NOVEL SYNTHETIC STRATEGIES TO PRODUCE BIOBASED POLYURETHANES

By

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ABSTRACT

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Polymers from renewable resources are gaining a lot of interest, especially with the high price and limited availability of crude oil. Polyurethane is one polymer that is widely used in various industries including packaging. Therefore it is desirable to be able to synthesize biobased polyurethane, especially with toxicity concerns from polymer production. The two main building blocks in polyurethanes are polyol and isocyanate.

One example of biobased polyol that is available commercially is soy-derived polyol. Catalytic ozonation of soybean oil has been investigated as one effective method to produce polyols. Ozone is known to be a powerful oxidizing agent, and is used in combination with ultraviolet (UV) light in many processes for oxidation of organic material to improve the effectiveness of the reaction. The combination of ozone and UV light in the ozonation reaction of soybean oil was investigated. It was found that the addition of UV light to the process did not change the rate of the ozonation reaction.

Two isocyanate-free and phosgene-free methods were utilized to synthesize biobased polyurethane: polyurethane synthesis from carbamate ester and polyurethane synthesis from ethylene carbonate. Dimethyl azelate was used as a model compound. Analyses were conducted on the end products of both methods. The polyurethane synthesis using ethylene carbonate was found to be a more direct approach to produce polyurethanes. This method is, therefore, recommended for further study of bio-based polyurethane synthesis.

DEDICATION

This thesis is dedicated to both of my family in Indonesia and in US.

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I would like to thank God for always giving me an abundance of blessings all my life. I thank my parents for their love, support, and prayers, also I want to thank both of my sisters for their love, support and companionship. I thank Don and Maurine for becoming my second parents, also for their love and support.

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Chapter 1

Introduction

Polyurethane is a polymer broadly used in various industries from building insulation, toys, furniture, and packaging, to airplane construction. The first polyurethane was synthesized by Otto Bayer in 1937 through the basic diisocyanate poly-addition process. In 1957, the introduction of polyether polyols increased the usage of polyurethane; previously only polyester polyols were used to produce polyurethanes. The progress in chemical research and processing technology has led to broad commercial use of polyurethane.

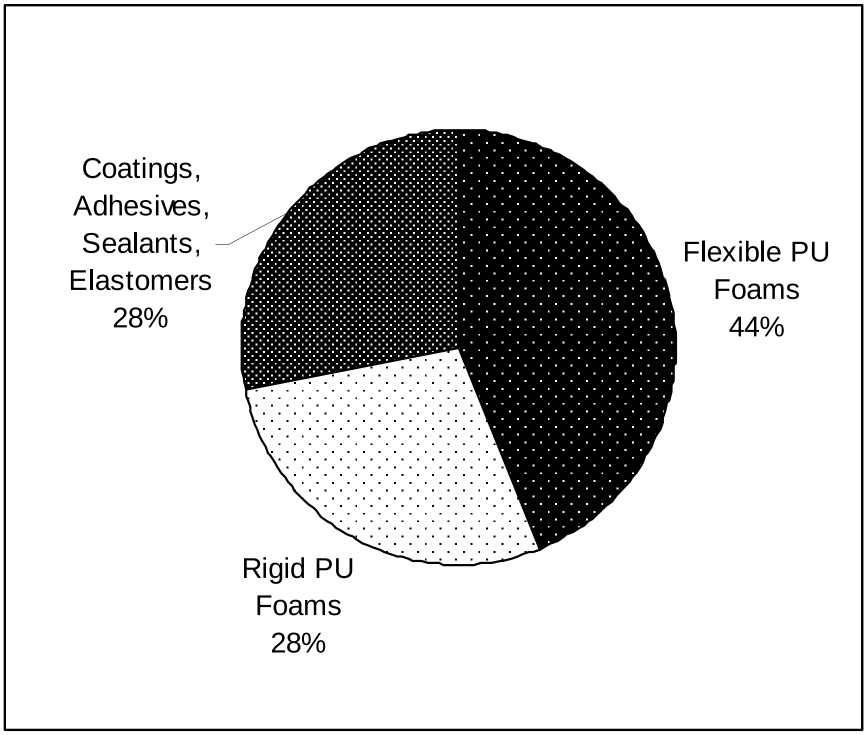

Figure 1.1. World Polyurethane Consumption, by products (2000-2002)[1]

The development of polyurethane flexible foams, semi-rigid foams, elastomers, films, and rigid foams helped to increase the importance of this polymer. Due to the flexibility in selection of monomeric materials (diols, diisocyanate, and chain extenders), and also the variation of preparation methods to meet the desired properties of the final product, the industry interest in this material keeps increasing.[2] The world consumption of polyurethane based products can be seen in Figure 1.1 above. Based on a market forecast by IBISWorld, the demand for polyurethane foam for the US alone will reach $12 billion in 2010, and the packaging applications of polyurethane foam account for 5.3% of the total of the US polyurethane industry revenue.[3]

Six main types of plastics dominate the packaging industry: PET (polyethylene terephthalate), HDPE (high-density polyethylene), PVC (polyvinyl chloride), LDPE (low-density polyethylene), PP (polypropylene), and PS (polystyrene). Polyurethane has an important application especially in foam packaging known as a foam-in-place system, where the foam is injected into a container and the product is placed inside surrounded by PE protective film. During the foaming process an additional layer of foam is injected prior to the container being sealed.[4] The foam acts as a shock absorber to protect the product during transportation. Polyurethane foam with an anti-static additive is a preferred material for electronics packaging.[5] A market study of the packaging polyurethane foam industry was conducted and according to this study, the demand for packaging polyurethane foam is estimated to reach $1.8 billion in 2011, as shown in Figure 1.2 below.[6]

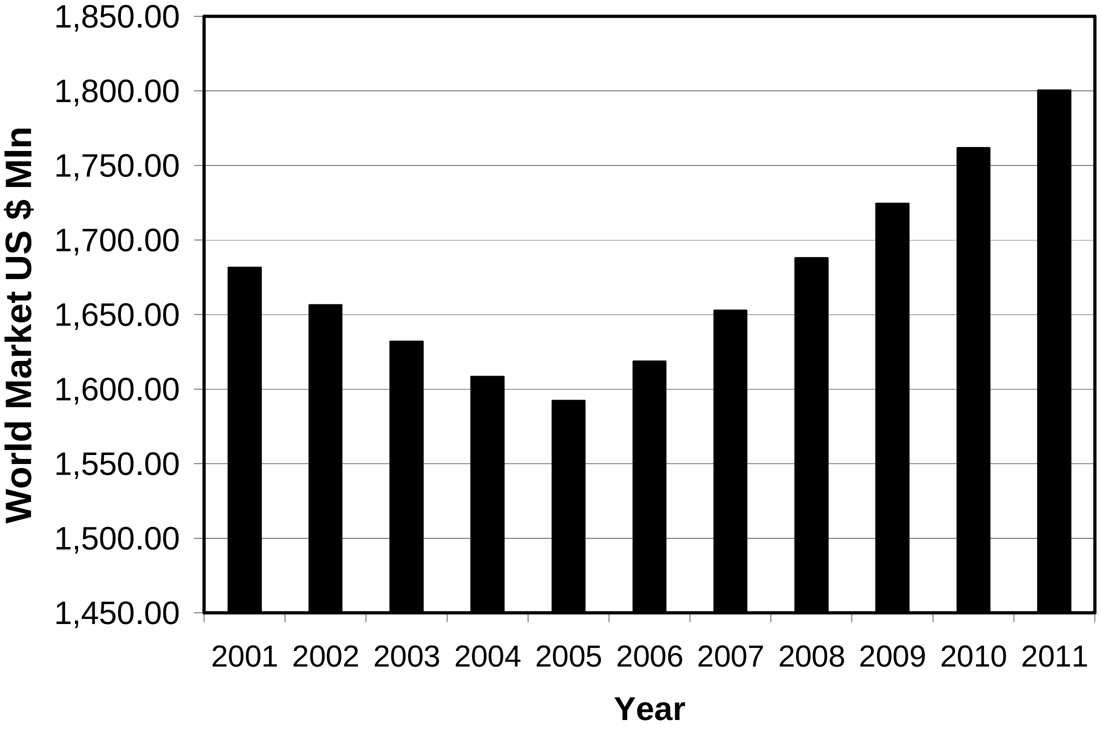

Figure 1.2. World Market for Packaging Polyurethane Foam Products[6]

Another major polyurethane application in packaging is as an adhesive for flexible packaging applications. Various categories of polyurethane adhesive including reactive adhesive, solvent-borne adhesive, and synthetic water-borne adhesive are used to laminate polyolefin films and aluminum, as well as paper.[7] Theoretically, strong bonds cannot be made between polar adherents with non-polar adhesives or vice versa; many non-polar adhesives have hydrophobic characteristics, and many polar adhesives have hydrophilic characteristics. Therefore, non-polar adhesives will have poor wetting and spreading in humid condition; polar adhesives will absorb the moisture, and provide sufficient wetting and spreading. Polyurethane adhesives both contain strong polar bonds and are hydrophilic, which make them a good adhesive with broad applicability due to their good wetting properties.[8]

Starting in the 1970s, when public attention was drawn to the high price and limited availability of crude oil, the development of polymers derived from non-petrochemical feedstocks has gained a great interest. It was estimated that about 7% of worldwide oil and gas are used for plastic manufacturing.[9] This motivates the interest in developing bio-based polyurethane products. Vegetable oil, soybean oil in particular, is very attractive as an alternative feedstock. These new biobased materials are expected to act as alternative raw materials and provide a more environmentally friendly solution to traditional petroleum-based raw materials. When compared to petroleum-based polyurethanes, the obstacles facing bio-based polyurethanes are cost and performance characteristics. However, recent significant development in bio-based products has made this material more cost-competitive with conventional products and has produced a wide variety of products such as fuels, chemicals, building materials, lubricants, fibers, and coatings. Other environmental issues that need to be addressed in the production of plastic packaging are air and water emissions, and chemical exposure. Exposure to some chemicals is harmful, especially if the exposure is above the threshold level.

Chemicals used in urethane production, such as isocyanates, raise some health hazard concerns. The toxicity problem can be minimized by good industrial practices. The Occupational Safety and Health Administration (OSHA) released regulations about the hazards and exposure limits of isocyanates. Isocyanates are known as strong irritants to the skin, eyes, gastrointestinal tract and the respiratory system. Common isocyanates such as MDI and TDI are reported to be harmful as they can enter the body through inhalation, skin (open wounds), eye contact, or mouth by swallowing or contaminated food and drink and by smoking.[10-13] The most common commercial process to produce isocyanates is the reaction of phosgene with amines; the reaction is called the phosgenation reaction. Phosgene is a colorless, highly reactive and highly toxic gas. Exposure to this toxic gas can cause severe respiratory effects; ocular irritation and burns to the eye and skin have been reported, and even death.[14] Therefore, replacement of phosgene in isocyanate production is highly desirable.

The goal of this thesis was to develop a method to synthesize biobased polyurethane that is intended for use in packaging applications. The phosgene-free synthesis of isocyanate and isocyanate-free synthesis of bio-based polyurethane will be covered in this thesis.

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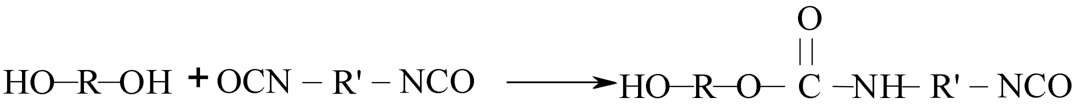
Chapter 2

General Background on Isocyanate, Polyols, and Polyurethane

This section will focus on the basic chemical reactions involved in the synthesis of polyurethanes. Specific background is discussed in appropriate sections. Polyurethanes are prepared by a condensation reaction of di- or poly-hydroxyl functional groups with isocyanates (Figure 2.1). The wide applicability of polyurethane is due to a long list of components such as diols, diisocyanates and chain extenders that can be combined to form the polymer. The two main important building blocks in polyurethane are polyol and isocyanate.

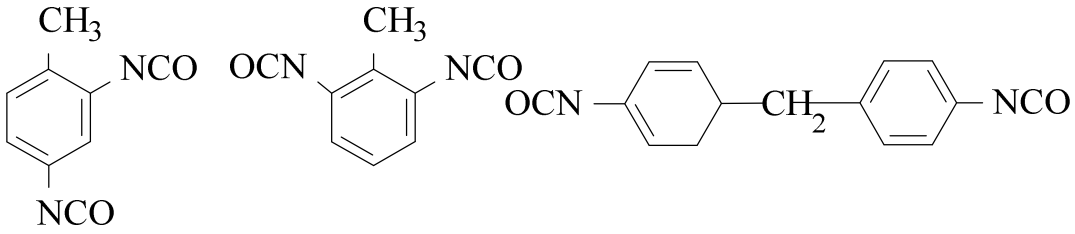


$$\mathrm{HO{-}R{-}OH} + \mathrm{OCN-R'-NCO} \longrightarrow \mathrm{HO{-}R{-}O{-}}\overset{\overset{\displaystyle \mathrm{O}}{||}}{\mathrm{C}}\mathrm{{-}NH{-}R'-NCO}$$

Figure 2.1 Formation of a urethane bond

2.1 Isocyanate

Toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI) are the two most common aromatic isocyanates that are used in polyurethane manufacturing (Figure 2.2). TDI is used primarily in the production of flexible polyurethane foams. It exists in two isomeric forms (2,4 and 2,6 TDI). Different isomer mixtures of TDI are offered commercially, TDI 80/20 (80% 2,4 TDI and 20% 2,6 TDI), TDI 65/35 (65% 2,4 TDI and 35% 2,6 TDI) as well as pure 2,4 TDI. MDI is used primarily in the production of polyurethane elastomers and in some flexible foams; polymers produced from MDI are usually stiffer compare to polymers produced from TDI.[1-6] Pure 4,4’ MDI isomer is a commercial product, and is commonly used in high performance polyurethane elastomers.[2] MDI is considered much safer to use than TDI, due to its lower volatility; however, MDI is harder to purify than TDI.



2,4-TDI 2,6-TDI 4,4'-MDI

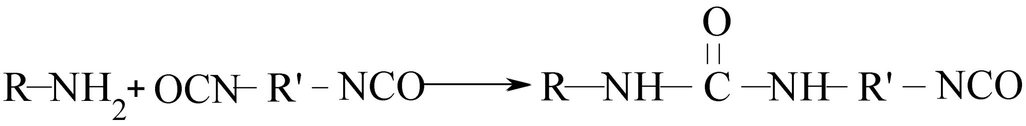
Figure 2.2 Commercial Isocyanates

Both TDI and MDI are produced by the reaction of phosgene with appropriate amines; TDI production involves nitration of toluene followed by a reduction step and then phosgenation. MDI production involves condensation of aniline with formaldehyde and phosgenation.[2] More details concerning phosgenation reactions will be discussed below.

Another type of isocyanate is aliphatic isocyanate, which has more specific applications than aromatic isocyanate. One of the reasons for the different applications is due to the reactivity differences between these two isocyanate groups. In general, aliphatic isocyanate, such as HDI (hexamethylene diisocyanate), has less reactivity than aromatic isocyanate. One common application for HDI is as the starting component for Spandex fiber production. Another example of aliphatic isocyanate is NDI, naphthalene diisocyanate, commonly used in elastomers for specific applications.[7] Aliphatic and aromatic isocyanates will form aliphatic and aromatic polyurethanes, respectively. Aromatic isocyanate is more sensitive to UV light than aliphatic isocyanate, which can cause yellowing of surfaces with exposure. Polyurethane production with aromatic and aliphatic isocyanates will produce rigid polymers and flexible polymers, respectively.[2]

2.1.1 Reactions of Isocyanate

Isocyanate is a very reactive compound. Isocyanate reactions can be categorized into two types: reactions with active hydrogen compounds and polymerization. Isocyanate can react easily with active hydrogen atoms. It attacks the oxygen atom of the hydroxyl groups or the nitrogen atoms in the case of amines; the most important isocyanate reaction is with hydroxyl groups which produces a urethane linkage, as was shown in Figure 2.1. The heat of reaction is 24 Kcal per mol of urethane formed.[1] The reactivities of various active hydrogen compounds are expected to be different; for example, the reactivity of secondary, tertiary or aromatic alcohols will be less than that of primary alcohols, and aromatic isocyanates are more reactive than aliphatic isocyanates.[2] The second fundamental reaction of isocyanate is the reaction between isocyanate and primary or secondary amines to form urea, as can be seen in Figure 2.3.



$$R{-}NH_2 + OCN{-}R'{-}NCO \longrightarrow R{-}NH{-}\overset{\overset{\displaystyle O}{||}}{C}{-}NH{-}R'{-}NCO$$

Figure 2.3 Urea Reaction

Polyurea is widely used in industrial coating applications that require good chemical resistance. The reaction of primary amines with isocyanate is much faster than the reaction with primary alcohol and, generally, no catalyst is required. Table 2.1 lists reactivities of different compounds with isocyanate.

Table 2.1 The Reactivity of Isocyanate with Hydrogen Active Compounds[1]

Hydrogen Active Compound	Formula	Relative Reaction Rate (non-catalyzed, 25°C)
Primary aliphatic amine	$R\text{-}NH_2$	2500
Secondary aliphatic amine	$R_2\text{-}NH$	500-1250
Primary aromatic amine	$Ar\text{-}NH_2$	5-7.5
Primary hydroxyl	$R\text{-}CH_2\text{-}OH$	2.5
Water	HOH	2.5
Carboxylic acid	R-COOH	1
Secondary hydroxyl	$R_2\text{-}CH\text{-}OH$	0.75
Urea	R-NH-CO-NH-R	0.375
Tertiary hydroxyl	$R_3\text{-}C\text{-}OH$	0.0125
Phenolic hydroxyl	Ar-OH	0.0025-0.0125
Urethane	R-NH-COOR	0.0025

Another fundamental reaction of isocyanate is the reaction with water. This reaction is important in low density flexible foam manufacturing because the reaction generates CO_2 gas that acts as a blowing agent during the foaming process.[3] Isocyanates react with water to form thermally unstable carbamic acids, which decompose and form amines and carbon dioxide. These are exothermic reactions that release heat at 47 kcal/mol.[1] The amine product can further react with isocyanate to form di-substituted urea.

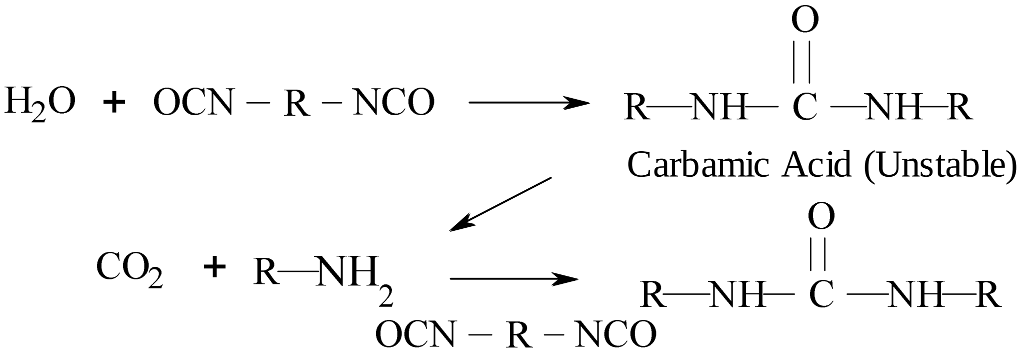


Figure 2.4 Isocyanate reaction with water

Due to the high reactivity of isocyanate, the products from the above reactions, which are urethane and urea, can further react with isocyanate (secondary reaction). The rate of the secondary reaction will be lower compared to the reaction with alcohol or amine, but under suitable conditions (temperature and relative humidity) the reaction can occur. Furthermore, urethane and urea can also react with isocyanates to form allophanate and biuret, respectively. Both secondary reactions need higher temperature, greater than 110^{o}C, for the reaction to occur, and both of these reactions are reversible.

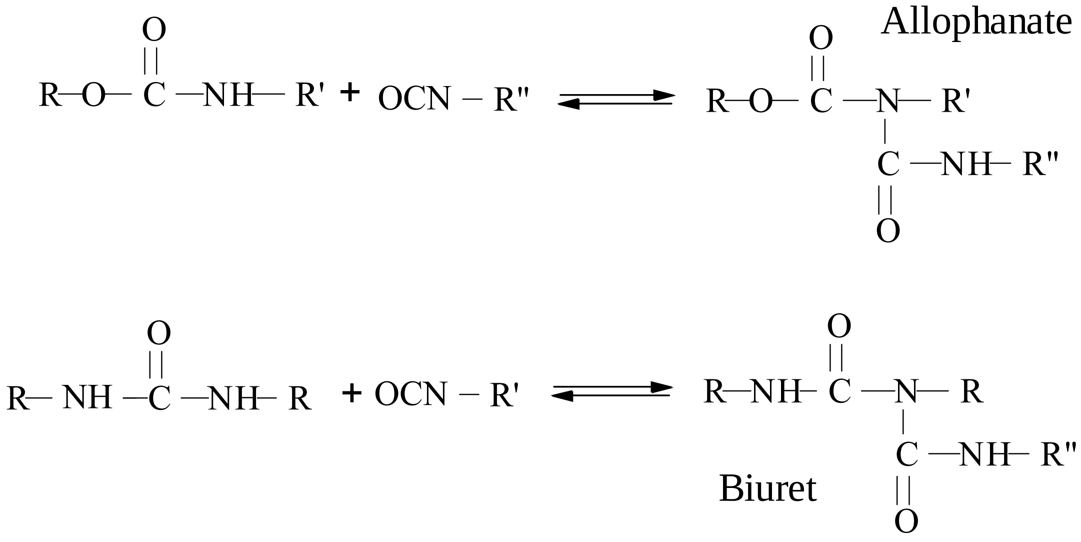


Figure 2.5 Secondary reactions of isocyanate with urethane (top) and urea (bottom)

Another category of isocyanate reaction is self-addition polymerization such as dimerization and trimerization reactions. Dimers and trimers of isocyanate can easily be formed at elevated temperature in the presence of a basic catalyst; the products are uretidinedione and isocyanurate respectively. The dimerization reaction is a reversible reaction, and can only occur with aromatic isocyanate. Aromatic isocyanates such as 4,4'-diisocyanate can dimerize slowly at room temperature. Other dimerization reactions of isocyanate can also form carbodiimides with carbon dioxide as byproduct; some types of carbodiimides can be used as stabilizers to prevent hydrolysis of polyurethane.[3]

Trimerization can occur with both aromatic and aliphatic isocyanates. This reaction forms a very stable isocyanurate ring in the presence of a strong base catalyst. It is used to produce isocyanuric foams and urethane-isocyanuric foams with high crosslink density.[1] The self-addition polymerization reaction for isocyanate is shown in Figure 2.6.

