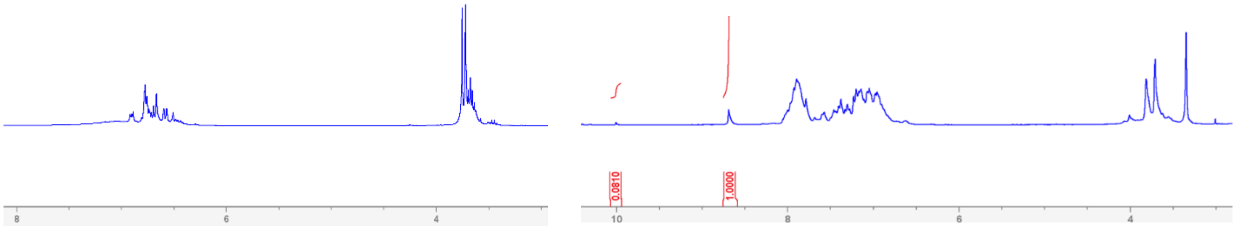


Figure 40: H-NMR of a) BGF and b) copolysulfone BGF.

Table 13 summarizes the results of the copolymers thus synthesized. These copolymers were recyclable, meeting the preliminary objective, however, were lower than PIS. The low T_g values were mainly attributed to the imine dissociation making the stoichiometry of copolymerization difficult to control. For the 100% BPA-alt polymers, the monomer ratio of BPA-alt to DFDPS was optimized accounting for the imine dissociation however, for the copolymer with the increase in variables it was difficult to optimize for the ideal monomer ratios. Additionally the BGF itself was a mixture of isomers of the o,p, m,p and p,p diol configuration further adding to the variables. This is likely the cause of the low T_g of the 100% BGF polymer.

Table 13: BGF-BPA alt copolymer synthesis

BGF (mol %)	BPA alt (mol %)	T_g (°C)
100	0	53.7
70	30	107.4
50	50	97.0
0	100	162.6

5.3.3 Copolysulfone- Divanillin

DV was synthesized according to protocol and polymerized. The synthesis of the monomer was confirmed via H-NMR. The key peaks were identified and marked with the aldehyde group presenting at 9.8 ppm and the methoxy group at 3.9 ppm (Figure 43). The monomer was then reacted with DFDPS in the presence of base catalyst KOH following the process outlined in the experimental section. The synthesis of divanillin based polysulfone was confirmed by determining the ether bond in C-NMR. It was used with BPA alt in various ratios to synthesize co-polyiminesulfones like BGF.

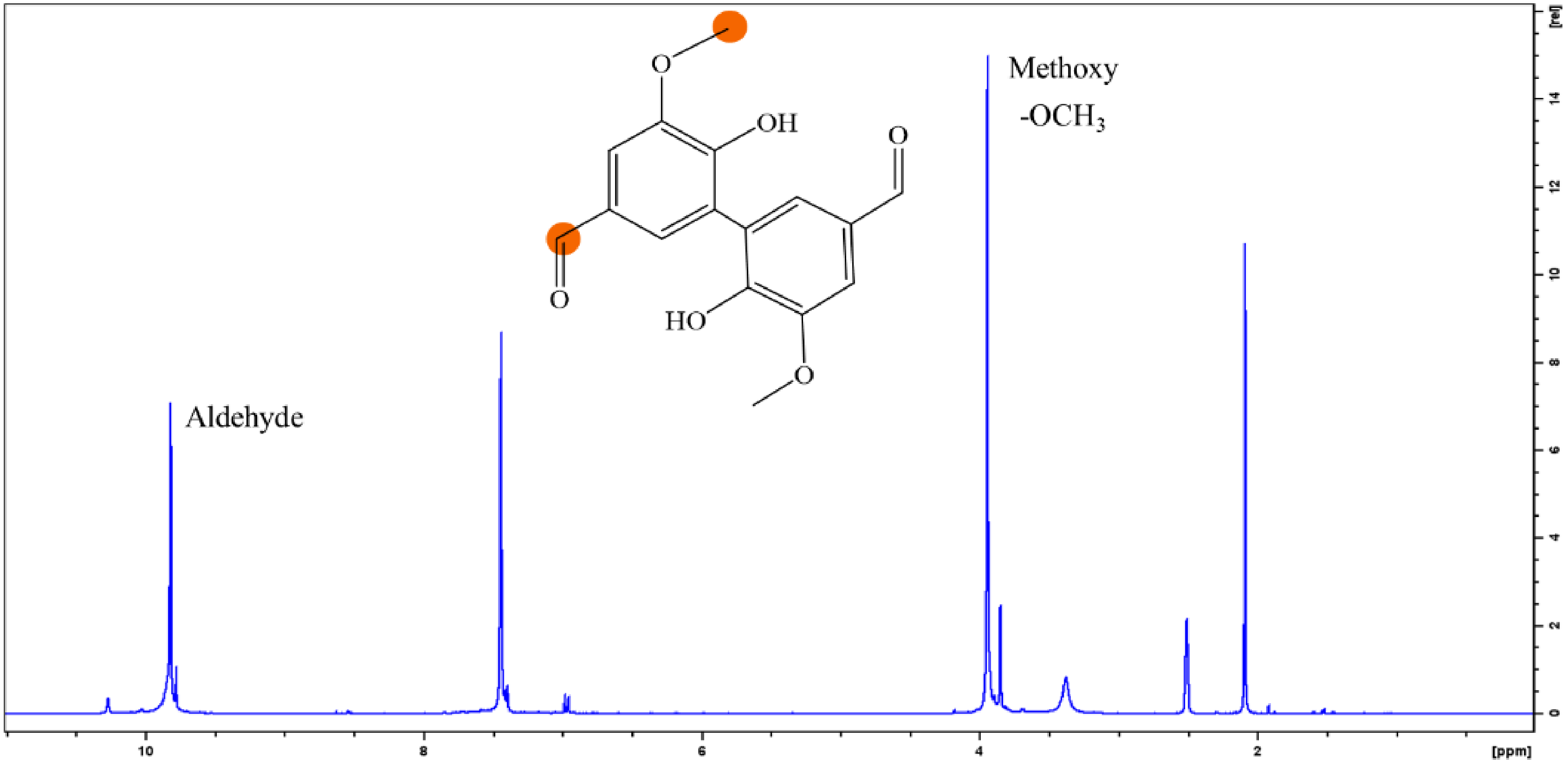


Figure 41: H-NMR Divanillin with labelled key peaks.

The copolymer synthesized was analyzed via H-NMR. The intensity of the methoxy and imine peaks are similar indicating that the majority if not all the polymerization if from the BPA alt monomer with the divanillin participation being negligible. The higher aldehyde peaks do indicate a part of divanillin reacting but is difficult to quantify because of possible imine dissociation being a part of it. Similarly, no clear conclusion can be drawn from the methoxy peak since the BPA-contribution cannot be determined with certainty.

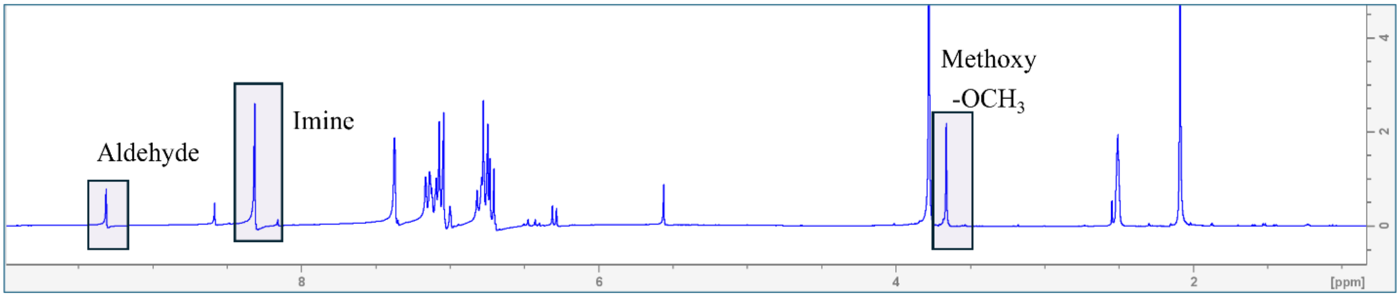


Figure 42: Divanillin Copolymer for 50/50 BPA alt to DV ratio.

Table 14 summarizes the results of the copolymers synthesized using divanillin. While the resulting copolymers were found to be recyclable, meeting the preliminary objective, no significant improvement in thermal property was noted. The T_g values were higher than the BGF copolymers. This is attributed to the higher flexibility of the methylene bridge to the brittle aromatic linkage in divanillin leading to lower activation energy for conformational changes. The T_g values while higher than BGF copolymers are still not comparable to PIS synthesized in chapter 3 and is likely due to both the imine dissociation making the stoichiometry of copolymerization difficult and the added steric hindrance of the additional bulky groups of aldehydes and methoxy on the monomer.