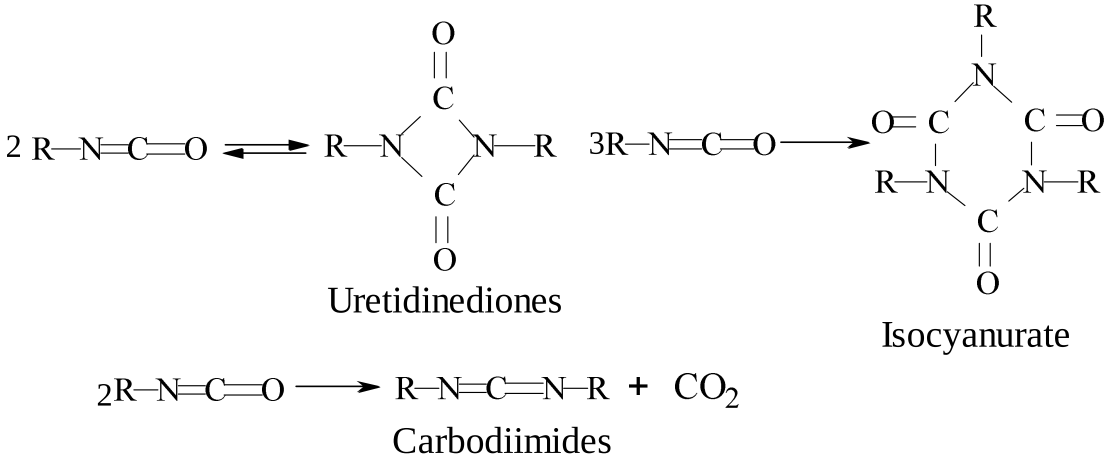


Figure 2.6 Poly-addition Reactions of Isocyanate

The high reactivity of isocyanate can lead to secondary reactions and undesirable formation of crosslinks. Therefore in order to increase the stability of isocyanate, it is reacted with other compounds, such as phenols, caprolactam, and oximes that create a thermally weak bond and prevent further isocyanate reactions. This process is called capping or blocking of isocyanate. Dimerized isocyanate is also considered as blocking the isocyanate process, called the self-block concept, and is the preferred reaction to avoid the release of volatile blocking agent.[5]

2.1.2 Phosgenation Reaction

Phosgene (carbonyl chloride) is commercially used to produce isocyanate from amines, chloroformate esters and organic carbonates from alcohols, and polycarbonate and acid chlorides from caboxylic acids. The use of phosgene as a reagent in isocyanate production makes the production of high yield and high purity isocyanate possible. Aromatic or aliphatic isocyanates are made by the reaction of phosgene and the corresponding amine or amine hydrochloride. The basic chemistry is shown in Figure 2.7.

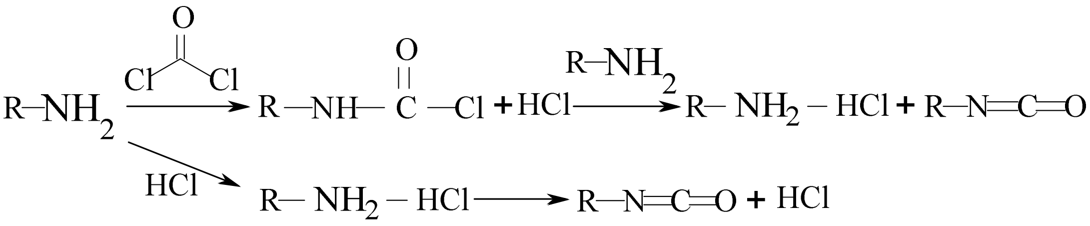


Figure 2.7: Isocyanate synthesis by phosgenation[7]

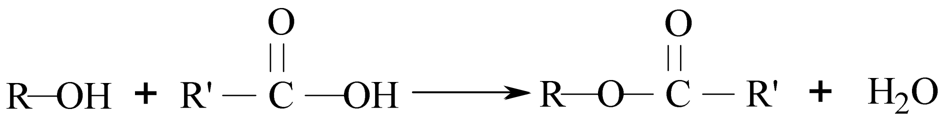
Amines react with excess phosgene and produce carbamyl chloride and hydrogen chloride which are then converted to amine hydrochloride and isocyanate. Undesirable secondary reaction can occur when the amine reacts with the isocyanate produced to form urea. In order to prevent urea formation, some process improvements were developed. The phosgenation reaction was conducted at a very low temperature with a high phosgene concentration. Jet and venturi mixers were used to provide high flow velocities during mixing in order to reduce by-product formation.[9]

2.2 Polyols

Polyols are defined as compounds that contain more than one hydroxyl group. Polyols are separated into two categories, low molecular weight and high molecular weight polyol. In polyurethane production, low molecular weight polyols are used as chain extenders, compounds with two hydroxyl groups (diols), and as crosslinkers, compounds with more than two hydroxyl groups. Higher molecular weight polyols, called oligo-polyols, are one of the main building blocks in the formation of polyurethane. The structure of polyols involved in the polyurethane formation determines the final product properties of this polymer. Therefore, selecting the right polyols to use is very important in order to achieve the desired end product properties. Two main categories of polyurethane are elastic polyurethane and rigid polyurethane. The structure of polymer that falls within any of those two categories is based on the oligo-polyol structure that formed the polymer. Polyurethane formed with high molecular weight polyol that contains low hydroxyl functionality (2-3 hydroxyl groups/mol) will fall into the elastic polyurethane category. This occurs due to the high mobility of the polyol chain that will act as a soft segment in the polymer. On the other hand, polyurethane formed with low molecular weight oligo-polyol and high functionality (around 3-8 hydroxyl group/mol), will form a rigid crosslinked polymer. The high functionality hydroxyl group will form urethane bonds with diisocyanate, high crosslinking will take place, and rigid polyurethane will be formed.[1] The two main high molecular weight polyols that are used commercially are polyester polyols and polyether polyols.

2.2.1 Polyester Polyols

In the beginning of polyurethane production, polyester polyols were the only polyols available. In general, polyester synthesis is conducted by condensation reactions between alcohols and organic acids (Figure 2.8).



$$R{-}OH + R'-\overset{\overset{O}{||}}{C}-OH \longrightarrow R{-}O{-}\overset{\overset{O}{||}}{C}-R' + H_2O$$

Figure 2.8 Condensation Reaction to Synthesis Polyester

Polyurethane that is produced from polyester polyols has better stability, solvent resistance and thermal resistance than polyurethane produced from polyether polyols. This is due to secondary forces in the ester chains that form crystalline structures in the urethane segments.[1] Therefore polyester-based polyurethane is preferred where wear resistance and environmental stability are important, such as in coating applications, paints, sealants, and adhesives. Flexible specialty foams for furniture, packaging and the automotive industry are the main applications for polyester polyols.[12] The downside of using polyester polyol is the high price and the sensitivity of the polymer to hydrolysis.[2] Addition of anti-hydrolysis substances can help to improve the quality of the material, but will increase the price of production Another way to increase the hydrolysis resistance is to increase the chain length and branching of the polyester chain.[13]

2.2.2 Polyether Polyols

Polyether polyols were introduced in 1957 and rapidly gained market share over polyester polyols in polyurethane production. Currently, polyether polyols account for almost 90% of polyurethane production. Polyether polyols have high hydrolysis stability, which is one property that polyester polyols lack, due to the ether linkages.[2] The main materials used to produce polyether polyols are alkylene oxide, and active hydrogen compounds usually called initiators. Initiators are defined as polyfunctional compounds of alcohols or amines, such as ethylene glycol, glycerol, triethanolamine, and sucrose. The wide choice of raw starting material to make polyether polyols, as well as the variety of types of processing, make this material easily tailored to desired properties and applications. In addition to the application flexibility and higher hydrolysis resistance, polyether polyols have lower viscosities than polyester polyols, which make these materials easier to process. The weakness of polyether polyols compared to polyester polyols is their lower oxidation resistance.[14]

2.3 Polyurethane

In polyurethane formation by polyaddition reaction, the ratio between the two reactive groups ([-NCO]/[-OH]) is important. High molecular weight polymers will form with an equimolar ratio between the two reactive groups; a slight excess of one of the reactants will significantly reduce the molecular weight of the resulting polymer. Several different polyurethane fabrication methods are commercially used; the different end applications determine which technique to pursue in making the polymer. Two well-known methods to produce polyurethane are the prepolymer method and the one-shot method.

2.3.1 Prepolymer Method

This is a solvent-free method, used in fabrication of polyurethane elastomers, coatings, flexible foams, sealants, mono-component polyurethane, and adhesives. A prepolymer with -NCO terminal group, which acts as an intermediate in the polyaddition reaction, is formed by reacting a diisocyanate with an oligo polyol (step 1). A high molecular weight polymer is then made by reacting the prepolymer with a chain extender (such as ethylene glycol) (Step 2),[1] as shown in Figure 2.9. Another similar method is called quasiprepolymer, where an excess of isocyanate is used during the making of the prepolymer. The prepolymer produced in this quasiprepolymer method will have a free isocyanate (16-32%). This technique is usually used in flexible polyurethane foam production.[1]

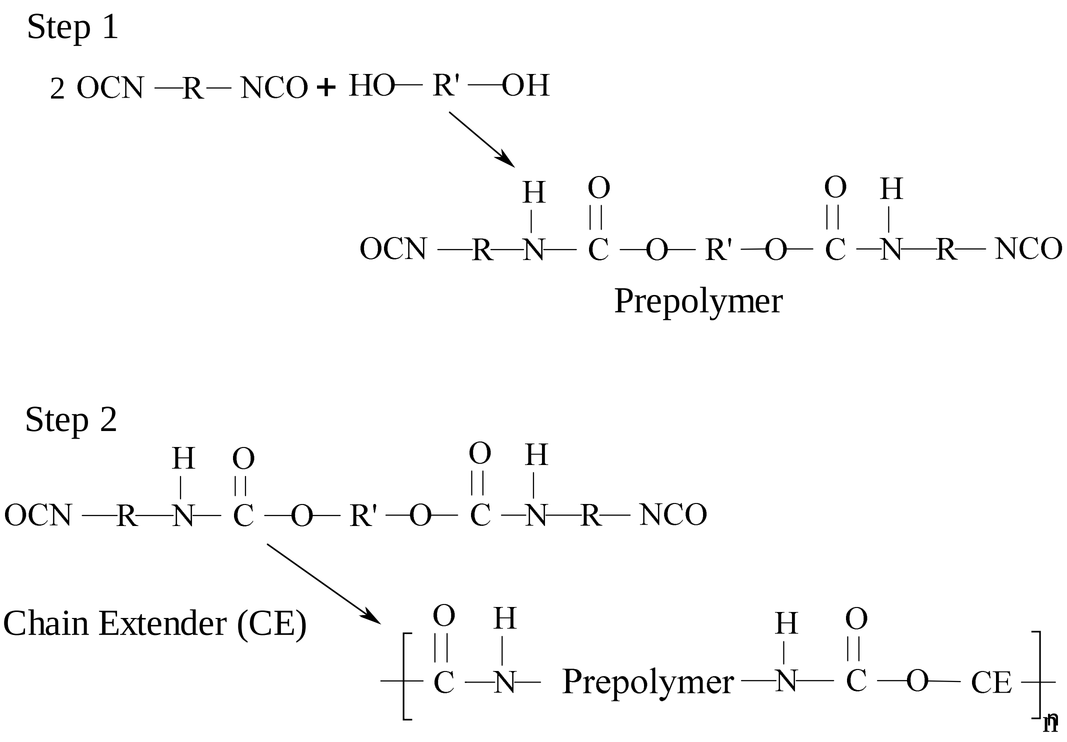


Figure 2.9 Prepolymer production reaction

One of the advantages of using this prepolymer method is the lower overall exotherm of the reaction.[11]

2.3.2 One Shot Method

This method, another solvent-free process, is the most commonly used in polyurethane production, due to the speed of the reaction, its simplicity and its economics. In this technique a master batch is prepared, which contains a mixture of polyurethane components that are not reacted with each other (such as polyol and modifiers) and is mixed with the other reactant components (i.e. isocyanate and catalyst). The key to this method is to have efficient mixing and perfect control of the amount of each component, because efficient contact between the reacting reagents is very important.[1] The disadvantage of using this method is the higher possibility of exposure to isocyanate which can cause health hazards, the expensive equipment due to the accuracy needed, and the sensitivity to the operating conditions. [11]

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Chapter 3

Effect of UV on the Catalytic Ozonation of Soy Oil to Produce Polyols

3.1 Literature Review

Petroleum based polymers find extensive applications in various industries and typically exhibit excellent properties. Due to the high cost of crude oil and its limited availability, substitute materials such as biobased products are expected to play a significant role as alternative industrial raw materials. Furthermore, the use of such biobased commodities should lessen the impact on the environment, provide a stable domestic source of raw materials and potentially could reduce the effect of global warming. Indeed, some biobased products are already being used as fuels, chemicals, construction materials, lubricants, fibers, coatings, and a host of other products.

One readily available source of renewable biomaterial is vegetable oils. These oils contain triglycerides, compounds that are composed of three fatty acids joined with glycerol. Some of the fatty acids are unsaturated, which provides active sites for chemical reactions that can be used to prepare polyols. These biobased polyols can then be used in the polymerization of polyesters and polyurethanes for various industrial applications including resins, elastomers, coatings, and foams. One of the earliest uses of natural biobased polyols was based on castor oil, which contains fatty acids having secondary hydroxyl groups (Figure 3.1)[1,2].

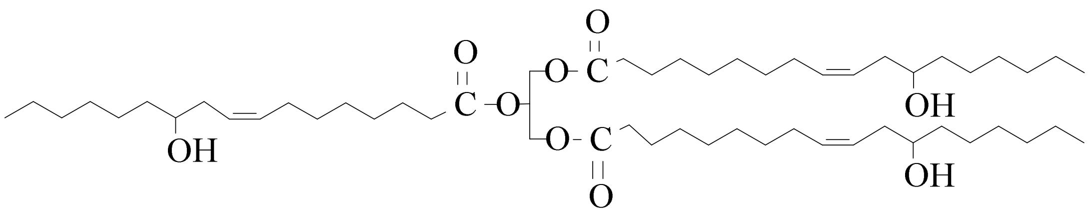


Figure 3.1: Castor Oil

Limited production and the relatively high price of castor oil led researchers to look at other vegetable oils such as soybean, canola, and sunflower oils. Among these different vegetable oils, soybean oil is most attractive since it is abundant and is available at a low price compared with the other vegetable oils. Furthermore, it contains a high degree of unsaturation, which can be used to produce higher functionality of polyols (see Table 3.1 for comparison of vegetable oil compositions). The triglycerides in soybean oil, however, do not contain any hydroxyl groups (Figure 3.2) and therefore further chemical modification is required to produce bio-based polyols from this soybean oil.

Table 3.1 Unsaturation Content of Different Oils[3]

Type of Oil	Soybean	Corn	Castor	Rapeseed
Iodine value	117-143	103-140	82-88	94-120

Soy-derived polyols could have a significant impact in the automotive industry since they are a key component in the manufacturing of polyurethane foams that are used in seat cushions, armrests and head restraints. The automotive industry estimated a saving of $26 million by converting petroleum-based polyols to soy-based polyols in the production of PU foams at high volumes.[4] The United Soybean Board reported in 2006 that the North American market opportunity for soy-based thermoset plastic was about 650 million pounds compared to the annual North America market demand of 3.6 billion pounds. Out of all of the potential industrial uses for soy polyols, packaging and other industries (footware, marine, etc) held 29% of the total 650 million pounds.[5] Packaging applications for soy polyols consist of soy-based thermoset plastics, coatings, adhesives and sealants.

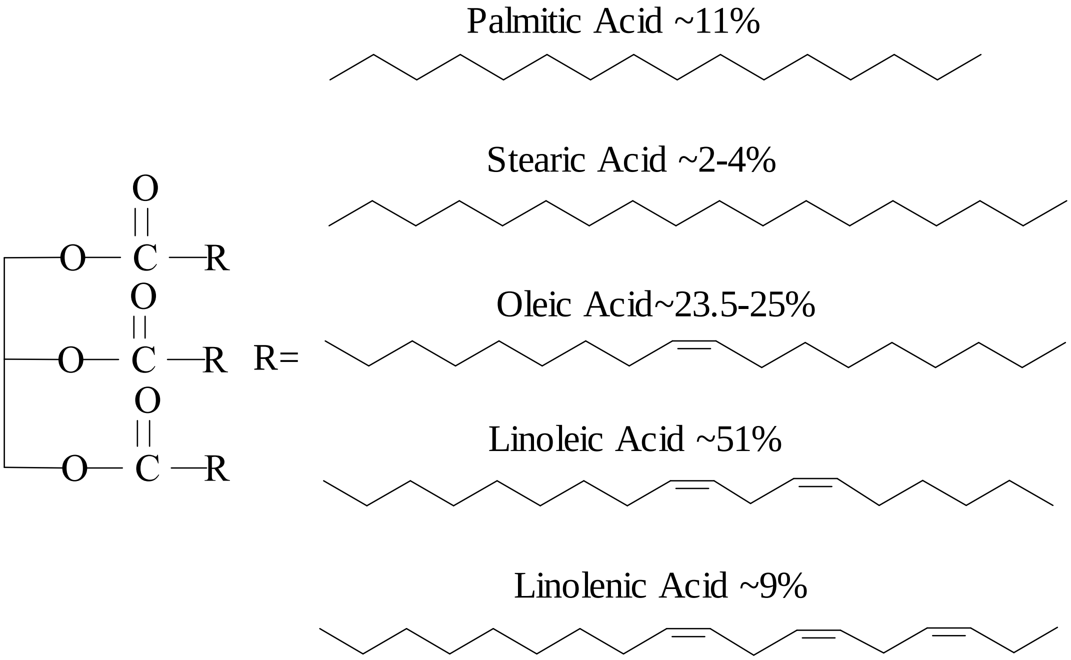


Figure 3.2: Composition of Soybean Oil[6]

Chemical modifications of soybean oil to polyols can be conducted in several ways; only the common approaches will be discussed. Soybean triglycerides can be modified by alcoholysis with glycerol, pentaerythritol, or α-methylglucoside that yield primary hydroxyls upon transesterification.[7] The downside of this synthesis is the high temperature and the length of the reaction which can cause degradation. Other common methods involve the conversion of double bonds to hydroxyl groups (Figure 3.3). Soybean oil averages 4.6 double bonds per molecule.[4] Epoxidation of the unsaturated bonds on the fatty acids of the triglyceride followed by ring opening of the epoxides will yield alcohols (B).[8-11] The epoxidized soy oils produce secondary alcohols, which have lower reactivity than primary alcohols. Similarly, multi-step processes are described where the double bonds are used in hydroformylation (A)[12] and ozone oxidation (C and D)[13] to yield polyols.

Ozone is known to react with the double bonds in olefins to form ozonide intermediates.[14] If no other reactants are present in the reaction mixture, these ozonides are quickly decomposed to aldehydes[15] and carboxylic acids.[16] The use of ozone as an oxidizing agent has distinct advantages over other oxidizing agents. It is known as one of the most powerful oxidation agents. It is produced on-site and does not require special storage, as do most other oxidizing agents. Any excess ozone that has not been reacted is spontaneously decomposed back to oxygen or can be decomposed in potassium iodide (KI) solution (Figure 3.4). Therefore there is no need to filter out waste by-products or neutralize and then remove the neutralization products, as is the case with other oxidizing agents.

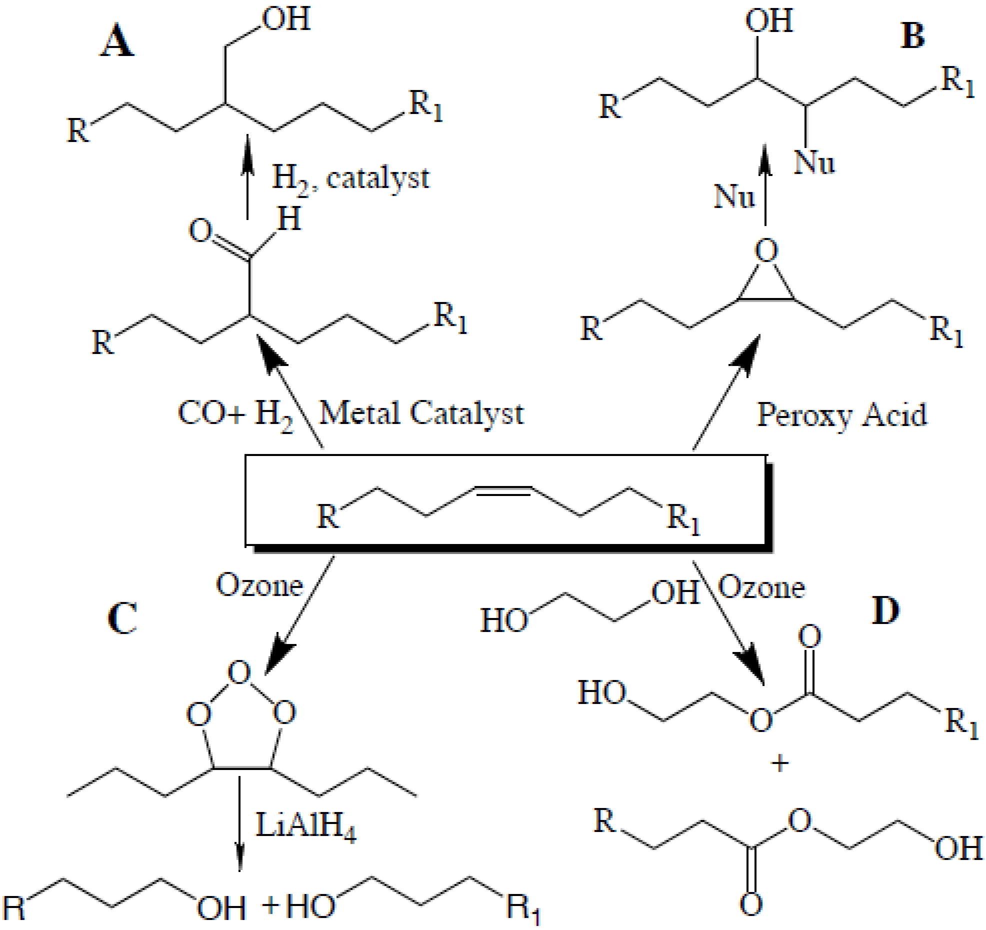


Figure 3.3: Double Bond Modification Pathways

$$2\,KI + O_3 + H_2O \longrightarrow 2\,KOH + O_2 + I_2$$

Figure 3.4: decomposition of ozone to oxygen in potassium iodide solution

Conventional ozonation (Figure 3.3-C) to produce polyols proceeds by a reduction process of the ozonide intermediates to yield polyols. However, this multi-step ozonation-reduction process requires expensive reducing agents and is not economical. Instead, it was shown that ozonation in the presence of sodium methoxide yields methyl esters and not the usual mixture of aldehydes and carboxylic acids. Such reactions were previously demonstrated with unsaturated ethers, esters, and amides[17] including the reaction of methyl oleate to produce methyl nonanoate and dimethyl nonanedioate. It was concluded that this one-step conversion of olefins to methyl esters in basic methanol solution appears to be general and does not depend on a required structure or a strained bond of the reactants. We have utilized this one-step catalytic ozonation to prepare soy oil polyols by reacting the oil with ethylene glycol[7] (Figure 3.3-D). This process appears very useful, is relatively simple, and led to high conversions of polyols without saponification of the triglyceride esters.

In many cases oxidation of organic materials is more intensive and rapid when a combination of ozone and UV are used. There are many publications describing a combination of ozone and UV light primarily for modification of polymer surfaces.[18,19] The motivation for those studies was to improve adhesion, initiate photo-grafting, or to enhance the dyeability and wettability. Generally, photolysis of ozone occurs on exposure to 200–300 nm UV light to form atomic oxygen and molecular oxygen. The rate of ozone photolysis is affected by the light intensity as well as ozone concentration.[20] In this reactive gaseous mixture (e.g. ozone, atomic oxygen and molecular oxygen), the atomic oxygen is the most reactive species and will react with water vapor to produce hydroxyl radicals:[21]

$$O_3 + h\nu \longrightarrow O(^1D)$$

$$O(^1D) + H_2O \longrightarrow 2\ OH\bullet$$

Figure 3.5: General mechanism of the reaction of ozone with UV

The hydroxyl radicals will then abstract a hydrogen atom from the organic polymer chain, leaving a free carbon radical site, or they may be inserted into C-H or C-C bonds to form hydroxyl and ether groups, respectively.[22] These hydroxyl radicals may further combine with such carbon radicals to form a hydroxyl group or they may abstract a hydrogen atom leaving an alkene unit in the polymer chain. The molecular oxygen species may also react with a carbon radical, forming a peroxy group, which then may abstract a hydrogen atom from a neighboring carbon to form a hydroperoxide unit. Subsequent oxidation will then yield aldehydes, ketones, ether or ester functional groups as well as crosslinks when a free radical is terminated by coupling with another free radical on a neighboring chain. Alternatively, extended oxidation may lead to chain scission and the formation of low molecular weight species.

Unlike atomic oxygen, ozone preferentially reacts with olefinic double bonds and the mechanism of this reaction is not via a free radical mechanism as before, but rather a 1,3-dipole cyclo-addition of ozone to the double bond as follows:[14]

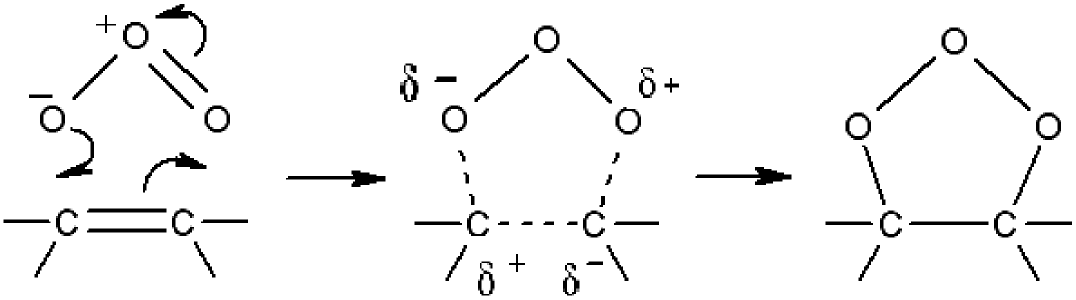


Figure 3.6: Cyclo-addition of ozone to double bonds

The overall reaction mechanism has been studied extensively and includes various oxygen containing intermediates with structures that depend on the type of olefins, the reaction conditions and the type of solvent used. However, it is generally agreed that the Criegee mechanism[23] (Figure 3.6) adequately describes the ozonolysis of alkenes.

It is apparent that the active species and, in fact, the reaction mechanism itself are quite different when ozone is used by itself or in combination with UV light. In this work the formation of polyols by catalytic ozonation of methyl soyate and related model compounds is investigated and compared with the same synthesis using UV assisted ozonolysis. In particular, we were interested on the effect of UV light on the kinetics and the mechanism of this polyol synthesis.

3.2 Experimental

3.2.1 Materials

Low saturated soybean oil was obtained from Zeeland Farm Services Inc., Zeeland, MI and was used without further modification. Methyl oleate (70% purity), triolein (65% purity), and calcium carbonate (99% purity) were purchased from Sigma-Aldrich, St. Louis, MO. All other chemicals and reagents used were analytical grade, and were used as received unless otherwise noted.

3.2.2 Equipment and methods

Ozone was produced by passing dry air through a Praxair Trailigaz ozone generator model OZC-1001 (Cincinnati, Ohio). The inlet air (20 psi) was passed through a desiccant column provided by W.A. Hammond Drierite Co. LTD (Xenia, Ohio) before entering the ozone generator. The ozone generator was set at 0.1 scfm flow rate and 500 volt power setting. UV light was produced by a Pen-Ray® UV lamp model 90-0012-01

(UVP, Upland, CA). The UV light source operated at 254 nm with 4.4 mW/cm^2 intensity. A 250-ml round bottom 3-neck flask equipped with magnetic stirrer was used as a reactor.

Ozone was introduced through a fine diffuser as fine bubbles through one of the necks and the UV light source was placed in another neck just above the reaction mixture. A condenser was attached to the middle neck to exhaust the air containing any excess of ozone. Any ozone that did not react was then bubbled through a KI solution before venting back out to the air. The reaction temperature was maintained at 0^{o}C with an ice/water bath.

A typical experiment consisted of adding soybean oil (10 g), ethylene glycol (20 g), calcium carbonate (1 g), sodium hydroxide (0.01 g) and dichloromethane (200 g). Sodium hydroxide was dissolved in ethylene glycol prior to the ozonolysis run to ensure homogeneity during the reaction. Ozone was then bubbled through the stirred mixture for a predetermined period of time and samples were collected every 5 minutes. The effect of UV was determined by comparing the reaction products with the UV light switched on to the ozonolysis products with no UV. Each sample was filtered to remove the calcium carbonate, and washed 3 times with 100 mL of distilled water to remove unreacted ethylene glycol. The oil phase was separated and dried over molecular sieves for 24 hours. Finally, the molecular sieves were filtered out and the dichloromethane solvent was evaporated.

3.2.3 Model Compounds

Methyl oleate (MO) and triolein (TO), as shown in Figure 3.7, were used as model compounds instead of soybean oil as described above. Here again, the ozonolysis reaction was run for 30 minutes with the UV light switched on and the products were compared to an identical reaction with the UV switched off. The separation steps were similar except that, with these model compound experiments, the dichloromethane was evaporated first. Excess ethylene glycol was separated by centrifugation. No water washing was conducted to prevent the loss of the water soluble, low molecular weight products. It is recognized that omitting the water-washing step in the separation procedure affects the hydroxyl value obtained from the titration due to the presence of ethylene glycol.

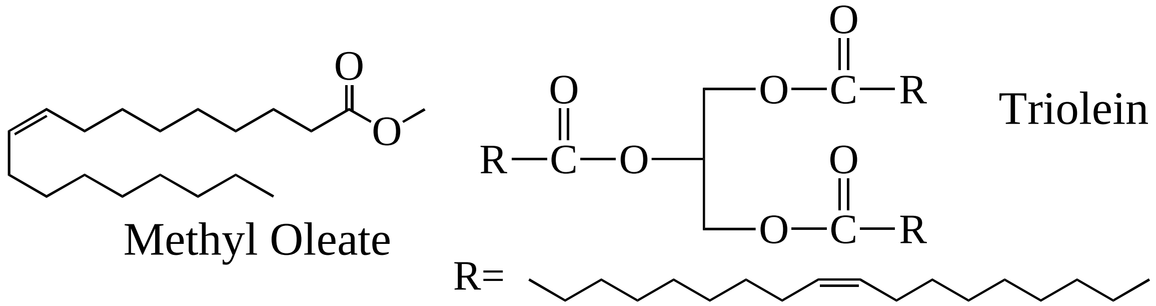


Figure 3.7 Model Compound Structures

3.3 Characterization

Infrared spectra were obtained with a PerkinElmer 2000 FTIR spectrometer with a diamond top ATR cell. Each spectrum was obtained with at least 16 scans to ensure a high signal-to-noise ratio. The hydroxyl value and acid value were determined by ASTM standard methods D1957[24] and D1980,[25] respectively. The presence of double bonds was determined by iodine value in accordance with ASTM D1959[26] and the ester linkages were determined by the saponification value based on ASTM D1962.[27] Samples for NMR spectroscopy were prepared by dissolving 50-100 mg of product in 0.7 ml of $CDCl_3$. Spectra were acquired on a Varian Unity plus spectrometer operating at 500 MHz. Standard acquisition parameters were used for the proton spectra and a recycle delay of 2 seconds was used for the carbon spectra. The solvent peak was referenced to 7.24 ppm and 77 ppm on the proton and carbon spectra respectively. Spectra were acquired at a constant temperature of $25^{o}C$.

3.4 Results and Discussion

As mentioned above, ozone is a very powerful oxidation agent. The exposure of soybean oil to ozone in the presence of ethylene glycol and NaOH caused the cleavage of carbon-carbon double bonds and further reaction with the hydroxyl groups, which yielded a mixture of polyols.

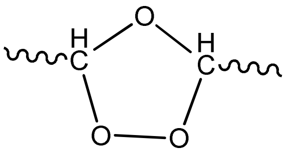
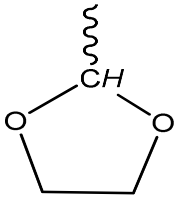
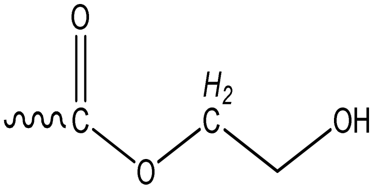
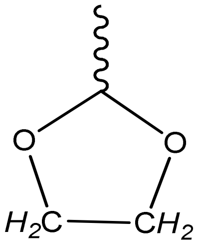
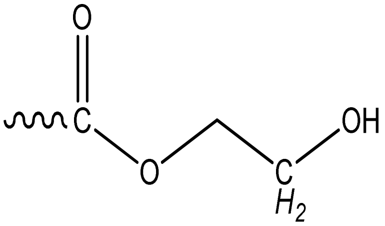
The combination of UV light and ozone during polyol synthesis was expected to increase the oxidation rate. Titration results from the model compounds MO and TO after 30 minutes reaction time can be seen in Table 3.2. Surprisingly, it is apparent from these data that there were no differences between the products in terms of the disappearance of the carbon-carbon double bonds, the amount of hydroxyl groups and ester linkages, indicating that the UV light does not have a significant effect on this reaction.

Table 3.2 Model Compound Study Titration Data

Properties	Methyl Oleate		Triolein	
	UV off	UV on	UV off	UV on
Hydroxyl Value (mg/g)	336.54	331.95	352.09	346.5
Iodine Value (mg/g)	0	0	0	1.5
Saponification Value (mg/g)	243.62	243.11	234.01	257.16

Further confirmation that UV has no apparent effect on this reaction was obtained from the chemical structure of the products by NMR (NMR spectra can be seen in Appendix A.2). The proton NMR spectra with and without the use of UV light for MO and TO are very similar. It is further apparent that the ozonolysis in all cases is essentially complete as seen from the absence of peaks at 5.34 ppm corresponding to the olefinic protons. The regions of interest along with the mole percentages are provided in Table 3.3. Integral areas were determined relative to the terminal methyl group as reference. The methyl group was chosen since it is up field of all other protons and thus errors are minimized. All reactants predominantly converted to acetals or ethers upon ozonolysis with ethylene glycol. However, in all cases the product distribution was not changed significantly by the UV light. It is also observed from the NMR that unreacted ethylene glycol is present in the product since water washing was not employed, which most likely contributed to the high hydroxyl values listed in Table 3.2.

Table 3.3 Model Compound Study NMR Data

^1H (ppm)	^{13}C (ppm)	Functional group	MO+ UV	MO	TO+UV	TO
5.0 – 5.2	105		6%	8.5%	12%	4%
4.6 – 4.9	108	 , other acetal	25%	34%	47%	58%
4.1 – 4.2	65		14%	15%	6%	8%
3.7 – 3.9	65 61	 , other ether 	-	-	-	-
2.4	44	$\sim CH_2CHO$	4%	8%	3%	2%

The carbon spectra for the samples confirmed the conclusions drawn from the proton spectra. Peaks corresponding to the ozonide (105 ppm), acetals (106-108 ppm), and carboxylic acid (178 ppm) were clearly observed. Also peaks corresponding to hydroxyesters (65, 61 ppm), dioxolane CH_2 (64 ppm) and unreacted ethylene glycol (63 ppm) were seen in the spectra. The aldehydes can be observed in the proton spectrum through the proton alpha to the carbonyl. Similarly, the carbon spectra showed the corresponding carbon (44 ppm). Apparently, the spectra for samples with and without the UV light were similar since the primary mechanism of this reaction is ionic in nature, whereas UV light is expected to affect primarily a radical mechanism as shown in Figure 3.5.

The effect of UV was further investigated in this catalyzed ozonolysis using soybean oil. Here, the oil with excess of ethylene glycol and catalyst was exposed to ozone to produce a mixture of polyols and the products were characterized at different times. FTIR was used to determine cleavage of the double bonds, the presence of hydroxyl groups and the formation of the ester groups (Figure 3.8).

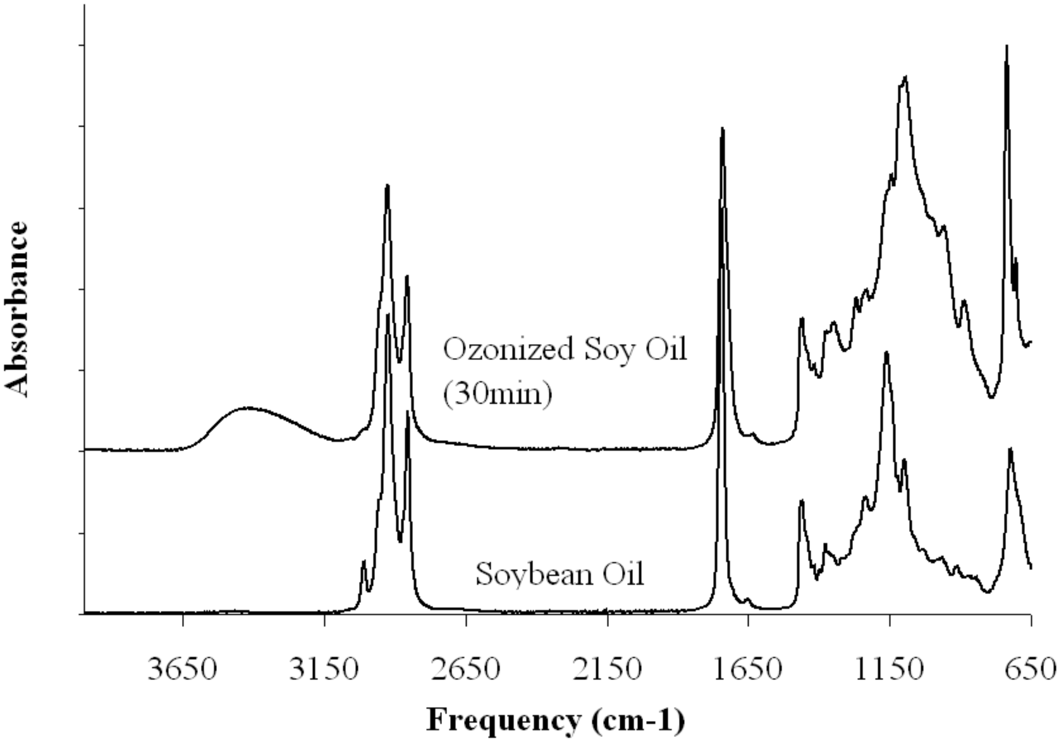


Figure 3.8: FTIR result of Ozonized Soy oil (Top) and Soybean Oil (Bottom)

It is apparent from these spectra that ozone readily attacked the double bonds and the new chain-ends reacted with one of the hydroxyl groups of the ethylene glycol through an ester linkage (Figure 3.9).

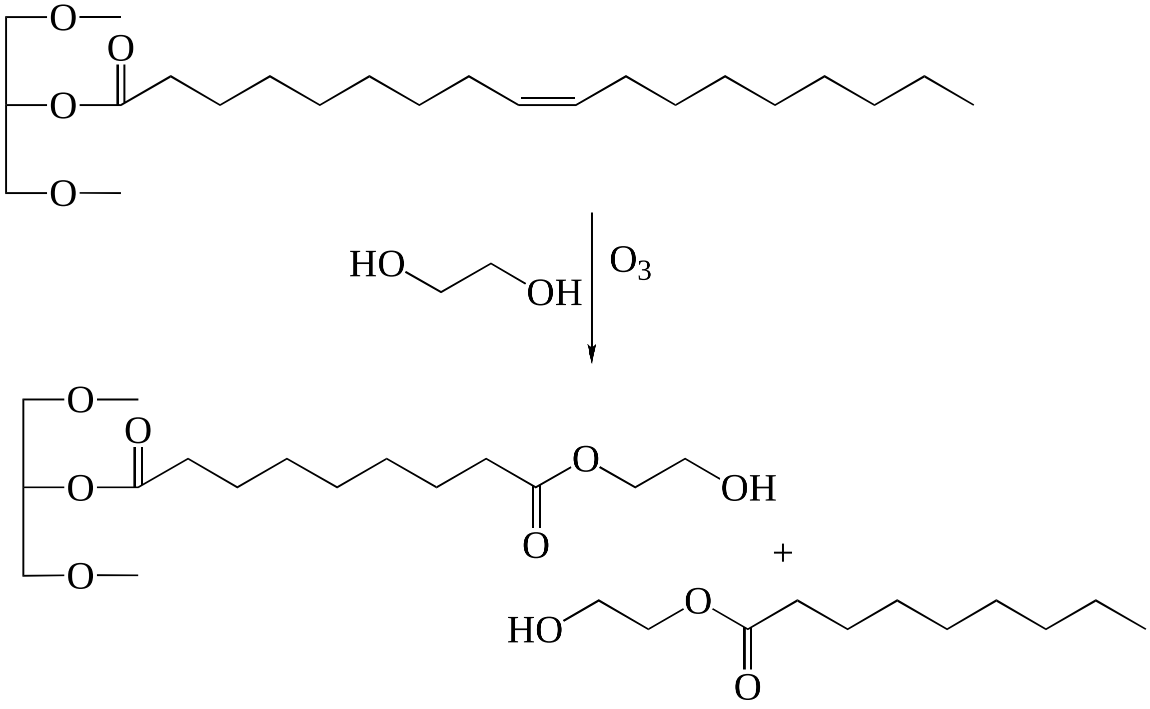


Figure 3.9: Catalyzed ozonation of unsaturated fatty acid in a triglyceride with ethylene glycol

The disappearance of the double bonds at 3000 cm^{-1} and the appearance of a broad hydroxyl peak around 3400 cm^{-1} as the ozonolysis reaction progressed were clearly observed. However, no apparent effect of UV was observed on these variables. Figures 3.10 and 3.11 show the double bond reduction curve and an example of the deconvoluted double bond spectrum, respectively.