Table 14: Divanillin-BPA alt copolymer synthesis

Divanillin (mol %)	BPA alt (mol %)	T_g (°C)
100	0	-
70	30	106
50	50	115
0	100	162.6

5.3.4 BGD-polysulfone

The focus was shifted to make crosslinked polysulfones. The bisguaiacol based polymers were not ideal for crosslinking due to the absence groups suitable for curing. The divanillin based polymers had two aldehyde groups that could be utilized for the crosslinking. The sample with 100% DV hereby referred to as PSU-DV was used for curing for maximum aldehyde group availability for crosslinking. Additionally, the idea of synthesizing a derivative of bisguaiacol with an aldehyde group was considered. This would serve as the site for the amine linking site to form imine crosslinks.

Initially the guaiacol was substituted for vanillin following the same procedure as BGF synthesis. Low yield of the product was recovered at the end. This was attributed to the unavailability of the favorable para position. From qNMR analysis it was found to be just 3.54% from the methylene bridge vs trioxane calculation (Figure 45).

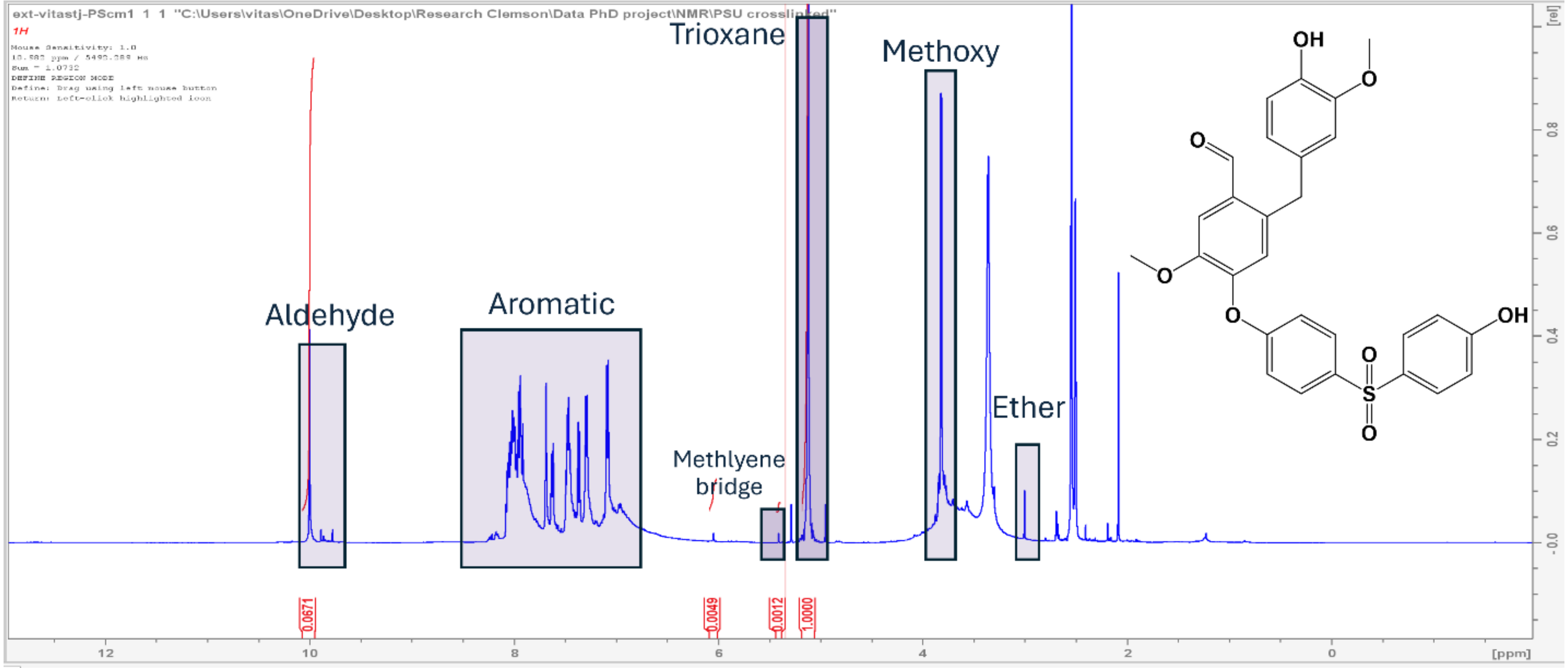
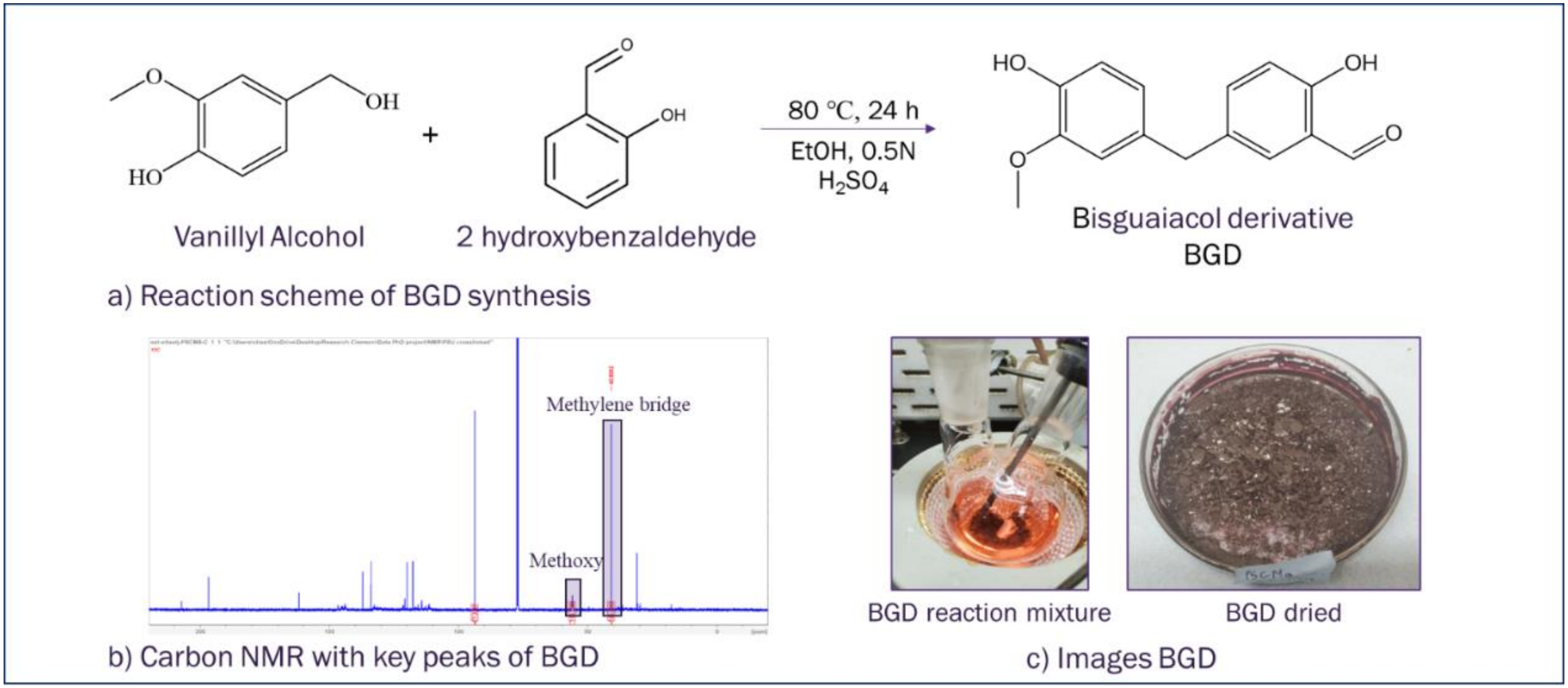


Figure 43: PIS prepolymer from vanillin based BGD.

Isovanillin was considered instead due to the availability of the para position to the hydroxyl group. The maximum yield for this was found to be just 67% though. This was likely due to the difficulty of adding a fourth substituent on the benzene ring of isovanillin. The bulky methoxy groups also contribute to the difficulty due to steric hindrance and lead to the low yield observed. An alternative was then selected with the aldehyde and hydroxyl moieties in a favorable ortho position relative to each other. The aldehyde group is meta directing and the hydroxyl group is o,p directing. With only 2 substituents and no steric hindrance due to the bulky -OCH_3 group salicylaldehyde was selected for the synthesis of BGF derivative (BGD). Salicylaldehyde is another byproduct of the lignin depolymerization process in addition to vanillin.

The synthesis of the BGD (MW 258 g/mol), was confirmed via H-NMR. The key peaks were identified and marked with the aldehyde group presenting at 9.8 ppm and the methoxy group at 3.9 ppm in the H-NMR. However, due to the potential overlap due to proximity a C-NMR was also performed to confirm synthesis. Using trioxane as an internal standard it was determined that the methylene bridge at 40.2 ppm was para to the -OH[23] as desired at 99.8% conversion (theoretical vs actual -CH_2 peak integration). BGD was then reacted with DFDPS (BGD-PSU) to make a polysulfone with an aldehyde group present for subsequent curing.



a) Reaction scheme of BGD synthesis

b) Carbon NMR with key peaks of BGD

c) Images BGD

Figure 44: a) reaction scheme BGD synthesis, b) C-NMR highlighting the methoxy and methylene group indicating para position of hydroxyl groups(ref), c) images of the reaction mixture and dried BGD monomer.