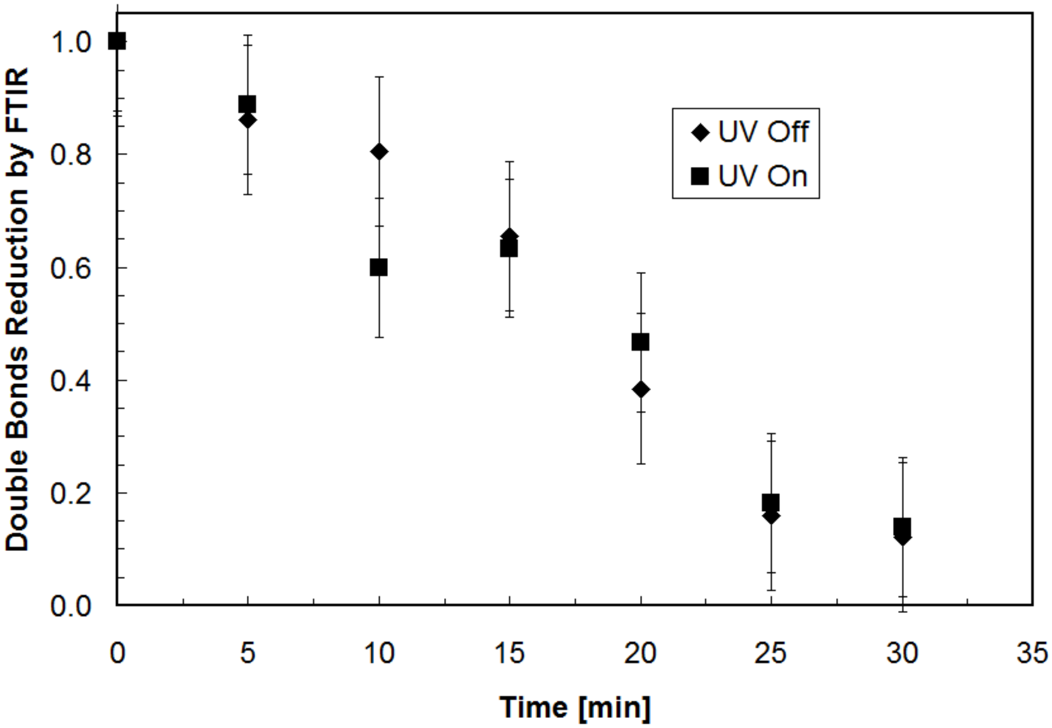
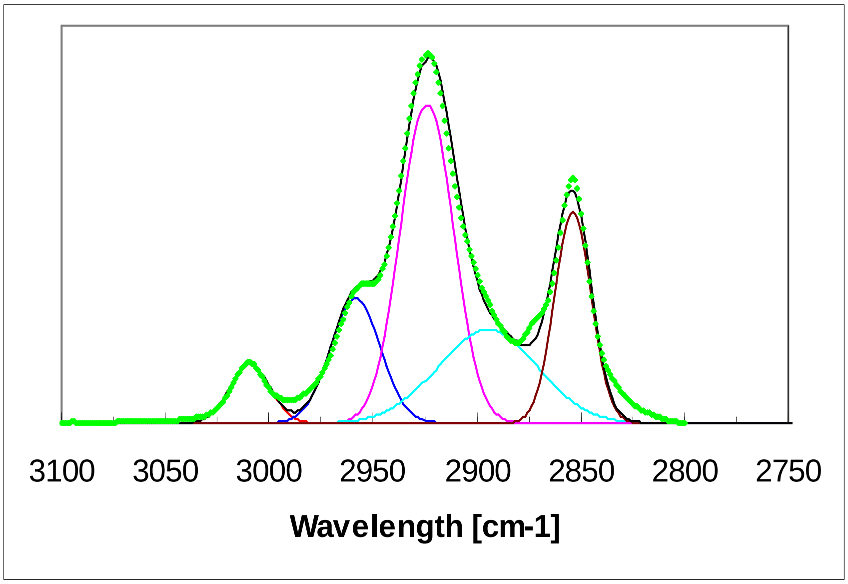


Figure 3.10: Double bond reduction comparison between UV on and UV off



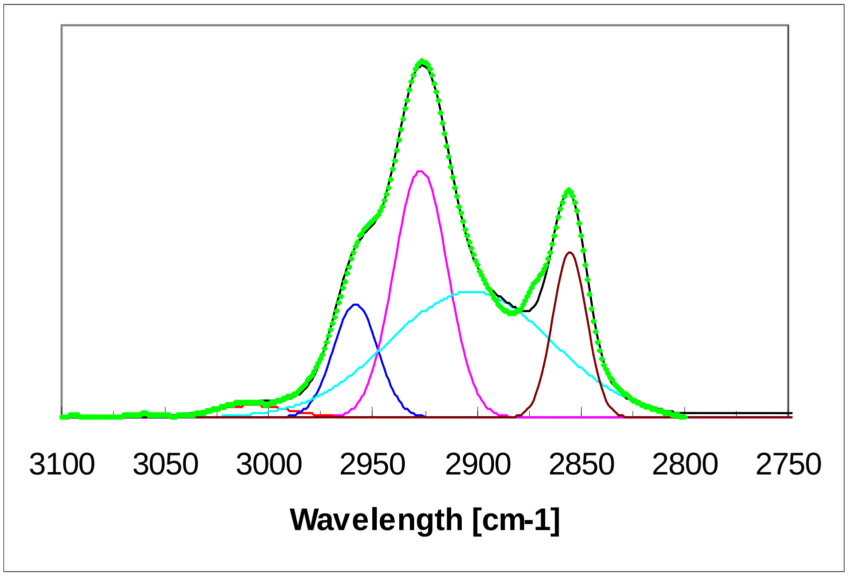
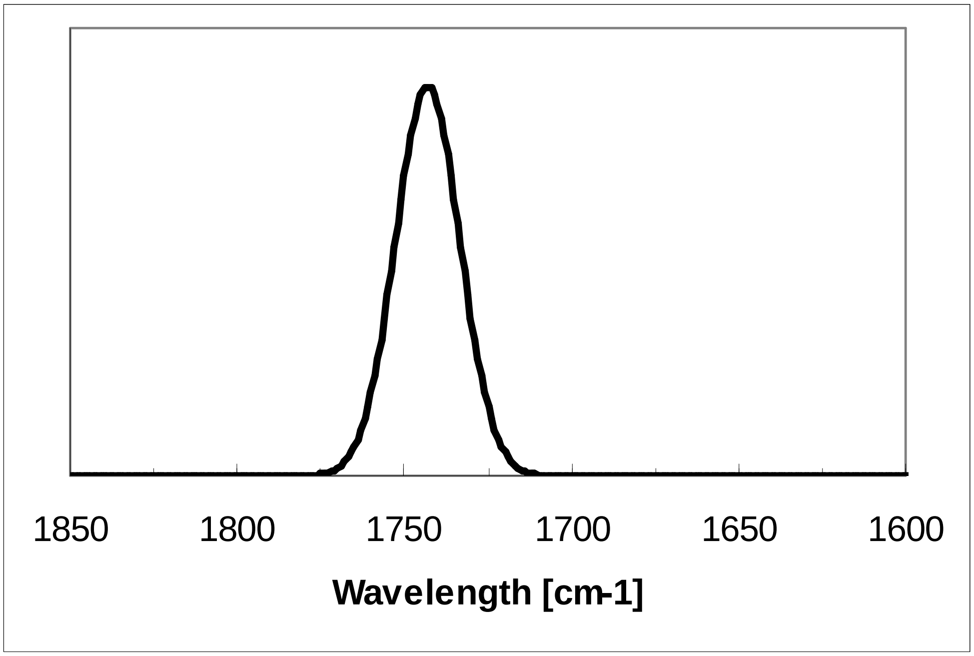


Figure 3.11: Deconvoluted double bond spectrum of Soybean Oil (Top), Deconvoluted double bond spectrum of soybean oil after 30 minutes ozonolysis with UV (Bottom) (For interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this thesis)

In order to better identify the reaction products and ensure that the product was not simply a blend of ethylene glycol and ozonized soy oil, the ester region in the FTIR was expanded and deconvoluted (Figure 3.12).



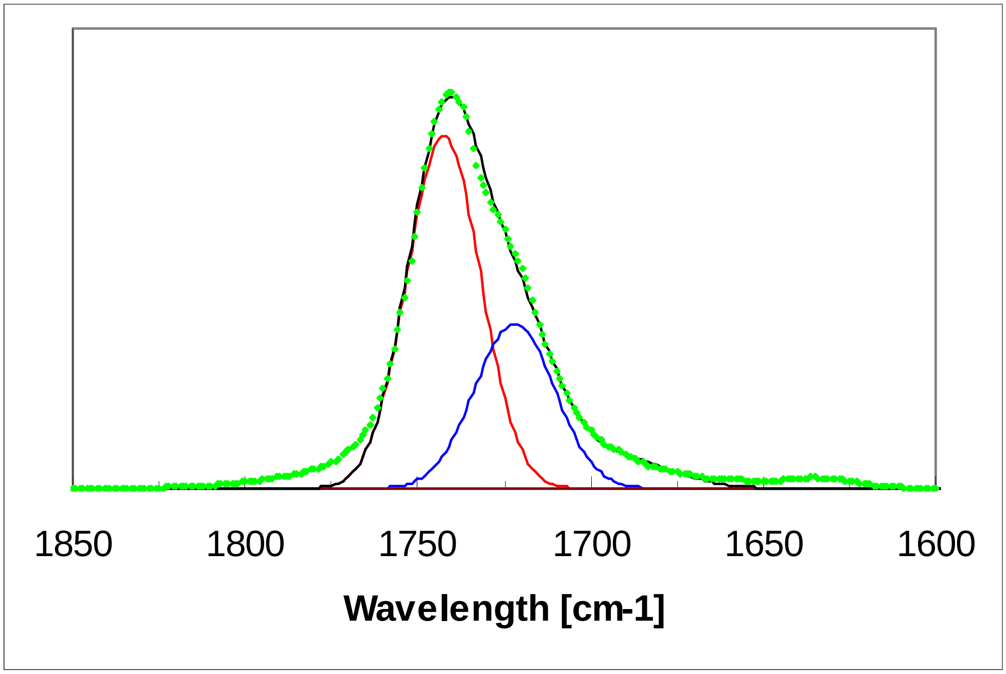


Figure 3.12: Ester peak of Soybean Oil (Left), Deconvoluted Ester peak of Soybean oil after 30 minutes ozonolysis with UV (Right)

It is observed that the new ester linkage of the new chain-ends and ethylene glycol appears as a shoulder on the original ester peak between the glycerol and the fatty acids in the triglycerides. The deconvolution allowed us to separate the contribution of the new peak and determine its relative area. It is apparent (Figure 3.13) that the area of this new ester peak is directly proportional to the extent of the reaction, indicating that the ester linkage is indeed due to the reaction of ethylene glycol with the new chain-ends of the fatty acids. However, the UV has essentially no effect on the rate of ester formation.

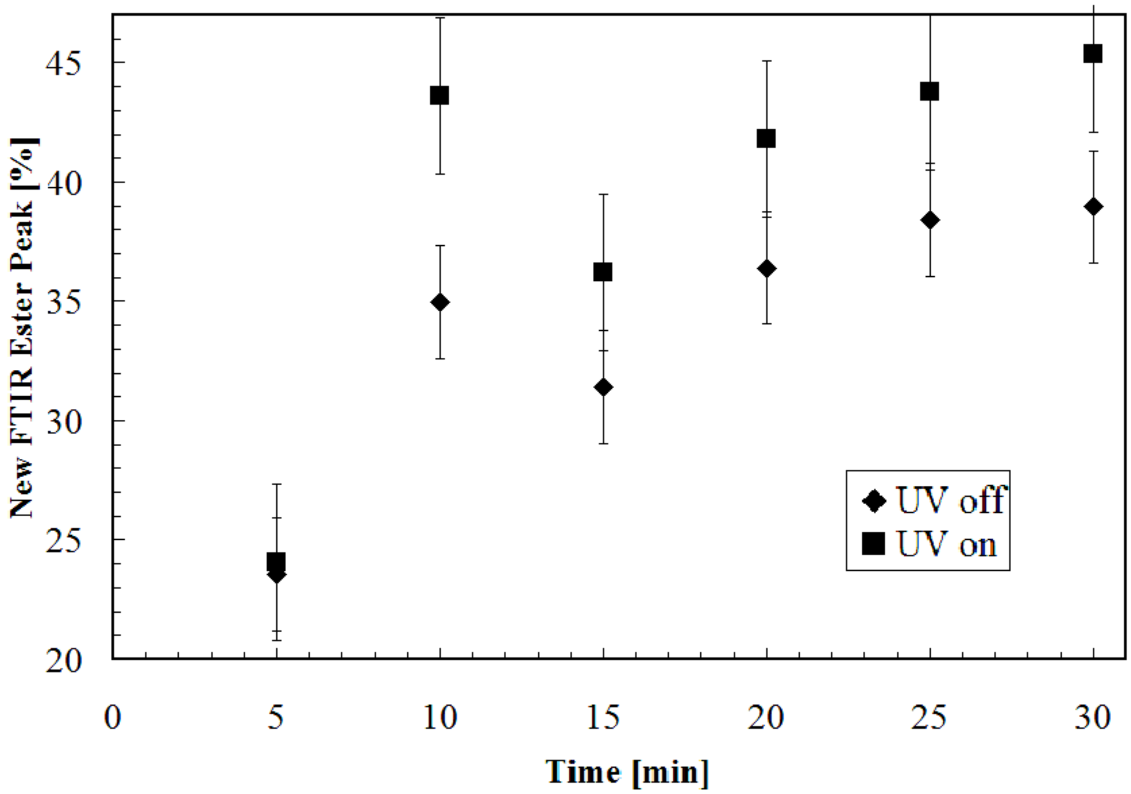


Figure 3.13: Ester functional group formation between UV on and UV off

Similar results were obtained from the titrations to determine the iodine values, hydroxyl values, saponification values and acid values (Figure 3.14-3.17 respectively) all indicating no effect on the rate of the reaction due to the UV.