5.3.5 Curing BGD-PSU and DV-PSU with Priamine

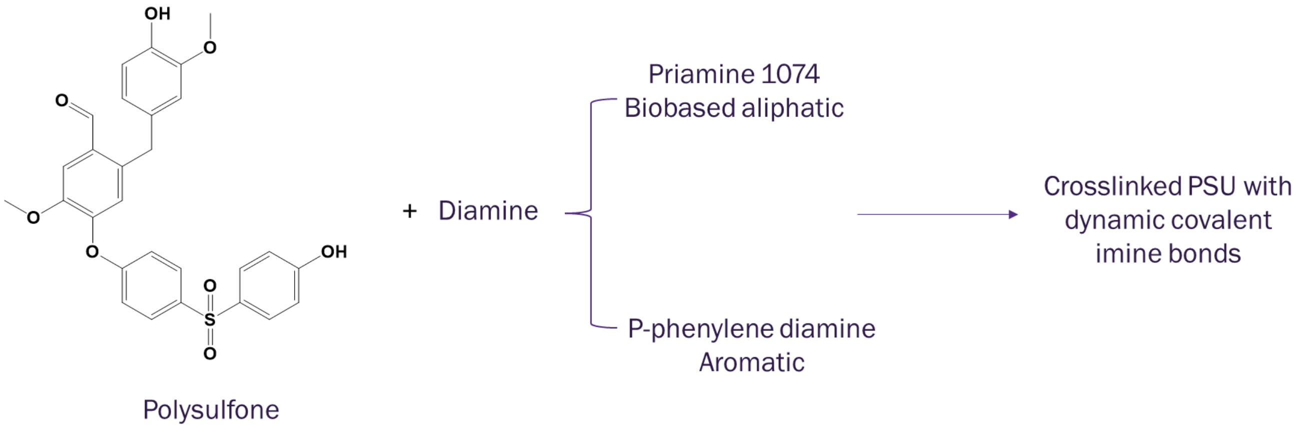


Figure 45: Curing Reaction Scheme.

The polymer curing was conducted by using imine association to crosslink the aldehyde groups with priamine, a biobased diamine. Initially p-phenylene diamine, an aromatic diamine and 1,10 diaminodecane, a short aliphatic diamine was also considered. It was found through DSC analysis that for 1,10 diaminodecane, the flash point is 127 ℃ and there were no exothermic peaks before then indicating that curing was not possible. P-phenylene diamine is highly aromatic and was found to be difficult to cure before polymer degradation temperatures. DSC was hence conducted to understand the curing temperature for BGD-PSU with priamine reaction system. An exothermic peak on the DSC scan revealed an optimum temperature of 167 °C for the curing of the system (Figure 48). The DV-PSU sample was also cured with priamine.

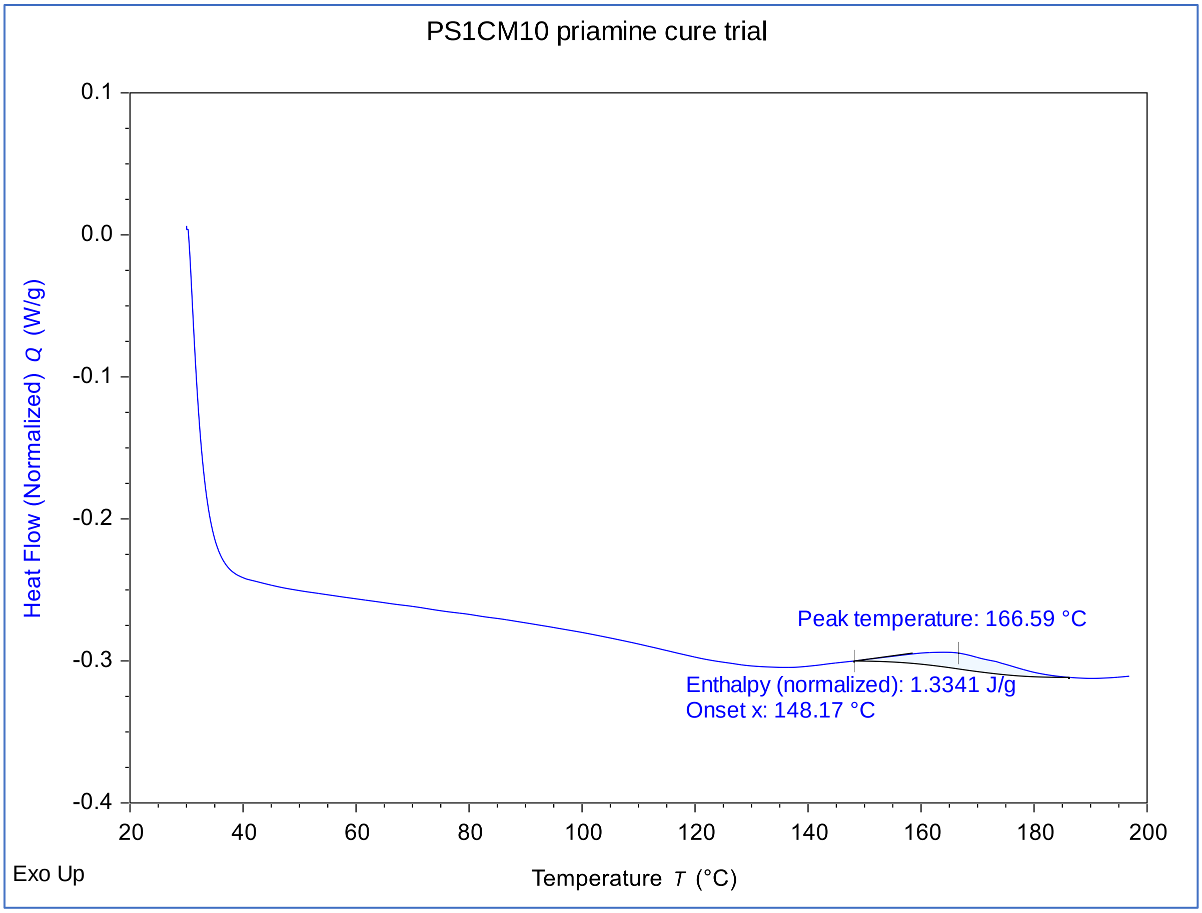


Figure 46: DSC to study curing of priamine and BGD-polymer.

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The curing chemistry was understood using FTIR as the cured polymers were insoluble in organic solvents without the use of acids at which point the imine bonds dissociated and were unable to be characterized via NMR. The FTIR had imine peaks in the 1640-1690 cm^{-1} region indicative of imine bond formation, suggesting the successful reaction between the aldehyde groups present in the polysulfone and the amine in priamine (Figure 49 and 50).

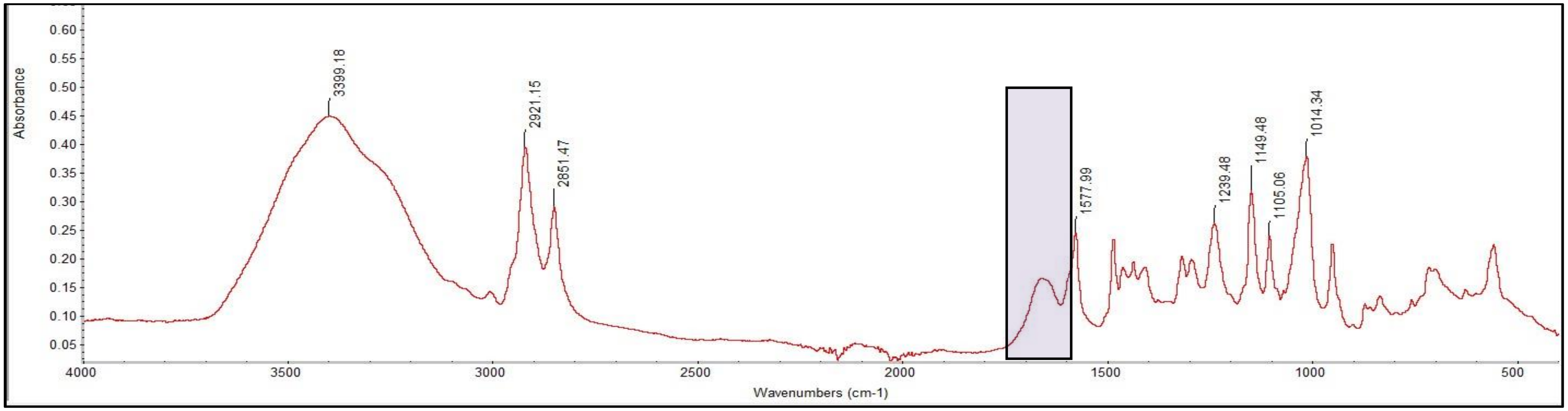


Figure 47: FTIR of BGD-PSU-Priamine with imine peak highlighted.

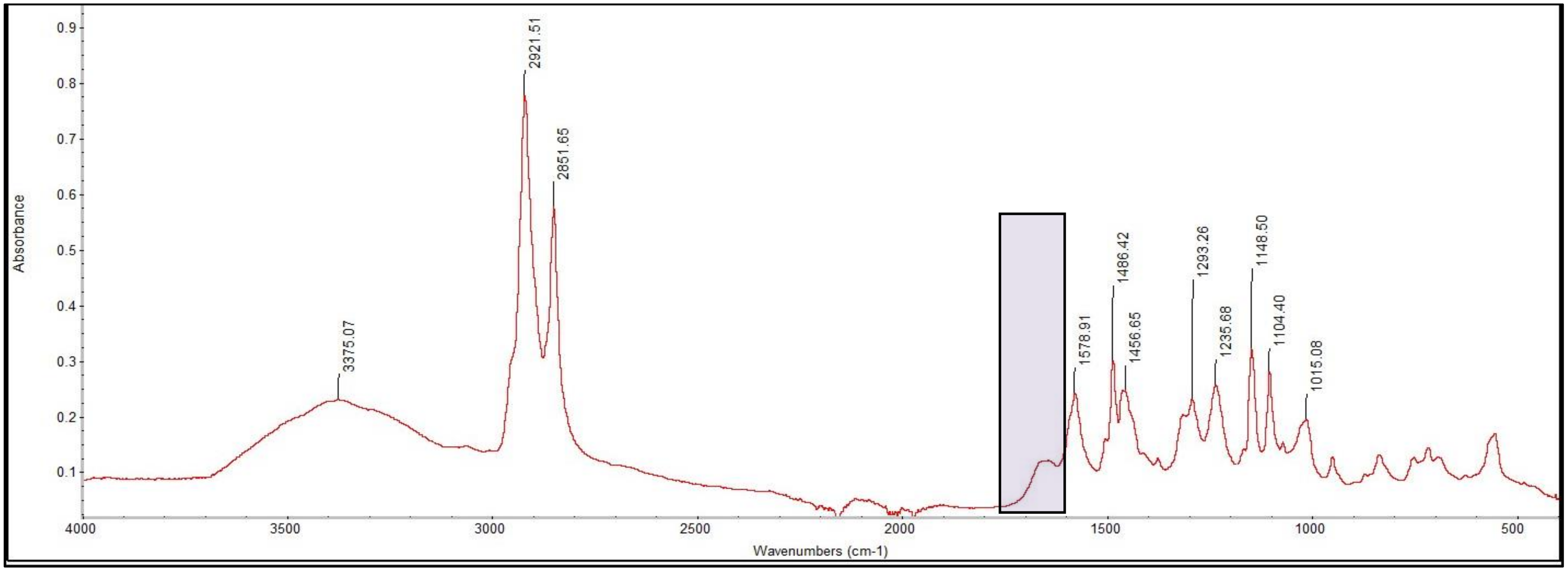


Figure 48: FTIR of DV-PSU-Priamine with imine peak highlighted.

A DSC run of the cured sample showed a step transition in the 1st heating curve for both the BGD and DV PSU-Priamine. From the imine peaks in the FTIR and the poor solubility observed experimentally, it can be determined that the samples have indeed formed networks. However, the network thus formed is not completely crosslinked as evidenced by the step transition. This can be attributed to the end chains of imine that didn't crosslink in the network.

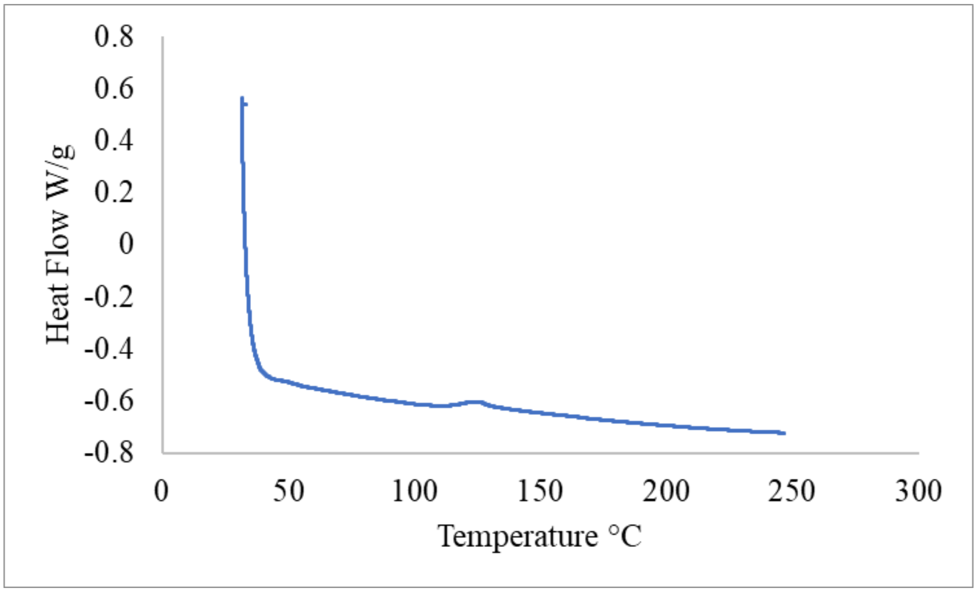


Figure 49: FTIR of BGD-PSU-Priamine with imine peak highlighted.

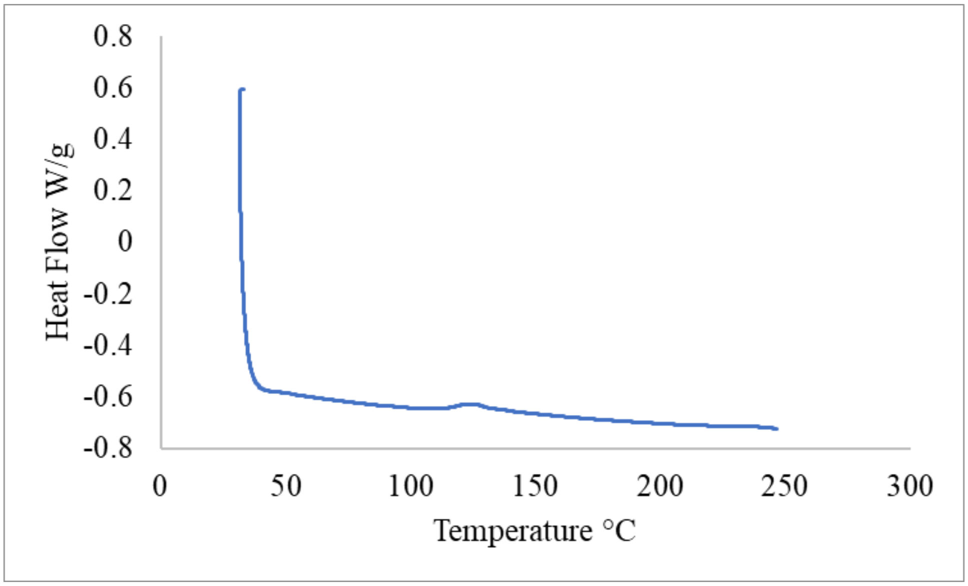


Figure 50: FTIR of DV-PSU-Priamine with imine peak highlighted.

5.4 CONCLUSION

In this study copolysulfones were successfully made using bisguaiacol and divanillin in different ratios with BPA alt. The copolymers synthesized were compared and the properties were as expected due to the structure of the BGF and DV monomers. Where the flexible methylene bridge of the BGF led to lower T_g than the DV copolymers. The DV copolymers were still not comparable to the BPA-alt polymers due to their lower reactivity from steric hindrance. While the copolymers were shown to be recyclable, the thermal properties were not comparable to the PIS synthesized in the previous study owing largely to imine dissociation, difficult to control ratios owing to imine dissociation, mixture of isomers for the BGF, and steric hindrance in the case of DV. PIS networks were considered as the next step to making derivative with different properties. A new monomer was synthesized based on the bisguaiacol procedure to add aldehyde groups necessary for curing in the polymer backbone. The synthesis of the various monomers and polymers was confirmed, and their thermal properties studied. Curing was successfully done with a biobased diamine, priamine 1024 albeit a complete crosslinking was not achieved.

5.5 FUTURE WORK

The priamine is expected to add flexibility to the brittle polysulfone main chain and a more detailed study of thermoset PIS's is the next step in this work. Additional diamines can be considered to obtain polymers with desired properties and check for recycling and self-healing observed in imine crosslinks. This can also be used in conjunction with imine metathesis to synthesize thermosets with a switch to change polymer properties on outside stimuli such as pH or temperature. Imine metathesis further opens a platform of materials after the use phase as it can be used to make new co-polymers using PIS, PIS thermoset, polyimines etc. where imine exchange is possible.