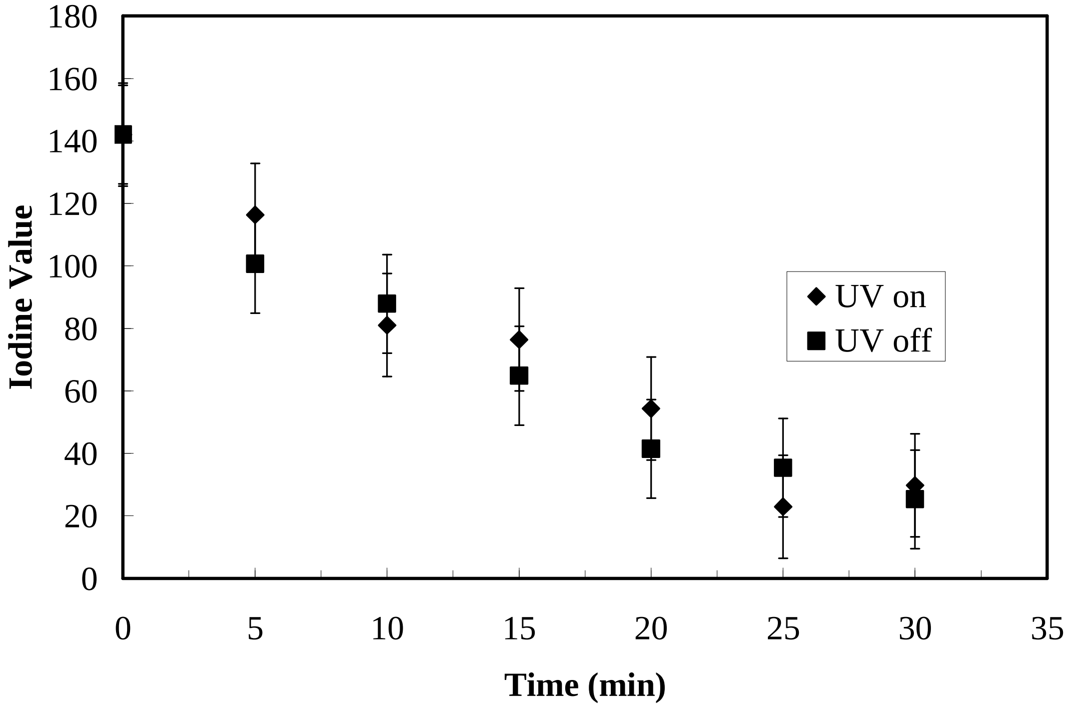


Figure 3.14: Iodine Value Titration Results

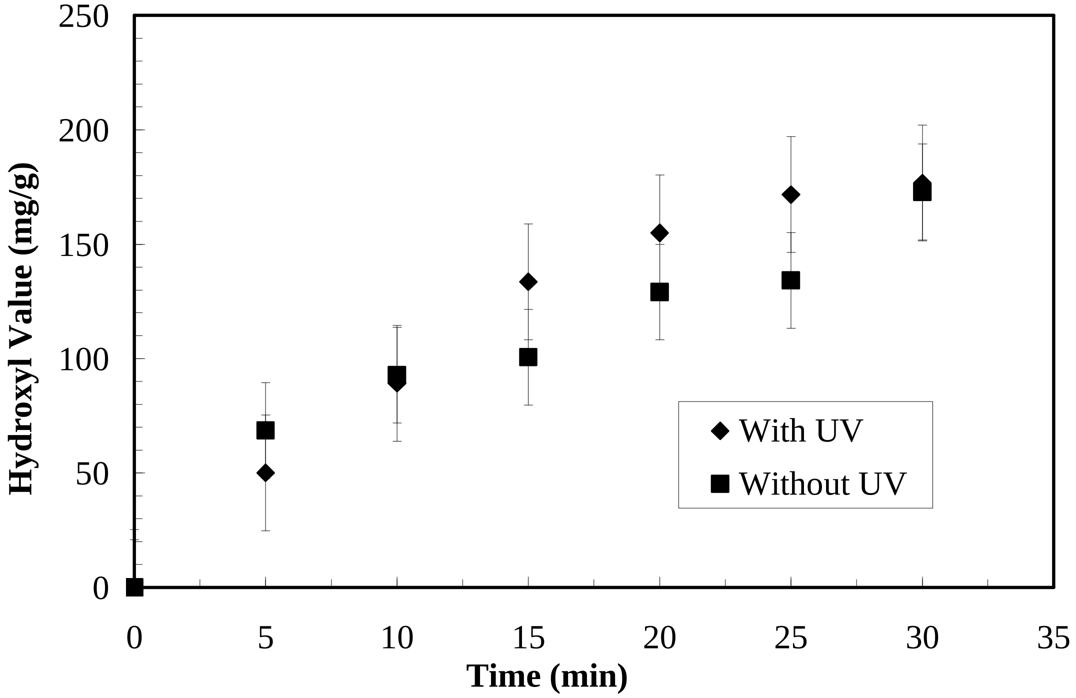


Figure 3.15: Hydroxyl Value Titration Results

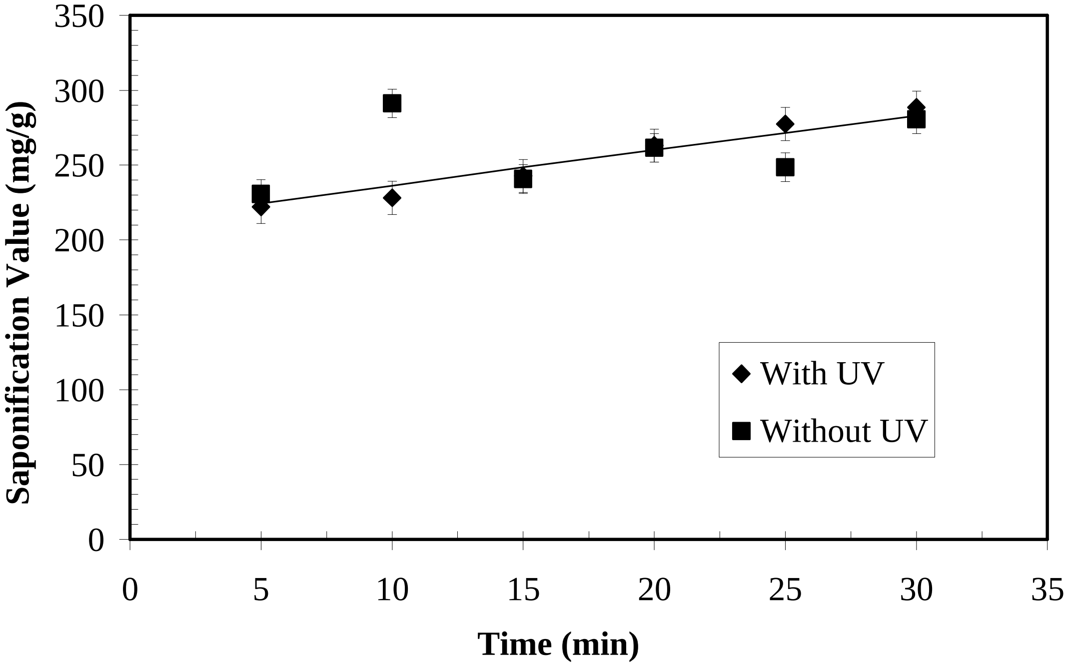


Figure 3.16: Saponification Value Titration Results

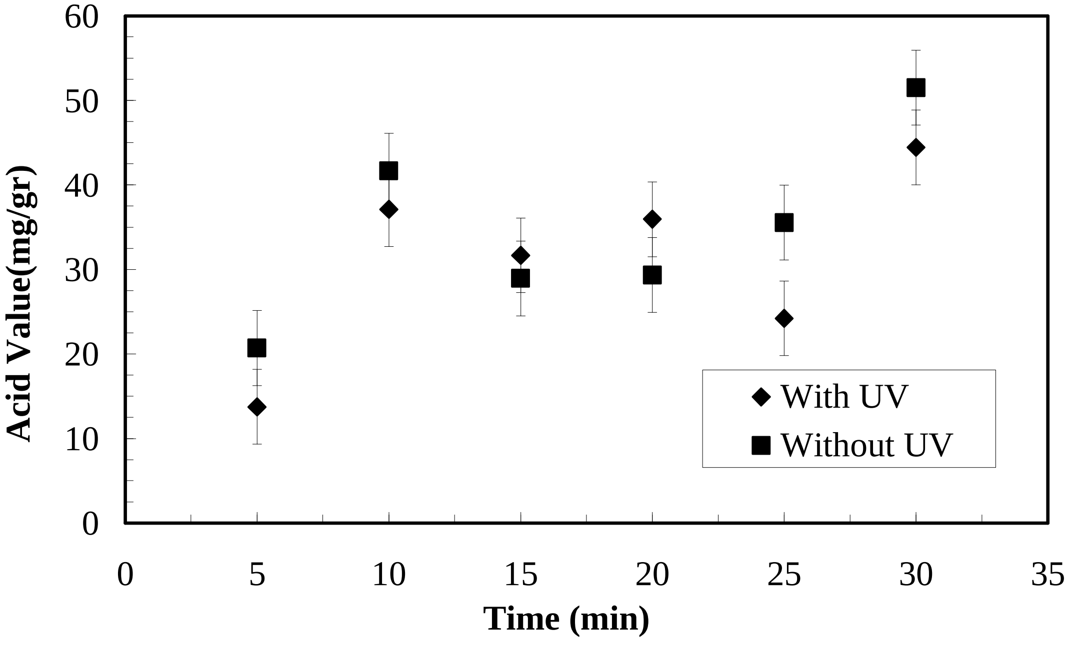


Figure 3.17: Acid Value Titration Results

The titration results were consistent with the FT-IR analysis as well as the model compound study. The reduction of double bonds that was observed with the FTIR and quantified with iodine value was proportional to the increase in hydroxyl value. The iodine value was used to measure the amount of unsaturation present. The hydroxyl value was used to measure the concentration of hydroxyl groups present. The reduction of double bond and the increase of hydroxyl were expected in a polyol synthesis from soy oil ozonolysis process. The water wash step during the ethylene glycol separation was conducted with dichloromethane present; therefore, a small excess of ethylene glycol might be present in the final soybean polyol samples, and the low molecular weight molecules were washed away.

The saponification value measures the free acids and saponifiable ester groups. The slight increase of the saponification value over the ozonolysis time indicates that the ozone did not cleave the triglyceride bond, which will lower the amount of ester produced. The ozone attacked the double bond to react with ethylene glycol to produce esters. This interpretation is supported by the increase in saponification value and no change in acid value.

It is well known that low UV wavelength light (~185 nm) leads to formation of ozone from oxygen. However, in this set of experiments 254 nm UV light was used. UV light in this wavelength is known to react with ozone to yield atomic oxygen as shown in Figure 3.5, which was expected to increase the rate of the reaction. However, no significant difference was observed. Possible explanations are that the oxidation reaction between ozone and the double bond was faster than the reaction between UV and ozone, and that the primary mechanism of the reaction is ionic whereas the UV light is expected to affect radical mechanisms. Thus, essentially all the ozone produced reacted with the double bonds independent of the UV light. Another possibility is that the intensity of the UV light was not sufficient and therefore the effect was minimal. In general, photolysis reactions are strongly dependent on the intensity of the light source and the distance of the source from the reaction medium. If this is the case here, more experiments may be needed with higher intensity UV light in order to verify the “no effect” conclusion observed with our data.

3.5 Conclusion

The study shows that adding UV to complement the catalyzed ozonolysis of soy oil and ethylene glycol to produce polyols did not change the rate of the reaction. The same conclusion was obtained whether soy oil or model compounds (e.g. MO and TO) were used. However, the simpler structure of the model compounds helped us to better identify the products of this complicated reaction. Irrespective of the exact mechanism, the catalyzed ozonolysis reaction appears to be useful in the synthesis of polyols from soybean oil. The polyols thus produced were characterized by iodine value, which confirmed the cleavage of the double bond due to the ozone attack; the hydroxyl value, which confirmed the presence of OH groups; and the saponification value, which confirmed the reaction linkage of the oil with ethylene glycol.

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Chapter 4

Synthesis of Bio-based Polyurethane

4.1 Literature Review

Polyurethane, a versatile polymer, can be produced in forms of very soft to very hard materials with a wide range of flexibility. Polyurethanes are prepared by reacting polyols and isocyanates. There are concerns about toxicity involved in polyurethane production particularly since phosgene is used in isocyanate production, as described in the introduction, and some of the isocyanate itself in polyurethane production. Those concerns have led to development of alternative methods of polyurethane synthesis. Another concern is related to the use of dwindling petroleum resources as basic materials in polyurethane production. Therefore, the alternative methods of polyurethane synthesis that are covered in this chapter will include isocyanate-free and phosgene-free methods. A biobased di-ester model compound was also used in this study, as a starting material. The results of this study are expected to be used as a basis for production of bio-based polyurethanes.

4.1.1 Bio-based Polyurethane

The synthesis of linear polyurethane includes the formation of prepolymer, followed by a chain extending reaction. As described in the previous chapter, the raw materials used in the production of polyurethanes, such as polyol, diisocyanate and chain extender, determine the properties of the final polyurethane product. Numerous biobased polyurethane products are prepared by combining petroleum-based isocyanate and biobased polyols.[1] These biobased polyols can be derived from renewable resources such as carbohydrates, lignin, and vegetable oils. Molecular weight, hydroxyl number and functionality requirement of biobased polyols thus produced are important in order to compete with the petroleum-based polyols.

The utilization of castor oil for polyurethane production has been studied. The properties of polyurethane produced vary with the isocyanate index used, which affects the glass transition temperature, tensile strength, and degree of elongation.[2,3] Commercial biobased polyurethanes that are formed by castor oil polyol have been used in telecommunications, electrical, and biomedical applications. The polyurethane produced from castor oil has good insulation properties, and good moisture resistance.[1] The formulation of biobased polyurethane derived from other plant oils, such as soy-based polyols, has similar advantages. The flexibility/rigidity of polyurethane produced is determined by the ratio of the hard segments to the soft segments. The degree of crosslinking is determined by the degree of functionality of each monomer. The hydroxyl value determines the required amounts of isocyanate and water.

As mentioned in Chapter 3, soy polyols can be prepared by different methods, hydroformylation, epoxidation, and ozonolysis. Detailed studies of polyurethane properties prepared by such methods with petroleum-based isocyanate have been conducted. Polyurethane produced from hydroformylated and hydrogenated epoxidized soybean oil polyols with the same functionality were compared. Polyols produced by hydroformylation are more reactive in forming urethane linkages than polyols produced from epoxidation.[4] Polyurethanes produced from polyols prepared by the epoxidation route are more rigid and have better mechanical properties. The lack of dangling chains in polyols prepared by the ozonolysis method produced polyurethane with good properties and higher T_g (glass transition temperature).[5] Detailed investigations of the foam properties of polyurethane derived from soybean oil polyols have also been published.[6-8]

Studies have been conducted concerning different polyurethane properties obtained from different ratios of diisocyanate to polyols, as well as different types of isocyanates used.[9-11] The ratio of isocyanate, with functionality more than two, to hydroxyl groups affects the crosslink density of the polymer produced, which also affects the T_g. Polyurethanes with the highest T_g are produced from aromatic triisocyanates, followed by aromatic diisocyanate, aliphatic triisocyanate, and aliphatic diisocyanate.

As mentioned, all the studies above were conducted using petroleum-derived isocyanate. Nevertheless, renewable resources have proven to be excellent alternatives capable of providing a wide range of polyol properties. As covered in previous chapters, biobased polyols derived from soybean oil offer a wide variety of chemical modifications, and provide a valuable, inexpensive and abundant source of raw material.

4.1.2 Isocyanate Synthesis

Isocyanates are very reactive compounds. They are derived from petroleum resources and require the use of phosgene during their production. Phosgene, a colorless gas, reacts with amines to produce isocyanates. (Figure 4.1)

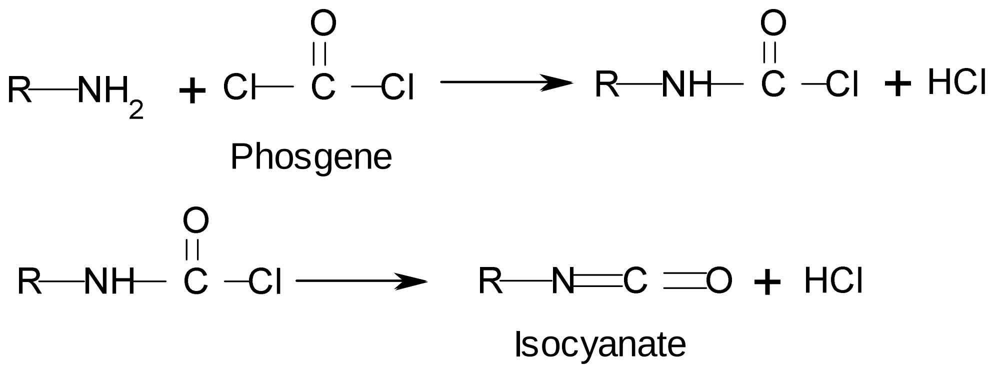

Figure 4.1: Isocyanate Synthesis

The high toxicity of phosgene, the high concentrations of the corrosive HCl by-product and the inherent risk involved in the isocyanate synthesis further contributed to the interest in development of an alternative method to produce isocyanates. Unique approaches to eliminate the use of phosgene in isocyanate production include diisocyanate synthesis from fatty acids[12], isocyanate synthesis from soybean oil[13] and direct synthesis from carbamates[17].

Isocyanates derived from fatty acids that are available commercially are based on dimers of the fatty acids. These isocyanates contain dangling chains that will result in further crosslinking.[12] In another study of isocyanate production from fatty acid, fatty nitrile and unsaturated nitrile were converted to a dinitrile compound, and then reacted with diamine to form diisocyanate.[14] A recent study to produce isocyanate from fatty acid (oleic acids) used the Curtius rearragement.[12] In this study the isocyanate synthesis was based on catalytic thermal decomposition of carbamate derivatives of biobased di-esters.

4.1.3 Alternative Methods of Polyurethane Synthesis

Some isocyanate-free methods have been investigated. Polyurethane can be obtained by reacting the cyclic derivative of carbonic acid (cyclic carbonate) with amines that yield urethane linkages and hydroxyl groups. Figure 4.2 is one example of the polyaddition reaction between bis(cyclic carbonate)s and diamines to produce poly(hydroxyurethane).[15-19]

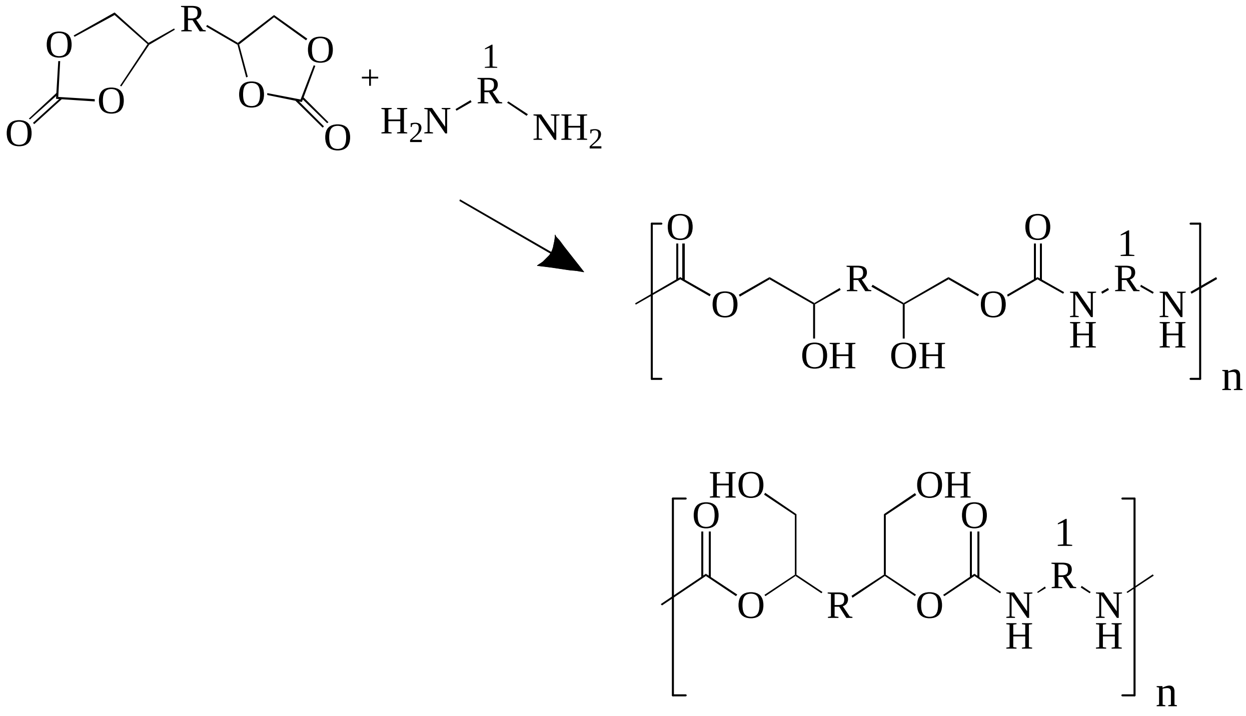

Figure 4.2: Isocyanate-free Method of Polyurethane Synthesis with Cyclic Carbonate

In another alternative synthetic method, aliphatic polyurethanes were prepared by a chain-growth reaction followed by a ring opening polymerization of aliphatic cyclic urethanes;[20-24] Such cationic ring-opening polymerization led to trimethylene urethane and tetramethylene urethane. Alternatively, amino alcohol was treated with two equivalents of phenyl chloroformate, and the resulting α-phenyl urethane-ω-phenyl carbonate was then treated with additional starting amino alcohol. In fact, di-tert-butyltricarbonate is known as a versatile and mild reagent in these syntheses. AB-type aromatic poly(oxycarbonylimino-1,4-phenylene) was synthesized[25] by pyrolysis of phenyl N-p-hydroxyphenylcarbamate as shown in Figure 4.3.

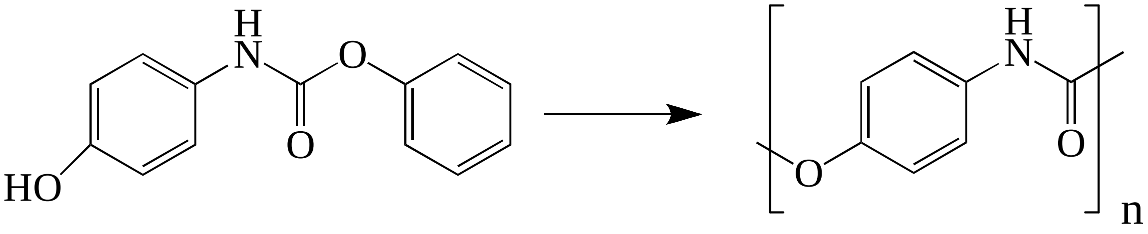

Figure 4.3: Preparation of poly(oxycarbonylimino-1,4-phenylene)

Two methods of isocyanate-free polyurethane preparation from diamine, diols and ethylene carbonate as a phosgene substitution method and polyurethane preparation from carbamate will be covered in this study. Details of the proposed reactions and methods will be discussed below.

4.1.4 Model Compound

Dimethyl azelate, diester that can be produced from ozonated methyl oleate, was used as a starting material in this research. Dimethyl azelate is a useful starting material for model polyurethane synthesis since it avoids the complexity typical of bio-based raw materials structures that often contain a mixture of compounds. Dimethyl azelate, on the other hand, is a well defined reagent that contains only two ester groups which can be reacted to form a di-functional prepolymer.

Ozonolysis of this biodiesel model compound (methyl oleate) is expected to produce two esters,[26] methyl hexanoate and dimethyl azelate. (Figure 4.4)

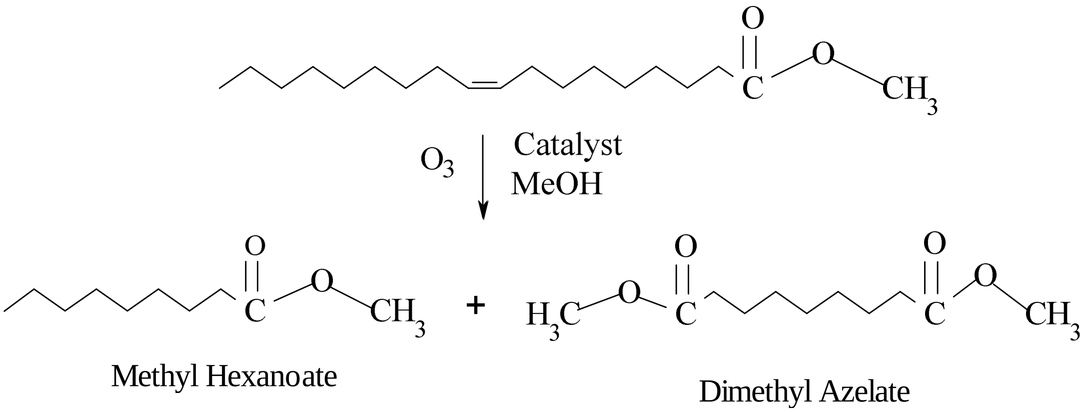

Figure 4.4 Ester products from ozonolysis of methyl oleate

4.1.5 Proposed reaction

4.1.5.1 Amidation reaction

An amidation reaction replaces the hydroxyl group in the terminal carboxyl groups with an amide group. Examples of the application of the amidation reaction are the reaction to produce aniline from nitrobenzene and the synthesis of polyamide from ester.

The first step is to react the ester group with diamine such that only one amine is reacted to form an amide, with the other amine group available for further reactions (Figure 4.5).

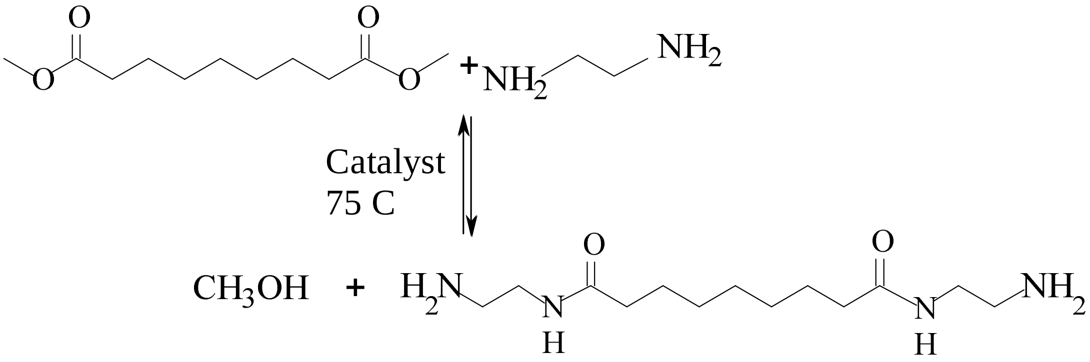

Figure 4.5 Dimethyl azelate amidation

4.1.5.2 Carbamate Synthesis

Carbamates are known as protecting groups in organic chemistry, particularly in peptide synthesis.[27-29] The conventional process of carbamate synthesis is based on phosgenation. Alternative routes for carbamate synthesis involve reacting amines with alkyl chloroformate in the presence of base or some Lewis acids.[30,31] Similarly alkoxycarbonylation of amines to carbamates has been proposed by treating carbon monoxide, alcohols or organic nitro compounds in the presence of platinum group metals as a catalyst.[32,33] Several catalysts are known to enhance the reaction of amine with chloroformates to yield carbamates; examples include zinc,[34] dimethylcarbonate with lead derivatives[35], and tin derivatives[36]. The catalyst that was used in this study was γ-alumina[37]. This catalyst was chosen because it does not generate salt, the reaction is simple, and additionally the catalyst is cheap, safe and can be reused after thermal activation.

Carbamate, also called urethane, is the monomer of polyurethane. Carbamates were prepared by reacting the product from the amidation reaction (Figure 4.5) with dimethyl carbonate. Details of the proposed reaction can be seen in Figure 4.6.