CHAPTER SIX:

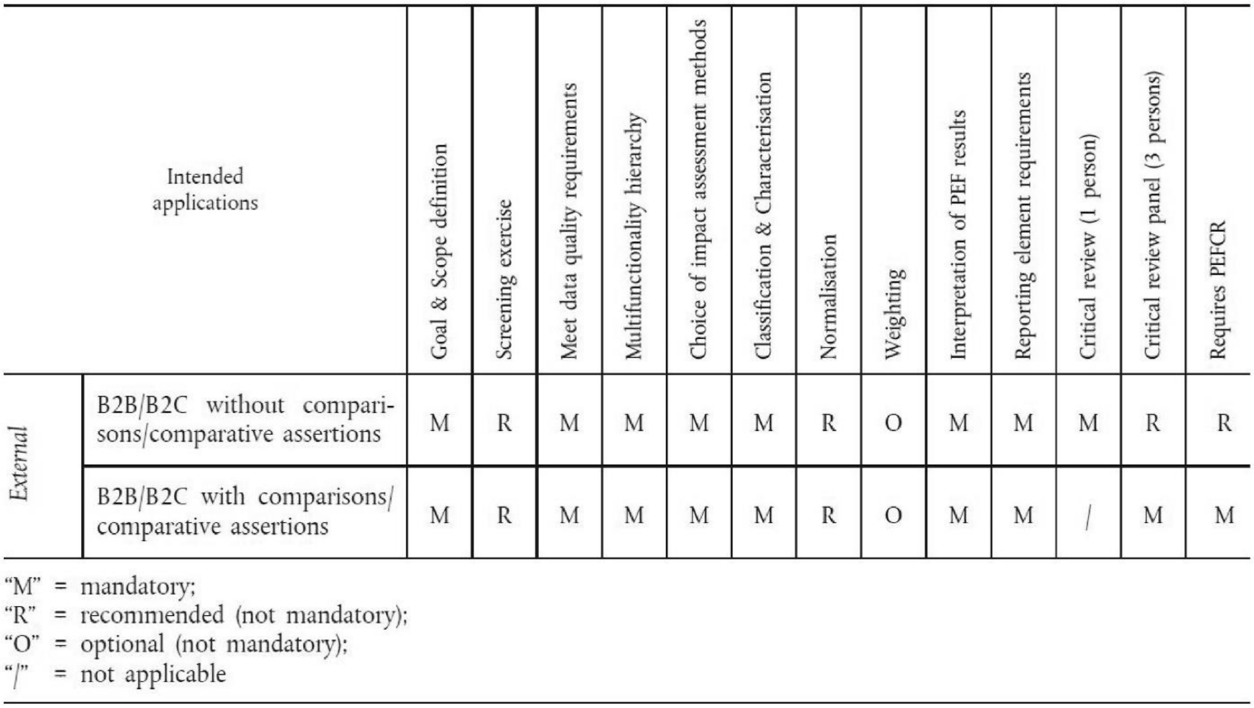
LIFE CYCLE ANALYSIS

6.1 INTRODUCTION

According to a study in 2015, polymers were the cause for 4% of the annual global greenhouse gas emissions (GHG) over their life cycle amounting to 1.8 Gt CO_2 eq. This number is expected to rise to 15% by 2050[1,89]. The use of nonrenewable resources in the synthesis of polymers poses an environmental challenge. In addition to that use of toxic chemicals in polymer synthesis leads to an increasing risk of polluting land and water resources upon the disposal of these materials. Some mitigation strategies have also been proposed such as making biobased plastics, using renewable energy, recycling, and reducing plastic demand[136]. While numerous technologies have been investigated to reduce the adverse impacts created by plastic waste, challenges in transportation of the plastic waste, cost of sorting, environmental impact of recycling, energy cost and economic considerations make the impacts of recycling plastic waste difficult to quantify and justify. Another concern when designing for sustainable materials is the competition with land or food sources. Selection of appropriate feedstock is essential as the impact of deforestation, resources in land cultivation, and the opportunity cost of food crops can all add to the impact of biobased materials from agro sources.

A study was carried out to evaluate the sustainability of biobased plastics from cradle to grave[137]. The study selected materials from a spectrum if biopolymers that were evaluated in a different study based on if the polymers were biobased, had the capacity for recycling using existing infrastructure and did not use or emit toxic chemicals in their production, use or disposal. While no impact analysis was done, they concluded that the current bioplastics are fully sustainable. They are simply either preferable due to their non-toxic chemicals from a health and safety perspective or are preferable from an environmental standpoint but might not meet property requirements. PLA, PHA and other starch-based polymers were still found to be the least toxic with lowest predicted impacts.

Another study was conducted where the authors reviewed the impacts of fossil based and biobased polymers from literature sources[138]. Based on the European Union Product Environmental Footprint (EU PEF), they considered full LCA only for the studies that met the nine mandatory, two recommended and one optional requirement illustrated in the Figure 53[139]. The studies analyzed in this review included those that followed the ISO 14040 and 14044 standards as well. They concluded that there was significant variation in data for both fossil fuel based and biobased polymers.



Intended applications		Goal & Scope definition	Screening exercise	Meet data quality requirements	Multifunctionality hierarchy	Choice of impact assessment methods	Classification & Characterisation	Normalisation	Weighting	Interpretation of PEF results	Reporting element requirements	Critical review (1 person)	Critical review panel (3 persons)	Requires PEFCR
External	B2B/B2C without comparisons/comparative assertions	M	R	M	M	M	M	R	O	M	M	M	R	R
	B2B/B2C with comparisons/ comparative assertions	M	R	M	M	M	M	R	O	M	M	/	M	M

"M" = mandatory;
"R" = recommended (not mandatory);
"O" = optional (not mandatory);
"/" = not applicable

Figure 51: PEF rules for comparative LCA studies[139].

Different methodologies, standards and interpretations can make life cycle assessments difficult to compare across the board. Additionally challenges in data quality and acquisition make for high uncertainties in the final analysis. This study seeks to evaluate the impact of the traditional polysulfone synthesis in comparison to the synthesis and recycling of the polyiminesulfones made in chapter 3 based on the ISO 14040 standards where possible. Factors such as raw material inputs, database selection, outputs, choice of recycling method were considered and applied throughout the study. The most significant impacts were identified and methods to mitigate them, thus reducing their effects were suggested as well. A comparative LCA was selected since there was no existing baseline for traditional PSU comparisons or any other comparable substitute material available.

6.2 MATERIALS AND METHODS

The present study was intended as a comparative analysis between the traditional polysulfone using BPA and the biobased recyclable polyiminesulfone synthesized in this work. OpenLCA, ELCD 3.2 Greendelta v2 database, TRACI, values from literature and Excel were used in the LCA inventory analysis and impact assessment. The LCA method comprises four major steps: goal and scope definition, inventory analysis, impact assessment, and interpretation.

The Appendix contains the list of inventory analysis from TRACI, ELCD, literature and the cut off methos, formulas, mass balances, recycling allocations and final data calculations.

6.2.1 Goal and Scope Definition

Goal

To compare the impacts associated with the recyclable biobased polyiminesulfones (PIS) synthesized in this work vs traditional polysulfones (PSU). The functional unit (fu) under the current investigation is 1 kg of polymer.

Scope

The cradle to cradle/grave approach is considered from raw material acquisition, product synthesis, end processing, use phase and subsequent recycling or disposal with transportation in between steps.

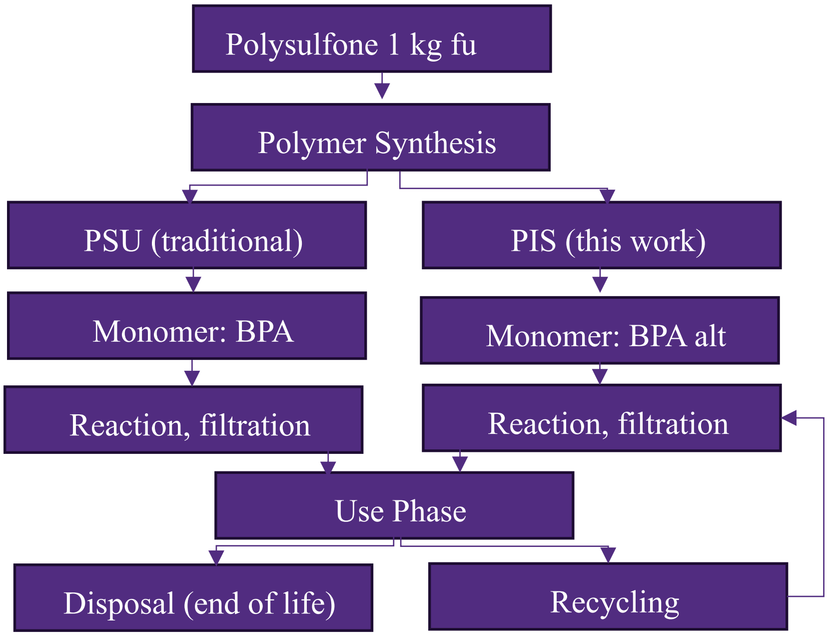


Figure 52: Flow chart for Life Cycle Assessment

List of assumptions:

- Elimination of common steps between the 2 products. This is applied to common raw materials (DFDPS), synthesis steps, processing, use phase and transportation.
- Cutoff method was utilized for BPA from the polycarbonate[140] and for 4 aminophenol from paracetamol[141] production due to availability.
- Literature values were used where database was unavailable.
- The European database and electricity values were used due to better data quality, compatibility with the database for other inputs and availability for the region.