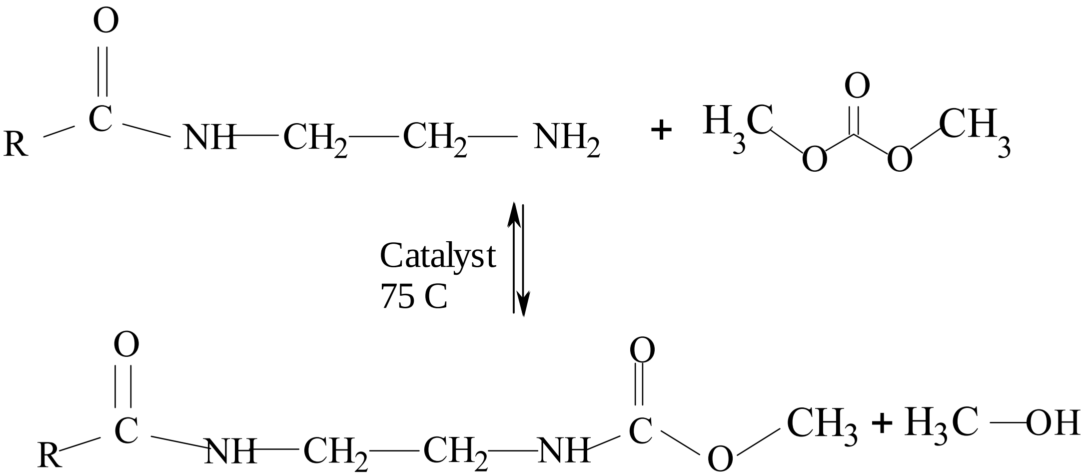

Figure 4.6 Carbamate synthesis

4.1.5.3 Isocyanate Synthesis

One alternative method to synthesize isocyanate is based on thermal decomposition of carbamates with an appropriate catalyst. Many catalysts have been suggested in the literature, including zinc, copper, aluminum, titanium, carbon groups and their oxides, and rare earths, antimony, bismuth and their oxides.[38, 39]

Uriz et al. investigated an alternative method of synthesizing isocyanate from carbamate. In their study, montmorillonite K-10 was shown to be an effective catalyst for the dealcoholysis process of carbamates to isocyanates (Figure 4.7).[40]

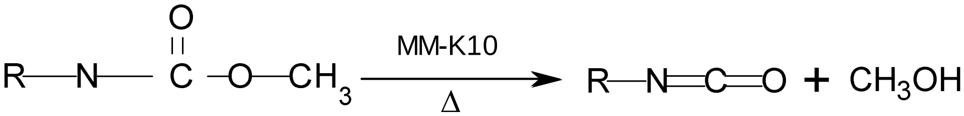

Figure 4.7 Dealcoholysis process of carbamate

The reaction is initiated with the protonation of the carbonyl group, which then yields an ionic intermediate followed by the elimination of the amidic proton to form the desired isocyanate.[40] The reaction must be run at elevated temperatures in order to remove the by-product (methanol) from the reaction mixture.

4.1.5.4 Polyurethane Synthesis from Carbamate

L. Ubags[41] has reported that polyurethane can be synthesized by polycondensation of bis(phenyl carbamate)s with ethylene glycol. This procedure can be applied to the carbamate produced from the previous reaction, with the proposed reaction shown in Figure 4.8 below.

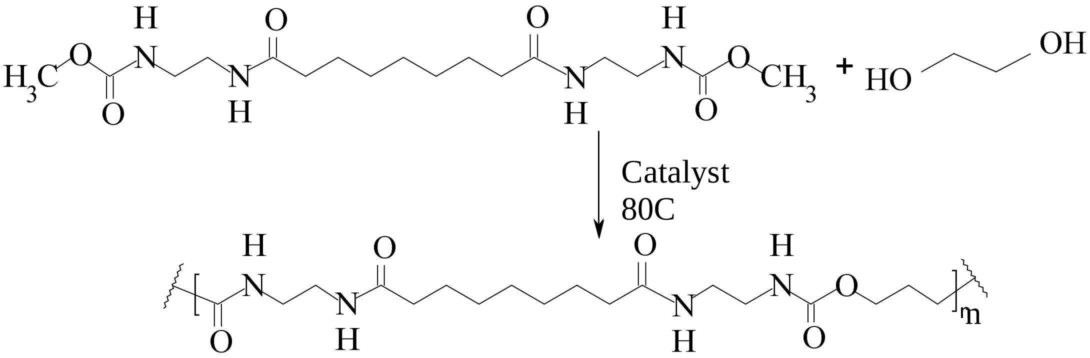

Figure 4.8: Polyurethane synthesis from carbamate

4.1.5.5 Polyurethane Synthesis with Ethylene Carbonate

Rokicki and Piotrowska[42] investigated an alternative polyurethane synthesis using ethylene carbonate as an alternative to phosgene. They reported success in synthesizing polyurethane without the use of isocyanate or phosgene. The detailed reaction beginning with the amidated product of dimethyl azelate is shown in Figure 4.9.

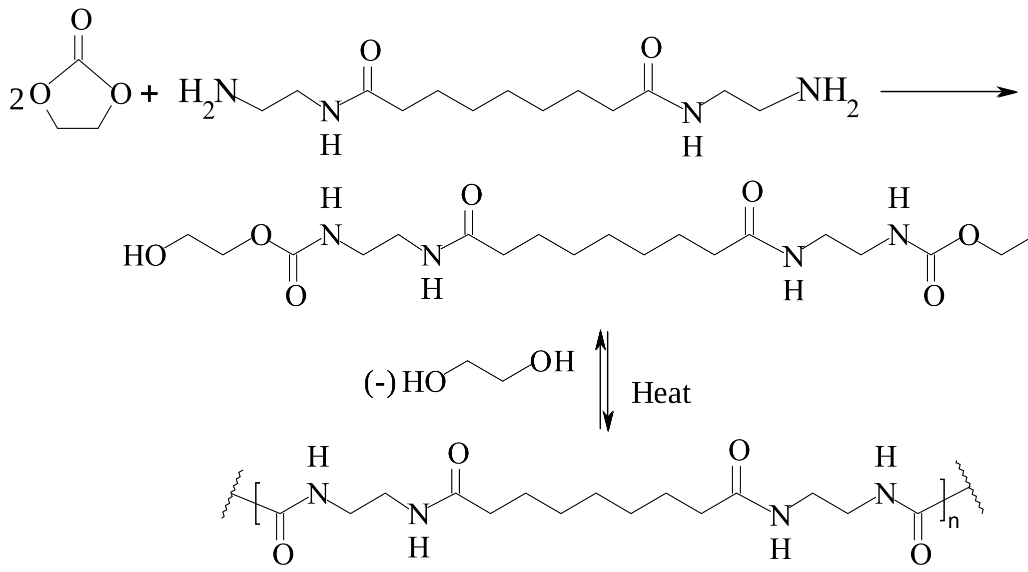

Figure 4.9: Polyurethane synthesis by the reaction of amine with ethylene carbonate

The prepolymer produced has functionality of two; therefore linear polyurethane will be produced in this model compound study.

4.2 Experimental Section

4.2.1 Materials

Dimethyl azelate (80% purity), ethylene diamine, dibutyltin dilaurate, and dimethyl carbonate were purchased from Sigma-Aldrich, St. Louis, MO. Gamma alumina was purchased from Inframat Advanced Material LLC, Manchester, CT. All other chemicals and reagents used were analytical grades, and were used as received unless otherwise noted.

4.2.2 Equipment and Methods

4.2.2.1 Preparation of Azelaic acid bis-[(2-amino-ethyl)-amide]

A typical experiment was conducted by mixing dimethyl azelate (0.5 mol), with an excess of ethylene diamine (2 mol) and 2% by weight of dibutyltin dilaurate in a three-necked round bottom flask. A Dean Stark trap apparatus and a water condenser were attached to one of the necks. A thermometer and a nitrogen purge blanket inlet were attached to the remaining two necks. The reaction temperature was maintained at 75^{o}C. This reaction is reversible; therefore, heating is required during the reaction to remove the by-product methanol. During the reaction, the methanol was collected in the Dean and Stark trap. At the end of the reaction the amount of methanol collected was determined. Unreacted ethylene diamine was then removed by distillation.

4.2.2.2 Carbamate Synthesis

Azelaic acid bis-[(2-amino-ethyl)-amide] (0.05 mol) from the above reaction was reacted with a large excess of dimethyl carbonate (1 mol) using γ-alumina as a catalyst in a three necked round bottom flask. The experimental set up was similar to the amidation reaction described in section 4.2.2.1. The reaction mixture was refluxed for 48 hours and the methanol by-product was collected in the Dean and Stark trap. At the end of reaction, unreacted dimethyl carbamate was removed by distillation.

4.2.2.3 Isocyanate Synthesis

Isocyanate was synthesized from carbamate by thermal decomposition. The product from the carbamate synthesis described in section 4.2.2.2 was converted to isocyanate by utilizing montmorillonite K-10 as a catalyst. Decaline was used as a solvent in the reaction. The mixture was heated to 190°C for 24 hours. After 24 hours, the decaline was removed by vacuum distillation.

4.2.2.4 Polyurethane Synthesis from Carbamate (isocyanate-free method)

Polyurethane was produced directly from carbamate. The carbamate product from section 4.2.2.3 was reacted with ethylene glycol, which acted as a chain extender, with mol ratio of 2:1. Dimethyltin dilaurate (2% by weight of carbamate) was used as a catalyst. The reaction was conducted in batch set-up in a three neck round bottom flask equipped with Dean Stark apparatus. A nitrogen blanket and thermometer were attached on the remaining two necks. The reaction was maintained at 80°C and stirred continuously as the polymerization progressed and the viscosity increased.

4.2.2.5 Polyurethane Synthesis from Ethylene Carbonate

This method consists of two steps, the formation of prepolymer from the amine product and the polymerization of this prepolymer. In the first step, the amidated product, azelaic acid bis-[(2-amino-ethyl)-amide] described in section 4.2.2.1, was reacted with ethylene carbonate at a 1:2 mol ratio using methylene chloride as a solvent. The mixture was stirred continuously at room temperature and the end of the reaction was determined by the disappearance of the 1800 cm^{-1} peak in the FT-IR spectrum. Methylene chloride was then removed by distillation. This intermediate was then polymerized in a three necked round bottom flask equipped with a Dean Stark trap and a water condenser, thermometer, and glass stopper, with xylene as a solvent. The solvent was used to reduce the viscosity and to advance the reaction to produce high molecular weight polymer.

Ethylene glycol was produced as a by-product and was collected in the Dean Stark trap as the reaction proceeded. The mixture of xylene and ethylene glycol formed an azeotrope with a boiling point of 145-150^{o}C. The xylene solvent was removed by distillation at the end of the reaction.

4.3 Characterization

Infrared spectra were obtained with a PerkinElmer 2000 FTIR spectrometer equipped with a diamond tip ATR cell.

NMR spectroscopy (proton spectra) was obtained using a Varian Inova spectrometer operating at 300 MHz. Unless otherwise stated, all samples were prepared by dissolving 50-100 mg of product in 0.7 ml of $CDCl_3$. The solvent peak was referenced at 7.24 ppm. All spectra were acquired at 25^{o}C.

Gas chromatography was used to characterize the mixture produced during each reaction, using a HP 5890 Series II GC, with Supelco Pta-5 column (30m x 0.25mm i.d.), film thickness 1 μm, and helium as the carrier gas. The GC temperature was set at 50^{o}C initial temperature, with 20^{o}C/min ramp to a final temperature of 300^{o}C.

Amine value titration was conducted per ASTM standard D2073[43] on the amidation end product. Hydroxyl value was conducted per ASTM method D1957[44] for the prepolymer in the ethylene carbonate polyurethane synthesis. DSC (Differential Scanning Calorimetry) analysis was conducted on the polymers produced, using a TA Q2000 DSC and aluminum sample pans. The experiments were run at 10^{o}C/min heating rate, and 50 ml/min nitrogen flow. TA universal analysis software was used to analyze the experimental data.

4.4 Results and Discussion

4.4.1 Amidation Reaction Results

The reaction between dimethyl azelate and ethylene diamine with a tin catalyst was expected to produce a compound with two terminal amine groups. The FTIR spectrum of the dimethyl azelate and the bis-[(2-amino-ethyl)-amide] derivative from the amidation reaction is shown in Figure 4.10.

The FTIR spectra show a shift of the characteristic carbonyl (C=O) band from 1730 to 1630 cm^{-1} and the disappearance of the band at 1200 cm^{-1} corresponding to C—O stretching. These two bonds represent the ester linkages of the dimethyl azelate structure. The shifts are caused by the formation of amides from the ester groups in the reaction with ethylene diamine. Furthermore, the formation of strong stretching and bending bands located at 3290 cm^{-1} and 1550 cm^{-1}, respectively, are characteristic of N—H groups obtained from the amidation reaction as shown in Figure 4.5.

The complete conversion was further confirmed by ^{1}H NMR spectroscopy. The ^{1}H NMR showed the peaks corresponding to the hydrogen of CH_2 attached to the ester group (~2.3ppm) were shifted to ~2.1 ppm after the amidation reaction. The full ^{1}H NMR spectra of the dimethyl azelate and the amidation product can be seen in appendix B, Figure B.1 and B.2, respectively. The by-product of this reaction was methanol. The presence of methanol was confirmed by GC (retention time = 1.736 minutes).

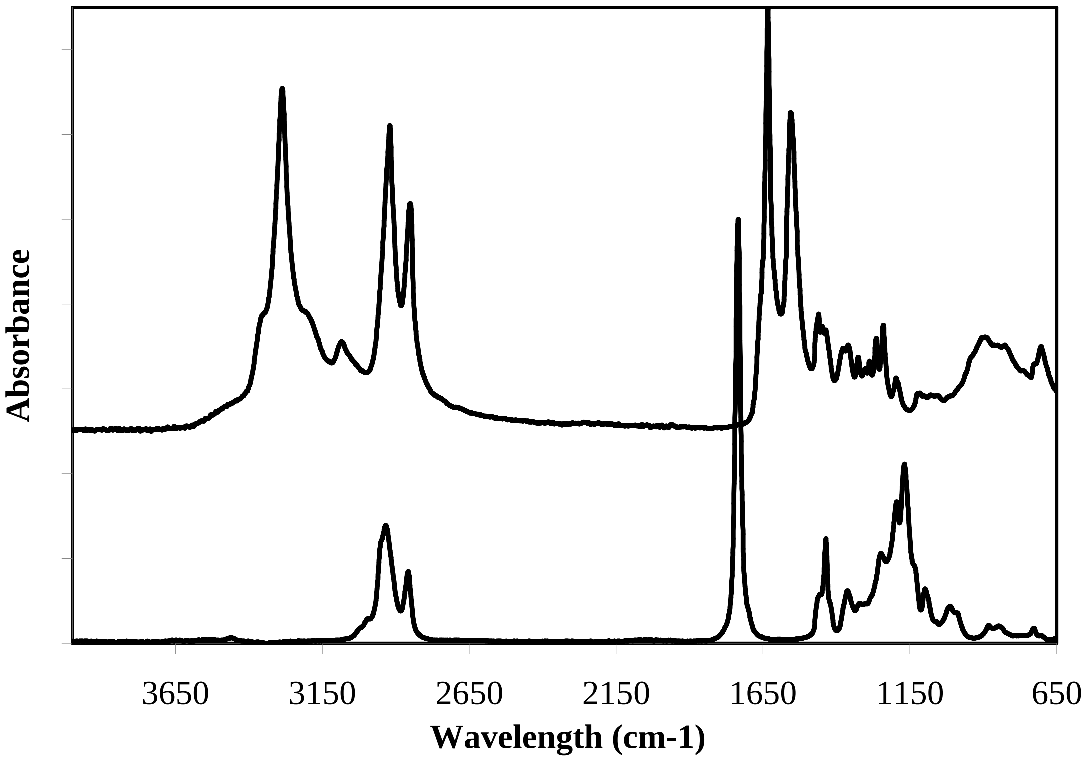

Figure 4.10 FTIR spectra of amidation product of dimethyl azelate (top) and dimethyl azelate starting material (bottom)

Amine value titration was conducted to determine the equivalent amount of amine. The theoretical amine value of the amidated product is 412.5 mg KOH/g. The total amine value that was calculated based on ASTM standard D2073 of this amidation product was 347.8±26.0 mg KOH/g sample. It is apparent from the above data that the amidation product of dimethyl azelate was successfully obtained.

4.4.2 Carbamate Synthesis

The carbamate derivative was synthesized from the bis-[(2-amino-ethyl)-amide] of azelaic acid by reaction of the terminal amines with methyl chloroformate. The FTIR spectrum was obtained from the carbamates produced (Figure 4.11).

The FTIR spectra of the carbamates produced show a new characteristic peak at 1700 cm^{-1} which corresponds to the stretching band of the C=O group caused by the reaction between the amine and dimethyl carbonate (Figure 4.6). The new peak around 1200 cm^{-1} is consistent with the existence of C—O stretching regions from the dimethyl carbonate structure. The stretching vibration of N—H at 3340 cm^{-1} exists for both structures, the amidation product and carbamate.

The ^1H NMR spectroscopy for the carbamate produced was in accordance with the structure proposed. The spectra can be seen in Appendix B, Figure B.3. This NMR spectrum showed the disappearance of the peak at 2.7 ppm, which represents the hydrogen in CH_2 of diamine and then shifted to 3.32 ppm due to the reaction with dimethyl carbonate. New peaks also appeared at 3.68 ppm, which represents the methyl group at the end of the carbamate structure. Another indication that the proposed reaction occurred as expected was the formation and removal of methanol by-product.

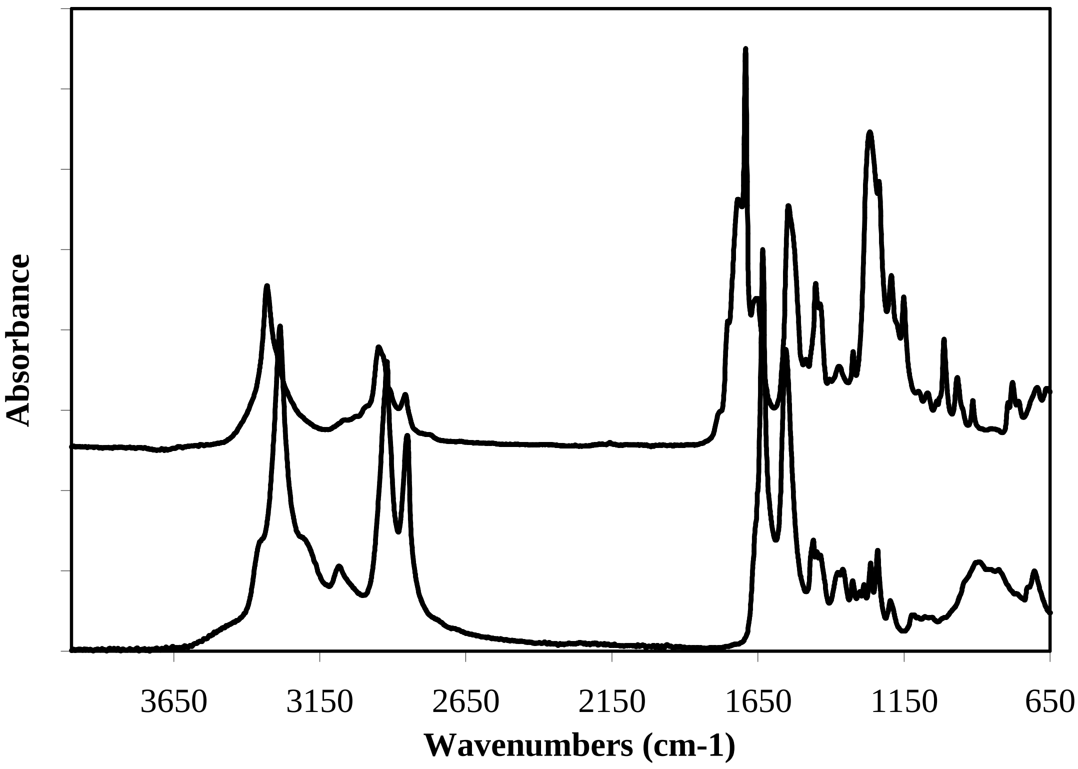

Figure 4.11 FTIR spectra of carbamates product (top) and amidation product of dimethyl azelate (bottom)

From all the results above, it can be concluded that the carbamate was successfully produced from the amidation product of dimethyl azelate.

4.4.3 Isocyanate Synthesis

The isocyanate was synthesized by thermal decomposition of the carbamate produced. The decomposition was conducted in the liquid phase at higher temperatures. An FTIR spectrum of the end product after the thermal decomposition reaction is shown in Figure 4.12.

The small peak around 2200 cm^{-1} of the thermal decomposition product spectrum is a distinct peak related to the stretching vibration of the isocyanate group (N=C=O). The presence of this peak in the end product spectrum indicates that the isocyanate was successfully produced during this thermal decomposition reaction. Unfortunately, the magnitude of the peak is much smaller than expected, indicating low yields. This poor yield could be due to the fact that isocyanate is a very reactive compound and reacted with moisture after it was produced or it further reacted with carbamate to form allophanate. To suppress these side reactions, the reaction was repeated at higher temperatures. However, although methanol was collected in the Dean Stark trap as expected, the yields were still low. Therefore, due to the low yield of isocyanate produced in this reaction, it was decided to prepare high MW polyurethane directly from the methyl carbamate intermediates. An alternative method was also investigated. These results are discussed in both sections below.

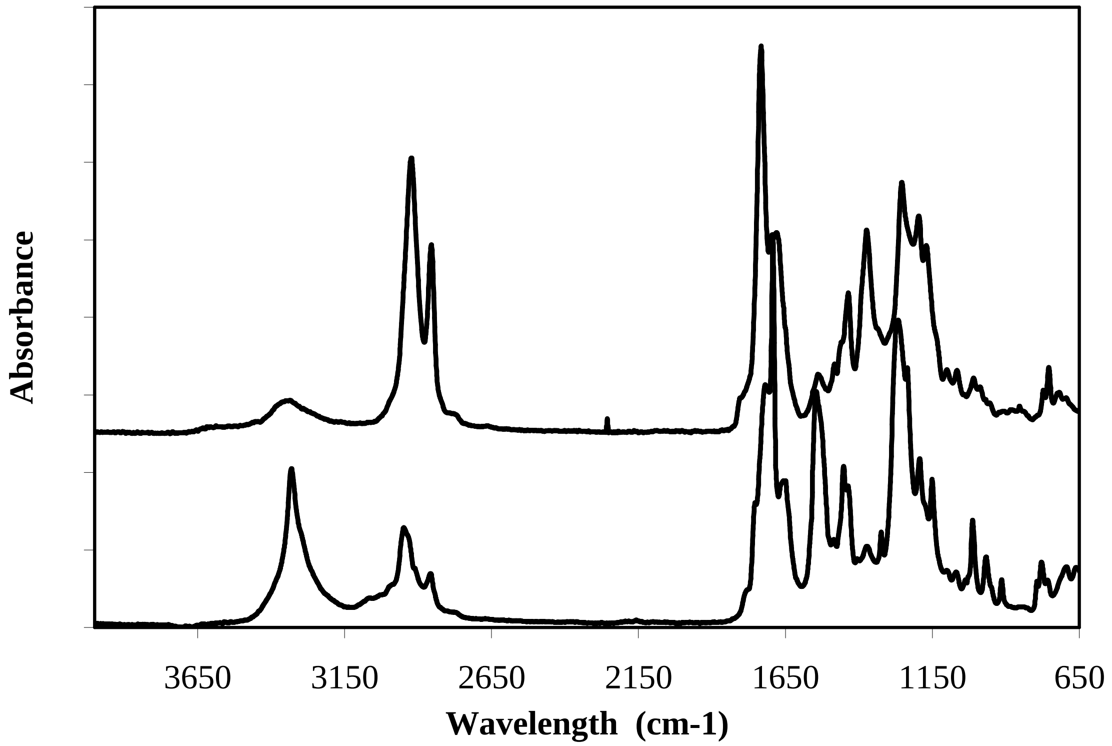

Figure 4.12 FTIR spectra of thermal decomposition product (top) and carbamates product (bottom)

4.4 Polyurethane Synthesis from Carbamate

Polyurethane was prepared from the carbamate intermediate by a chain extending reaction with ethylene glycol. The FTIR spectrum of the polyurethane produced by this route is shown in Figure 4.13 below. This reaction produced the desired polyurethane. As mentioned above, carbamate is the monomer of polyurethane; therefore the FTIR spectrum produced was very similar, since the same functional groups exist in both compounds.

The ^{1}H NMR spectra of the polymer produced are shown in Appendix B Figure B.4. The ^{1}H NMR spectra of the polyurethane produced were compared with the spectra of the carbamate starting material. Since the carbamate is the monomer of polyurethane, the NMR spectra showed similar peaks. A new peak showed on the polyurethane spectra around 4.2 ppm, this peak represents the hydrogen attached to the methylene of the ethylene glycol that reacted with the carbamate. An extra peak around 3.8 ppm indicates unreacted ethylene glycol present in the mixture. Determining the exact amount of ethylene glycol used is one of the challenges in this method. Ethylene glycol has a high boiling point, which makes this compound difficult to remove from the mixture. The presence of ethylene glycol even in small amounts will significantly reduce the molecular weight of the polymer produced.

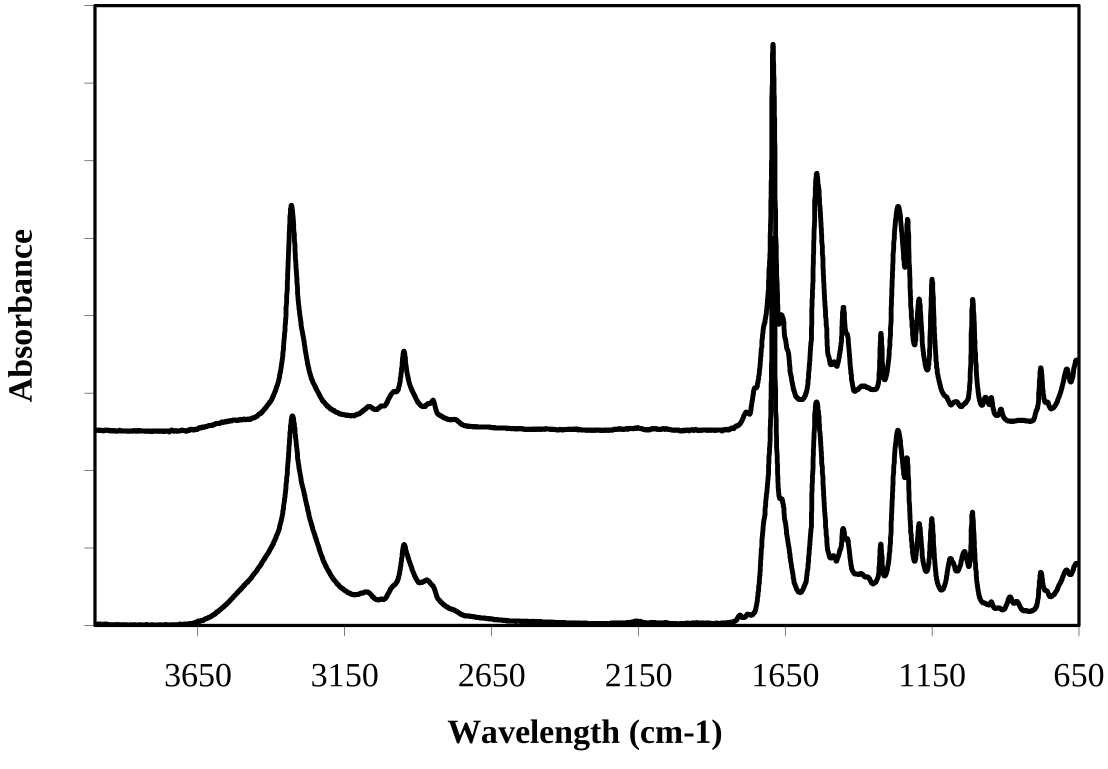

Figure 4.13 FTIR spectra of polyurethane produced (top) and ester-carbamates starting material (bottom)

Differential scanning calorimetry was used to analyze the polymer end product. Figure 4.14 shows the result of the heat flow versus temperature curves obtained from the polyurethane sample. The glass transition temperature (T_g) of this polymer was around -23.9^{o}C and melting temperature was 43.1^{o}C.

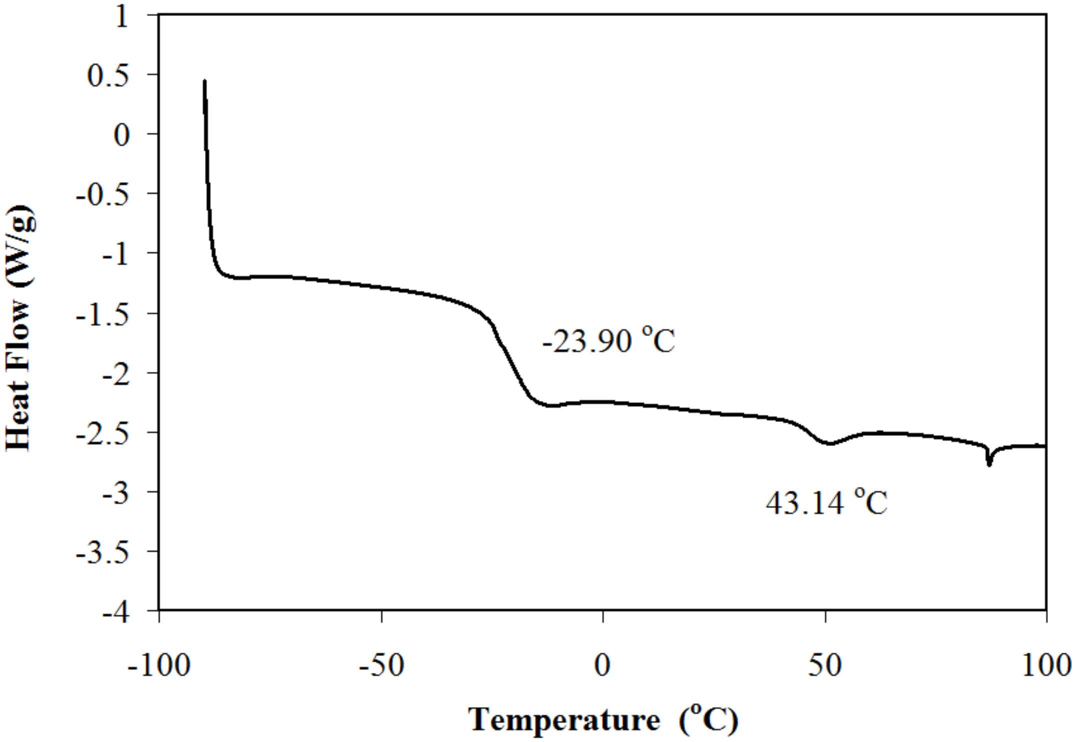

Figure 4.14 DSC result for polyurethane from carbamate

4.5 Polyurethane Synthesis with Ethylene Carbonate

Another synthetic route to polyurethane without utilizing any isocyanate was examined. This polyurethane synthesis method in which polyurethane was directly produced from the amidation product of dimethyl azelate was a simpler process than the previous method. Details of this reaction are shown in Figure 4.8. The FTIR spectra of the polymer produced by this method were compared to the FTIR spectra of the polyurethane produced from ester carbamate. These spectra are shown in Figure 4.15.

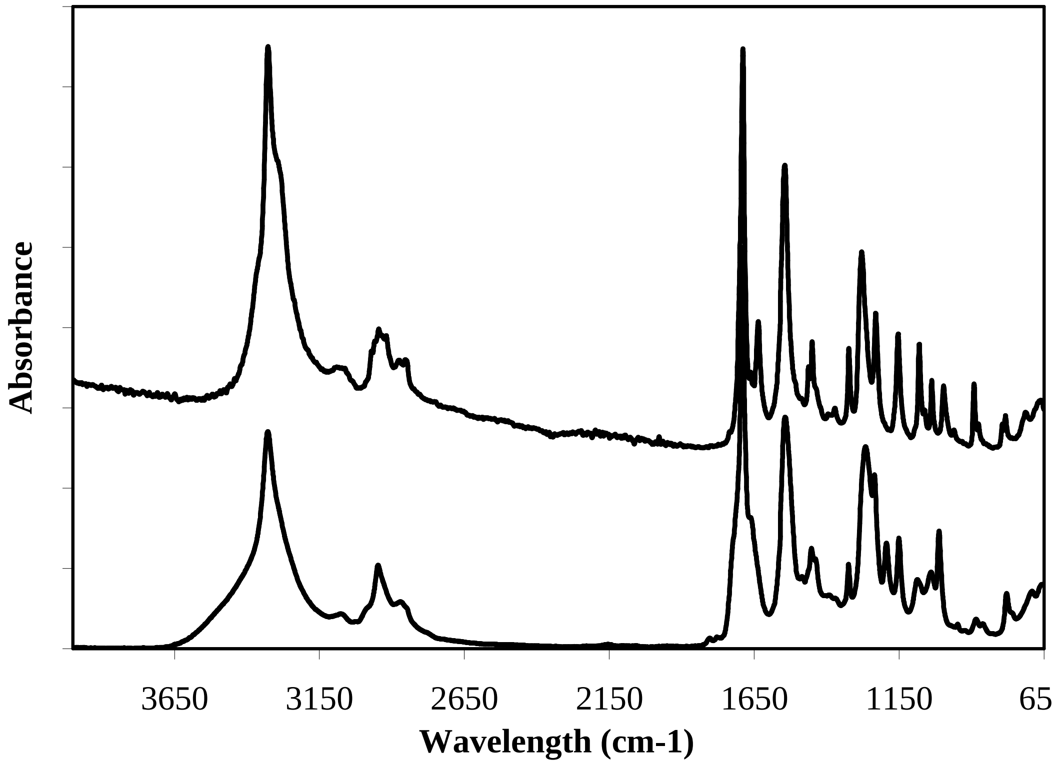

Figure 4.15 FTIR spectra of polyurethane produced with ethylene carbonate (top) and polyurethane produced from ester-carbamate (bottom)

Based on the FTIR spectra, it is apparent that the polyurethane produced by both methods had the same functional groups. The structure of the polymer was further confirmed with ^{1}H NMR spectroscopic analysis (Appendix B, Figure B.5). The ^{1}H NMR spectrum showed peaks at 4.1 ppm and 3.3 ppm, representing the hydrogen on the two methylene groups of the ethylene carbonate that attached to the amine reactant. The peaks at 2.76 ppm that represent the hydrogen attached to the methylene that exists on the amidation product NMR spectra were reduced, but still appeared, which indicate an unreacted amine, and a new peak at 3.67 ppm represents the same hydrogen bond on methylene already attached to the ethylene carbonate group. The small peak at 4.1 ppm shows the hydrogen attached to the methylene group after the removal of ethylene glycol necessary for the monomer to polymerize. This shows that the polymerization occurred and a high molecular weight of polymer was produced. This proposed method has fewer steps from converting the starting material to polyurethane and can be used to prepare high molecular weight polymer

The glass transition temperature (T_g) and melting temperature (T_m) values of this polyurethane were obtained from DSC (Figure 4.16). The polyurethane exhibited a glass transition temperature of 40.85^{o}C and melting point of 128.55^{o}C.

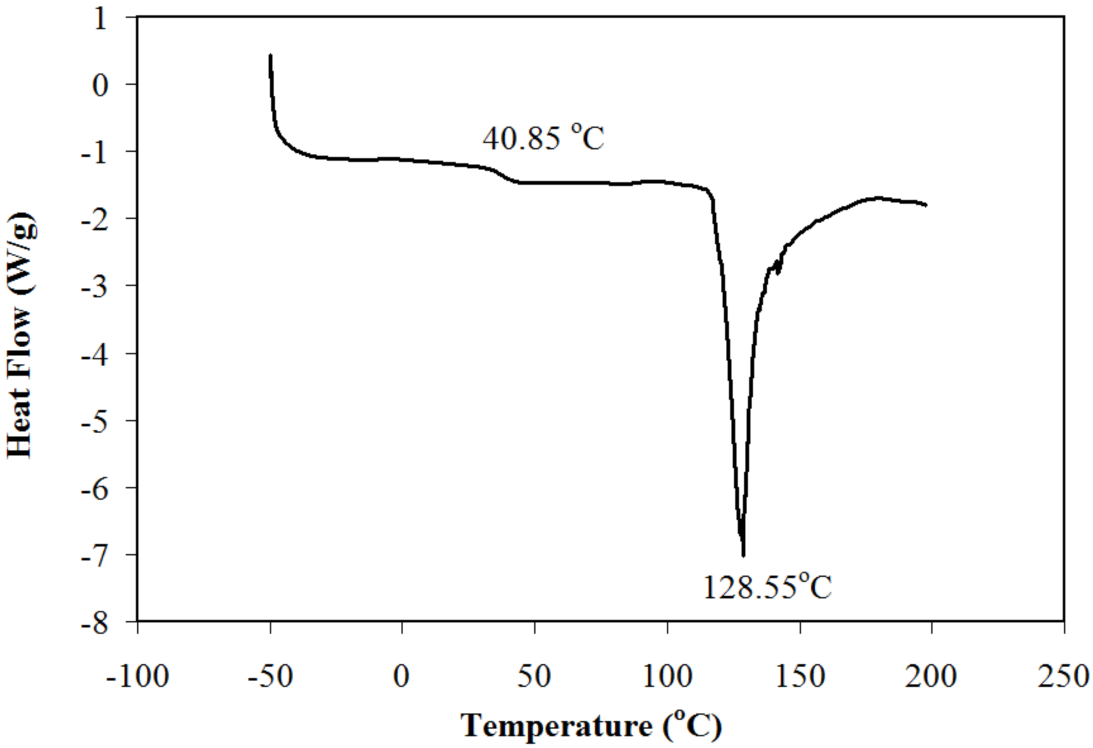

Figure 4.16 DSC result for polyurethane produced with ethylene carbonate

Based on the end product results from both methods, it was clearly observed that both methods successfully produced polyurethane. There is greater probability of the polymer resulting from the carbamate method containing impurities, due to the additional steps required. Each step in this carbamate method was also time consuming. It was harder to obtain a high molecular weight of polymer with the carbamate method due to the requirement of a specific amount of ethylene glycol addition to the pre-polymer mixture. On the other hand, the polyurethane synthesis method with ethylene carbonate is a much faster process, it contains fewer steps than the carbamate method and it produced higher purity polymer.

4.6 Conclusion

In order to avoid the use of hazardous monomers such as phosgene and isocyanates, alternative polyurethane synthesis methods were investigated. Dimethyl azelate was used as a model compound to produce polyurethanes by two different routes; the first method involves chain extension reaction of a carbamate intermediate with ethylene glycol and the second method involves formation of urethane pre-polymers by the reaction of terminal amines and ethylene carbonate followed by re-equilibration. The data indicate that high molecular weight polyurethanes can be successfully produced by either method starting from dimethyl azelate. Two different synthetic isocyanate-free polyurethane synthetic methods were also investigated. The polyurethane synthesis using ethylene carbonate is a more direct approach to production of polyurethanes. This method is, therefore, recommended for further study of bio-based polyurethane synthesis.

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Chapter 5

Conclusions

The urgent necessity to develop and improve new synthetic routes to synthesize polymeric materials from renewable resources has driven a great amount of research. The renewable resource based polymers have economic and environmental benefits. Polyurethane has two main building blocks, polyols and isocyanate. Biobased polyols are available commercially. Ozonolysis is one method that can be used to produce soy-based polyols.

One study was done to evaluate the effect of ultraviolet (UV) light to improve the synthesis of soy-based polyols with ozonolysis. The study showed that addition of UV to complement the catalyzed ozonolysis of soy oil and ethylene glycol to produce polyols did not change the rate of the reaction.

In the study of this thesis, two methods were used to synthesize bio-based polyurethane. The simpler structure of a model compound, dimethyl azelate, helped us to better identify the products of this complicated reaction. Based on the results, it can be concluded that polyurethane can be successfully produced from dimethyl azelate. Two different synthetic isocyanate-free methods to produce polyurethane were successfully demonstrated. The polyurethane synthesis method using ethylene carbonate is the more direct and preferred approach to the production of this polymer. This method is, therefore, recommended for further study of bio-based polyurethane synthesis. For future work, other chemicals like biodiesel can be used as starting material in replacement of dimethyl azelate with the recommended method above.