6.2.2 Inventory Analysis

As this study uses chemicals from biobased sources (lignin production), consistency and data quality were a challenge. Detailed process information was obtained from the empirical data at the lab-scale, process inputs, outputs, the electricity consumption for the polymer reaction primarily for the drying and recycling steps using the oven and stirrer. The ELCD 3.2 database was used to collect impacts of emissions and production of inputs such as BPA, reagents, solvents etc. And finally, data from literature was used where no other data source was available. Table 15 lists the inputs used for the analysis. The balance is waste and consists of unreacted monomers, water, solvent, salts and is accounted as emissions to the environment in the assessment.

Table 15: Input and output of materials and energy

Inputs	Abv.	Unit	PSU	PIS
Bisphenol A	BPA	kg	0.52	0
Potassium Carbonate	K_2CO_3	kg	0.31	0
Bis 4 florophenyl sulfone	DFDPS	kg	0.57	0.55
N-Methyl-2-pyrrolidone	NMP	kg	5.14	0
Deionized water	DI-H_2O	kg	10.00	10.00
Vanillin	Van	kg	0	0.43
4-aminophenol	4AP	kg	0	0.31
Potassium Hydroxide	KOH	kg	0	0..24
Dimethyl sulfoxide	DMSO	kg	0	5.50
Hydrochloric acid	HCl	kg	0	0.006
Electricity	Electricity	kWh	4.80	5.52

6.2.3 Impact Assessment

The aggregated input and output scores are converted to different environmental impacts. The EF 3.0 method was employed to assess the potential environmental impact of polymer synthesis and recycling in categories comprising abiotic depletion (AD), climate change (CC), human toxicity non-cancer (HT), freshwater ecotoxicity (FAE), acidification (ACI), eutrophication (EU), ozone depletion (OD) and photochemical oxidation (PO). EF, Environmental Footprint is the method maintained by the European commission and uses midpoint method for assessment. This was chosen due to data availability.

6.3 RESULTS AND DISCUSSION

6.3.1 Life Cycle Impact Assessment

The aggregate data are summarized in Table 16 and Figure 55. The main categories are human toxicity and freshwater ecotoxicity.

Table 16: Life Cycle Impact Categories PSU vs PIS

Categories	Abbv.	Units	PSU	PIS
Climate Change	CC	kg CO_2 eq	158.82	155.94
Freshwater Ecotoxicity	FE	CTUe/kg	30.16	45.47
Human Toxicity (non-cancer)	HT	CTUh/kg	6.33E-06	0.04
Acidification Potential	AP	Mol H^+ eq	0.71	0.86
Abiotic depletion (non-fossil)	AD	kg Sb eq	2.37E-07	0.08
Eutrophication	E	kg N eq	0.81	1.04
Ozone Depletion	OD	kg CFC 11 eq	1.02E-05	0.12
Photochemical Oxidation	PO	kg NMVOC eq	12.65	19.15
Abiotic depletion (fossil)		MJ	1478.21	1619.22

The method used to incorporate recycling for PIS is the 50/50 method for 50 cycles of recycling where the impact of the first cycle is 1/50 fraction of the impact and from 2nd to 50th cycle, the recycling inputs and outputs are considered. The offset for the material loss during recycling is accounted for as emissions. 50 cycles were selected from experimental data where 98% of the PIS material was successfully recovered consistently[142].

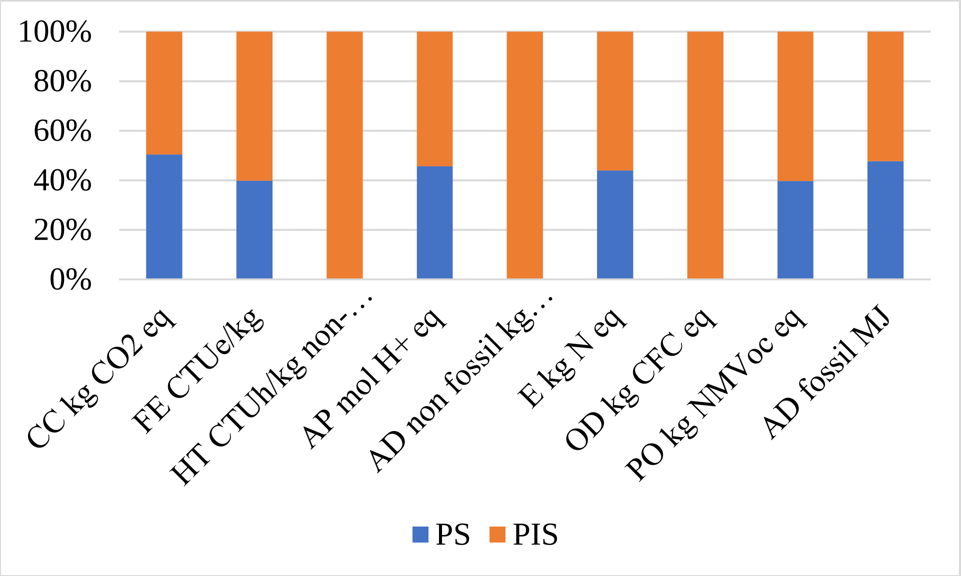


Figure 53: PSU vs PIS Impacts

The human toxicity, abiotic depletion for non-fossil resources and the ozone depletion were primarily attributed to the PIS process, largely due to lack of compatible data for the solvent NMP. For the human toxicity factor this is believed to be due to lack of available data of BPA on the human body and lack the data for NMP. Various studies have pointed out the acute impacts of BPA accumulation, it is believed to be a xenoestrogen, a thyroid mimicker and has been linked to various other problems. However, the HT value for BPA emission was just 1.07E-10 CTUh/g. While compatible data or a reliable conversion factor for NMP could not be found, the HT value for NMP was 146 mPt from modelling the production process in Simapro[143]. For the PIS system, contributor to this value were the solvent DMSO, 4 aminophenol and electricity.

Similarly for the AD non fossil and OD values, lack of compatible NMP data led to this estimation of impacts. The impacts are largely due to electricity and solvent and the values for electricity are of the same order of magnitude.

6.3.2 Comparison of Impact Categories

The major impacts are associated with the climate change, freshwater ecotoxicity and abiotic depletion fossil fuels. The major contributor to these is electricity. The electricity data was considered for a mix grid of which approximately 40% is from fossil fuel in the EU[144]. This factor would be much higher depending on geography as the electricity source is predominantly fossil fuel globally. Figures 56 shows the various impact categories for PSU vs PIS systems. Since some categories are harder to see in Figure 56, a zoomed in Figure 57 is included. The units for y-axis are different for each category and are noted in the labels for the bars on the x-axis.

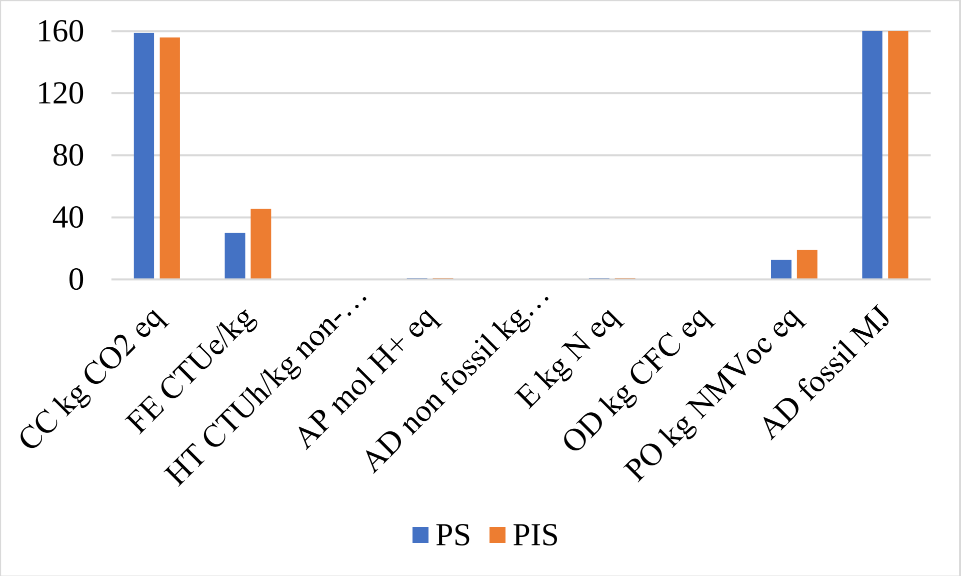


Figure 54: PSU vs PIS impact factors. The AD fossil has a higher value and is not representative.

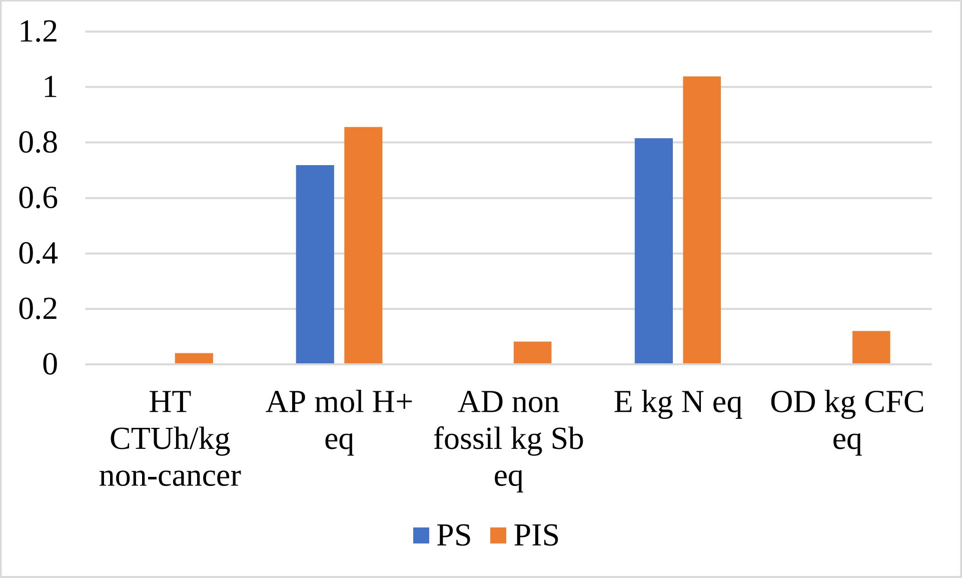


Figure 55: PSU vs PIS impact factors for human toxicity (HT), Acidification Potential (AP), Abiotic depletion non fossil (AD-nf), eutrophication (E) and ozone depletion (OD).

The human toxicity, abiotic depletion for non-fossil resources and the ozone depletion were primarily attributed to the PIS process and expanded on in the previous section. In this section the rest of the impacts are discussed.

Climate Change:

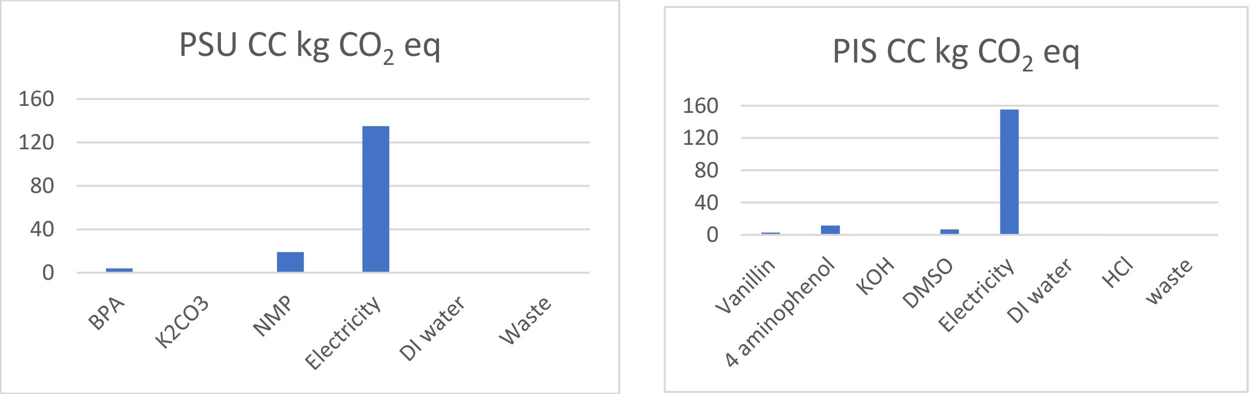


Figure 56: Bar graph for major contributors to climate change for PSU and PIS.

The y-axis in kg CO_2 eq for Figure 58 is compared for PSU and PIS across different system inputs. The major impact for climate change is due to electricity for both the processes. And while DMSO has a lower impact than NMP, in the overall scheme, electricity is the predominant factor. The overall impact for CC is lower for PIS and that is despite the extra electricity needed for recycling due to the solvent contribution.

Freshwater Ecotoxicity:

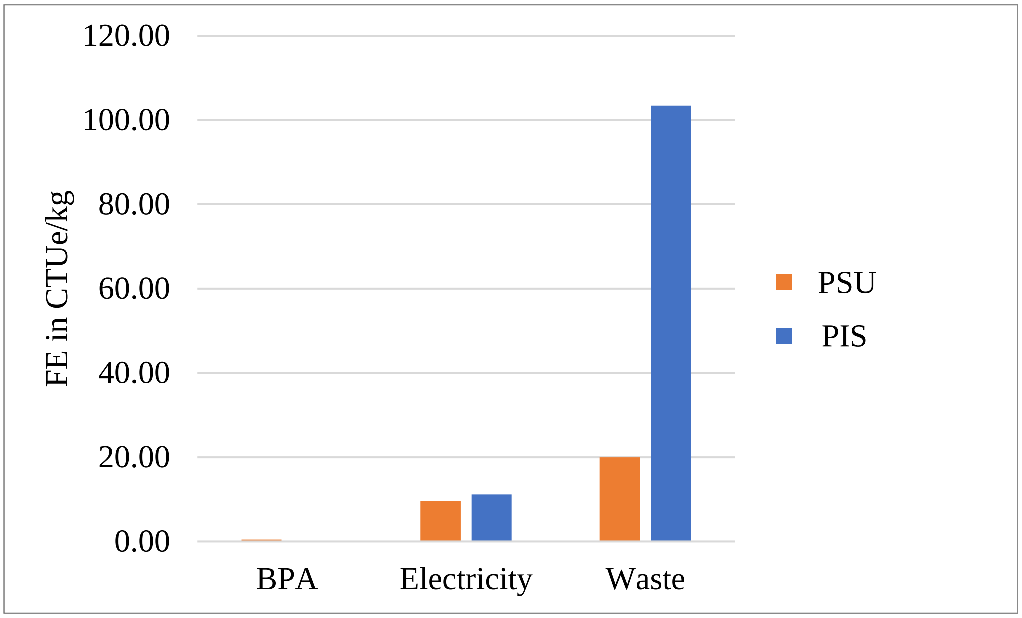


Figure 57: Freshwater Ecotoxicity by component.

The major contributor to this impact is the waste emission. The FE value for 4 aminnophenol for the PIS system is 45 CTUe/kg. Another factor is the solvent. The NMP emission value for FE is 3.02 CTUe/kg whereas for DMSO it is almost 3 times higher at 9.38 CTUe/kg. This makes the recycling of the solvents, specifically for PIS a process to consider reducing the impact and perhaps make it comparable to the traditional PSU synthesis.

Abiotic Depletion fossil:

The abiotic depletion largely originates from the detrimental effects of natural gas and crude oil utilized in electricity generation[145]. Unsurprisingly electricity has the highest contribution to this category. Due to the higher electricity usage for the PIS process, the AD fossil for PIS system is 1619 MJ and is 1478 MJ for the PS system.

Acidification Potential, Eutrophication, Photochemical Oxidation

The acidification of PIS is higher due to the use of residual HCl emissions and due to higher electricity usage. The eutrophication factor is also largely due to the electricity usage. For the photochemical oxidation, the major contributors are BPA, electricity, and solvents. Lack of data of NMP makes this a difficult comparison. However, this further lends to the need for solvent recycling.

6.3.3 Comparison of Polymers

Through this study it can be seen that recycling is not feasible from an environmental perspective. The largest factor to that conclusion is electricity followed by solvent use. The chemicals used in synthesis and recycling have minimal impact on the overall assessment. However, it must be noted that this analysis made several assumptions and simplifications that are not representative of the process on a whole. These assumptions were made for the sake of simplicity and the lack of availability of quality data. Various studies have pointed out the acute impacts of BPA accumulation in the human body. The FAE value for BPA is 7.55 CTUe/kg, much higher than the human toxicity value of 0.062 CTUe/kg.

In addition, the electricity distribution towards greater sustainability would also dramatically shift this assessment to make PIS more viable. Much work is being done to minimize the impact of vanillin synthesis and values ranging from 6.27E+01 CO_2 equivalent from plant-based production, 4.45E+03 natural production from vanilla bean pod[146], 7.5E+04 from guaiacol to 2.8E+04 CO_2 equivalents from guaiacol simply by replacing ultrapure water to industrial water and recycling solvents[147] have been reported.

6.3.4 Expanding LCA Scope

The LCA in this study only considered environmental impacts based on limited data as the aim was to gauge the viability of chemical recycling currently. Further studies will need to be undertaken to make a more comprehensive assessment. Additional economic and logistic factors of recycling need to be considered. The cost of raw materials, transportation, additional costs due to recycling process need to be taken into account before recycling can be achieved on a commercial scale.

6.4 CONCLUSION

In this study, LCA was carried out to determine the feasibility of chemically recycling polysulfones. From just the climate change perspective, PIS and its recycling is slightly better than the traditional PSU synthesis. However, the PSU system had lower impact factors than PIS in the remaining categories. The largest impact factor was the abiotic depletion of fossil fuels during electricity production 1619 MJ for the PIS system and 1478 MJ for the PSU system.

The results suggested that further work needs to be done both in a more comprehensive analysis and in reducing impacts of inputs such as electricity by switching to renewable sources which could make recycling a more efficient method of dealing with waste polymer. Additionally, solvent recycling must be considered and compared for decision-making. Current research into reducing the environmental impacts of lignin biorefinery process would also have the potential to make the PIS system more attractive due to the reduction in costs associated with vanillin and DMSO.

CHAPTER SEVEN:

CONCLUSION AND FUTURE WORK

7.1 CONCLUSION

Current polymer waste disposal methods are unsuitable. Chemical recycling has emerged as a promising way to deal with waste and close the loop on plastic production for a more sustainable future. As the demand for sustainability increases, the focus will shift to technologies that reduce our impact on the environment while fulfilling the material needs.

The efforts in this work to design an alternative to polysulfones that are recyclable and sourced from biobased feedstock are a step forward towards circularity. The choice of vanillin, bisguaiacol, salicylaldehyde, DMSO as lignin-based compounds was done with the intent to incorporate and upcycle lignin as opposed to using it as a low value fuel. The introduction of the dynamic imine bond was selected to enable the recycling of the polysufone, the copolymers and the thermoset polymers. The materials thus synthesized and recycled were characterized using NMR and FTIR techniques. The properties of recycled PIS were studied using DSC and TGA to determine structure-property relationships and confirm the impact of recycling on the material.

And finally, a life cycle analysis was undertaken to test the impact of recycling. The major impact of electricity and solvent use on polymer production and recycling must be noted. Further work will need to be undertaken to optimize multiple processes across various industries to design a truly greener alternative to the plastic waste problem.

7.2 FUTURE WORK

In the design for recyclable polysulfones, different dynamic covalent chemistries can be studied. Further work on making blends and testing their processability for practical applications can be done. Solventless methods, or methods that enable re-use of solvents can be applied to reduce the environmental impact of the process.

For the derivative polymers, other biobased monomers can also be studied to make a variety of copolymers. Similarly various diamines can be tested to enable tunable thermoset synthesis. The curing kinetics of various diamine can also be studied. Imine bonds undergo metathesis, i.e. imine exchange. This can be exploited to design thermosets that on exposure to external stimuli such as pH or light can exchange to form smart materials. Additionally, it can be used to expand the post recycling products available as various polysimineulfones and polyimines can be integrated to make new materials.

Finally, for the LCA, a more comprehensive analysis with a wider scope can be performed. Inclusion of methods such as solvent recycling to reduce impact can be employed. Further work on the pre-processes such as vanillin production, sourcing electricity from renewables etc. also greatly impact the results. Further work on the PIS system for better atom economy or different starting monomer replacing 4AP would also reduce the impact and make for a greener biobased chemically recyclable alternative to the currently used petroleum derived polysulfone. This serves as a future area of research for the current study.

APPENDIX

LIFE CYCLE ANALYSIS

A. 1 LIFE CYCLE ANALYSIS

The LCA calculations were performed in excel due to use of various data sources. This was done since no database was found that had the data for the entire inventory analysis. From the Open LCA database ELCD 3.2 greendelta version 2.18 hereby referred to as ELCD, elementary flows were used for emission data for chemicals emitted to the environment. TRACI, literature, and carbon cloud were also utilized under similar conditions where available (temporal, geographical, methodology etc.) and added in the inventory analysis in the next section.

A. 1.1 Mass Balance calculations for the inputs and outputs of the PSU and PIS system:

Functional unit of PSU and PIS: 1 kg

PSU Molar Mass: 442.52 g/mol

PIS Molar Mass: 457.51 g/mol

Table 17: PSU inputs per functional unit

PSU inputs	Molar Mass g/mol	Density g/ml	Amount in kg. (per functional unit)
BPA	228.29		0.52
DFDPS	254.25		0.57
K_2CO_3	138.21		0.31
NMP	99.13	1.028	5.14
DI water	18.02		10
Electricity	-		4.8 kWh

Table 18: PSU output/ emissions per functional unit

PSU outputs/ emissions	Molar Mass g/mol	Amount in kg. (per functional unit)
BPA	228.29	0.52
DI water	18	10.08
NMP	99.13	5.14
KF	58.10	0.26
H_2CO_3	62.03	0.28

*No data was found on the impact of PSU; it was approximated from the impact of its monomers. DFDPS was not added since the impact for the PSU and PIS are the same and because no data was found on the impact of DFDPS production or disposal or of a reasonable substitution.

Table 19: PIS Inputs per functional unit.

PIS inputs	Molar Mass g/mol	Amount in kg. (per functional unit)
Vanillin	152.15	0.43
4 aminophenol (4AP)	109.13	0.31
DFDPS	254.25	0.56
KOH	56.11	0.25
DMSO 1	78.13	5.5
DMSO 2(recycling)		2.75
HCl	36.46	0.00595
DI water	18.02	10
DI water 2 (recycling)	18.02	5
Electricity		11.04 kWh

*Note: HCl 5 µl of 38% conc

Table 20: PIS outputs/ emissions per functional unit.

PIS outputs/ emissions	Molar Mass g/mol	Amount in kg. (per functional unit)
Vanillin	152.15	0.10
4 aminophenol	109.13	0.071
DI water	18	10.08
DI water 2		5.0
DMSO 1	78.13	5.5
DMSO 2(recycling)		2.75
KF 1	58.10	0.25
KCl 2	74.55	0.32
Vanillin (post recycling)	152.15	0.006
4 aminophenol (post recycling)	109.13	0.004
KOH 2 (recycling)	56.10	0.01

*Note: 2 (recycling) are in Tables 19 and 20 refer to the inputs and outputs required for recycling. (post recycling) is for the lost material in the recycling since 98% recycled polymer is recovered, this is the 2% lost per cycle.

A. 1.2 Inventory Analysis:

Table 21: Inventory Analysis.

List of Inventory	Production / Emission	Database and Reference
BPA	P	Allocation from Polycarbonate:[140] Polycarbonate: ELCD
DFDPS	P	-
K_2CO_3	P	GHG data only: CarbonCloud Potassium hydroxide (KOH). E525 · 0.77 kg CO_2e/kg | Verified by CarbonCloud
NMP	P	Literature[143]
DI water	P	Literature [143]
BPA	E	ELCD
NMP	E	ELCD
KF	E	-
H_2CO_3	E	ELCD
Vanillin	P	Literature [148]
4 aminophenol	P	Allocation and data from Paracetamol literature: [149]
KOH	P	GHG data only: CarbonCloud https://apps.carboncloud.com/climatehub/product-reports/id/1394351136979
DMSO	P	Literature[143]
HCl	P	ELCD, TRACI
Electricity	P	ELCD: Grid mix EU AC EF 3.0 adapted
Vanillin	E	ELCD
4 aminophenol	E	ELCD
DMSO	E	ELCD
KCl	E	GHG data only: CarbonCloud https://apps.carboncloud.com/climatehub/product-reports/id/3316104472076

*P=Product; E=Emission

CarbonCloud: Technical report in the format requested by the ISO 14067 and GHG protocol Product Life Cycle Accounting and Reporting Standard are available in the links given.

ELCD: Open LCA database ELCD 3.2 greendelta version 2.18 calculated using the EF 3.0 method.

TRACI: From the EPA website version 2.2 (https://www.epa.gov/chemical-research/tool-reduction-and-assessment-chemicals-and-other-environmental-impacts-traci)

Literature: The data collected was consistent with EF units for data quality.

A. 1.3 LCA Analysis and Interpretation:

The LCA impacts were calculated for all the inputs and outputs given their impacts in different categories from the inventory analysis and the mass balance. For the recycling, a 50/50 method was selected[150]. The summary of data analysis and interpretation is in chapter 6.

Table 22: Impacts from PSU and PIS by chemical in climate change and freshwater ecotoxicity.

	Climate Change kg CO_2 eq	Freshwater ecotoxicity CTUe/kg
PSU		
BPA	4.13	0.48
K_2CO_3	0.35	0.00
NMP	19.12	0.00
Electricity	135.12	9.68
DI water	0.09	0.00
Waste	0.00	20.00
PIS		
Vanillin	2.71	0.00
4 aminophenol	11.78	0.00
KOH	0.48	0.00
DMSO	7.00	0.00
Electricity	155.39	11.13
DI water	0.09	0.00
HCl	0.01	0.00
Waste	0.00	103.43

*Data for Figure 58. Waste stream includes all the output chemicals from Table 18 and 20.

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Fig. 3. Hierarchy of Polymer materials according to their temperature, chemical, and mechanical stability.

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