APPENDICES

APPENDIX A

CHAPTER 3 DATA

A. 1. FTIR Spectra of Soybean Oil Ozonolysis

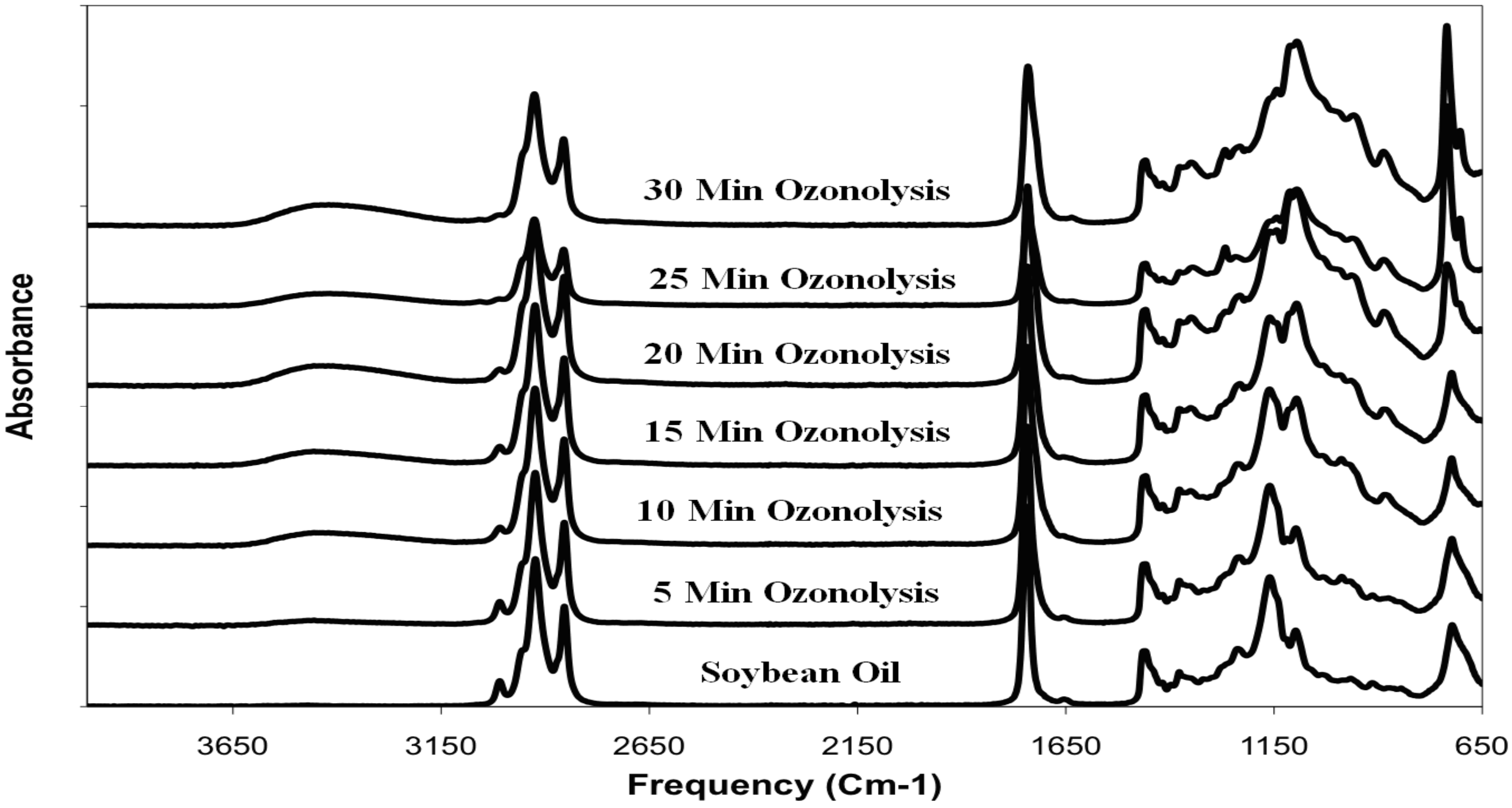


Figure A.1 FTIR results of soybean oil ozonolysis with UV

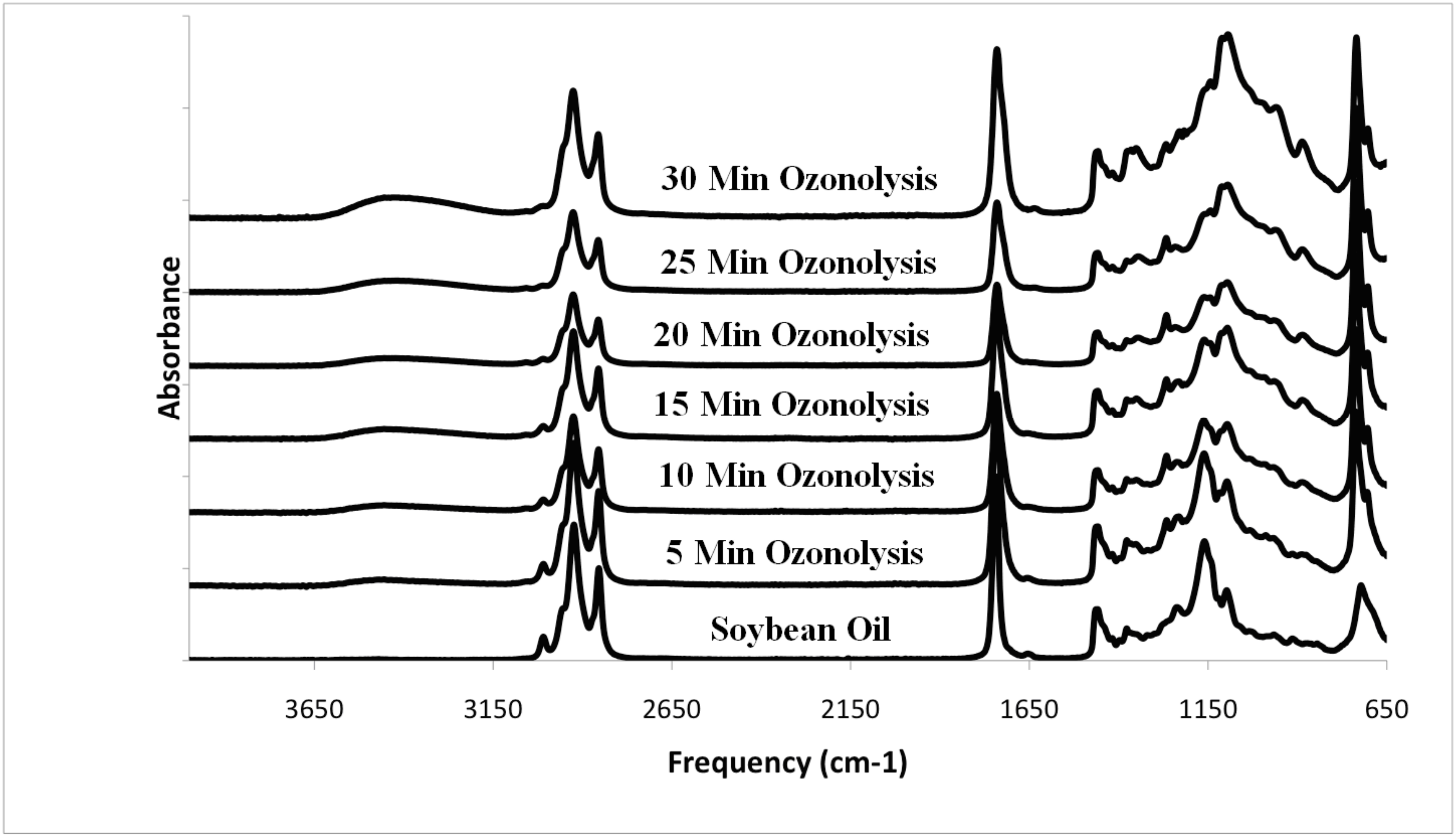


Figure A.2 FTIR results of ozonolysis of soybean oil without UV

A.2. NMR Spectra of Model Compounds

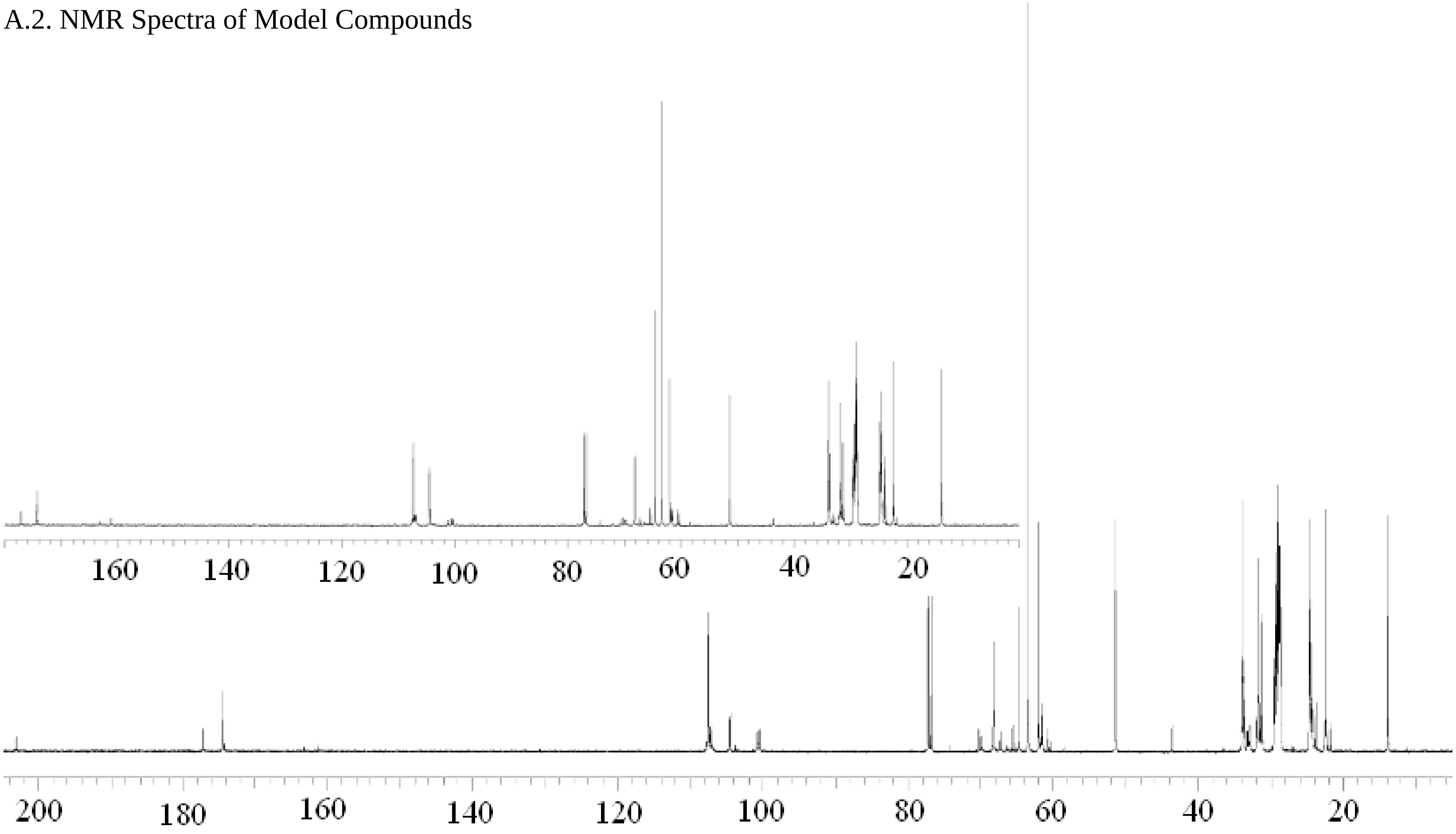


Figure A.3 ^{13}C NMR spectrum of methyl oleate – ozonated with ethylene glycol with UV light. Inset shows the spectrum of the product without UV light

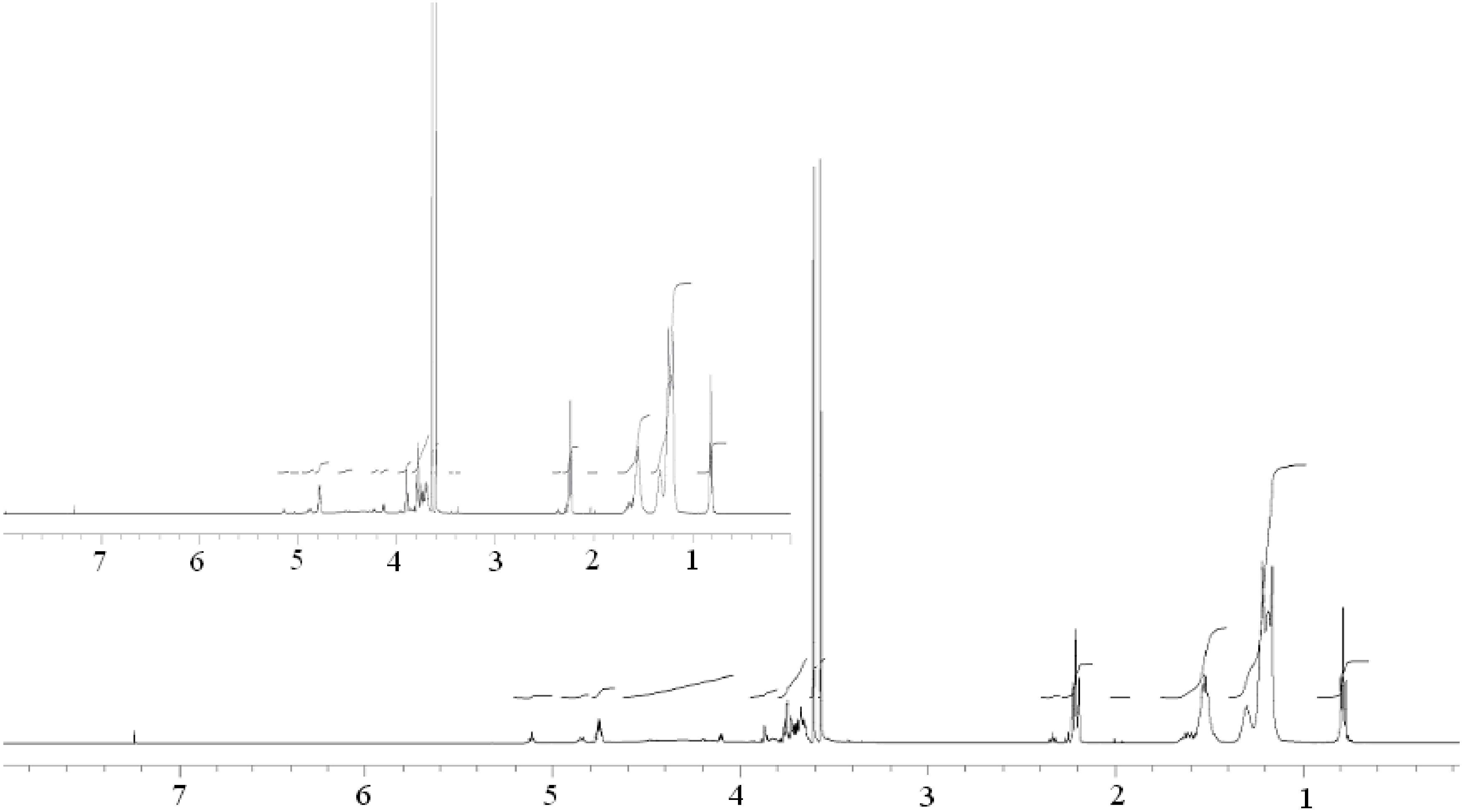


Figure A.4 ^{1}H NMR spectrum of Methyl oleate –ozonated with ethylene glycol with UV light. Inset shows the spectrum of product without UV light.

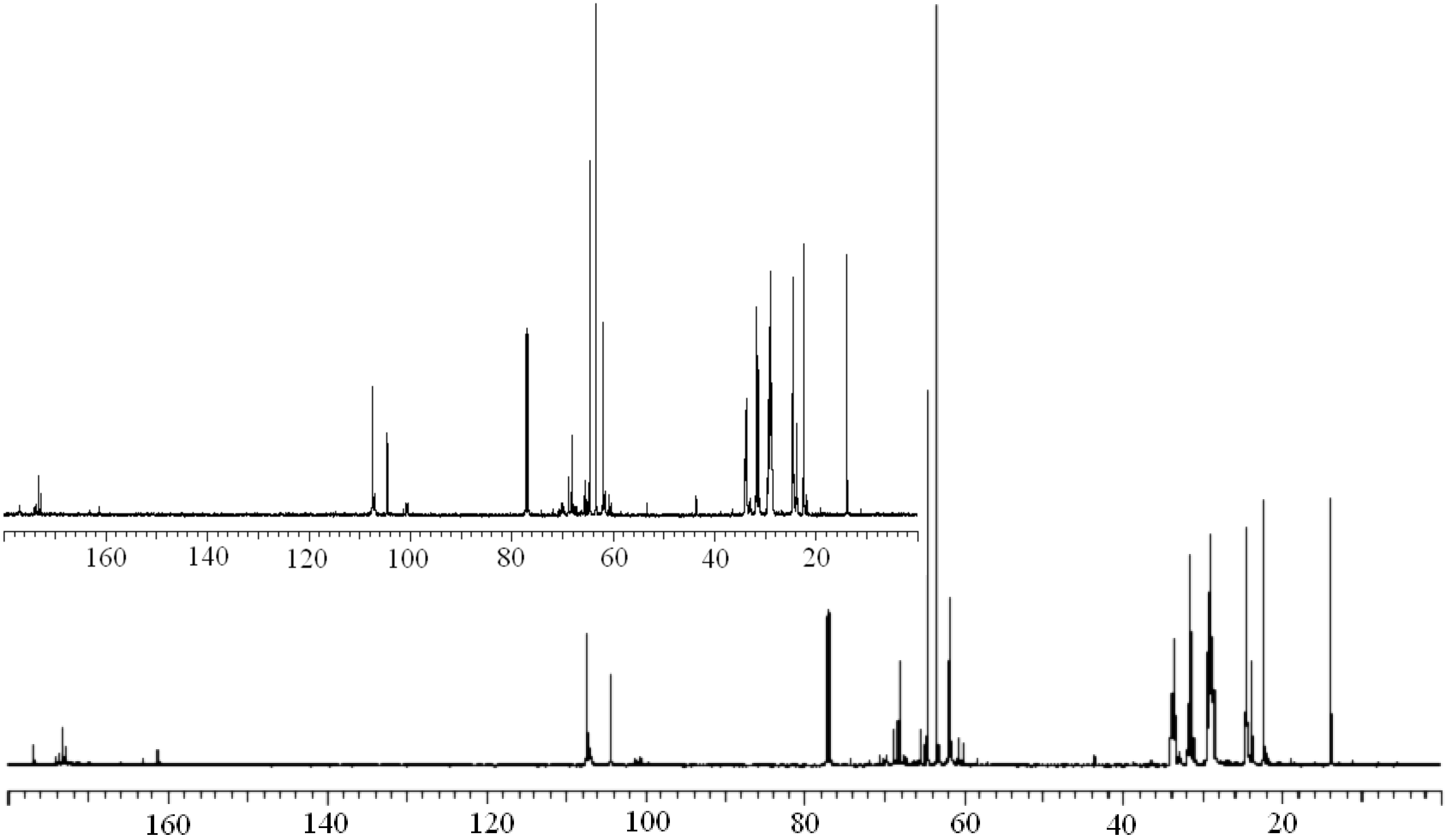


Figure A.5 ^{13}C NMR spectrum of triolein-ozonated with ethylene glycol with UV light. Inset shows the spectrum of the product without UV light

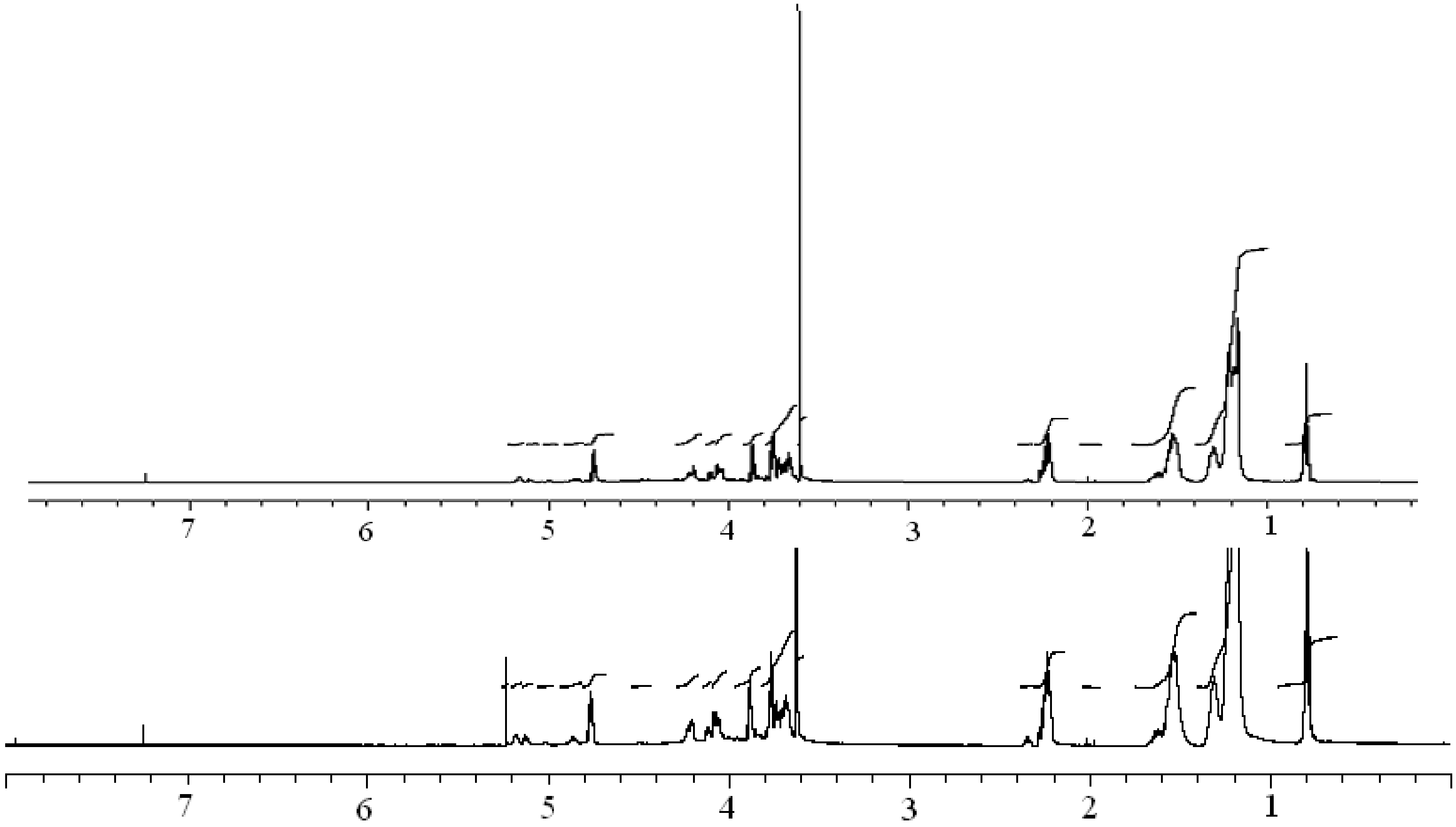


Figure A.6 ^{1}H NMR spectrum of triolein –ozonated with ethylene glycol and UV light (Bottom). Top spectrum shows the spectrum of product without UV light

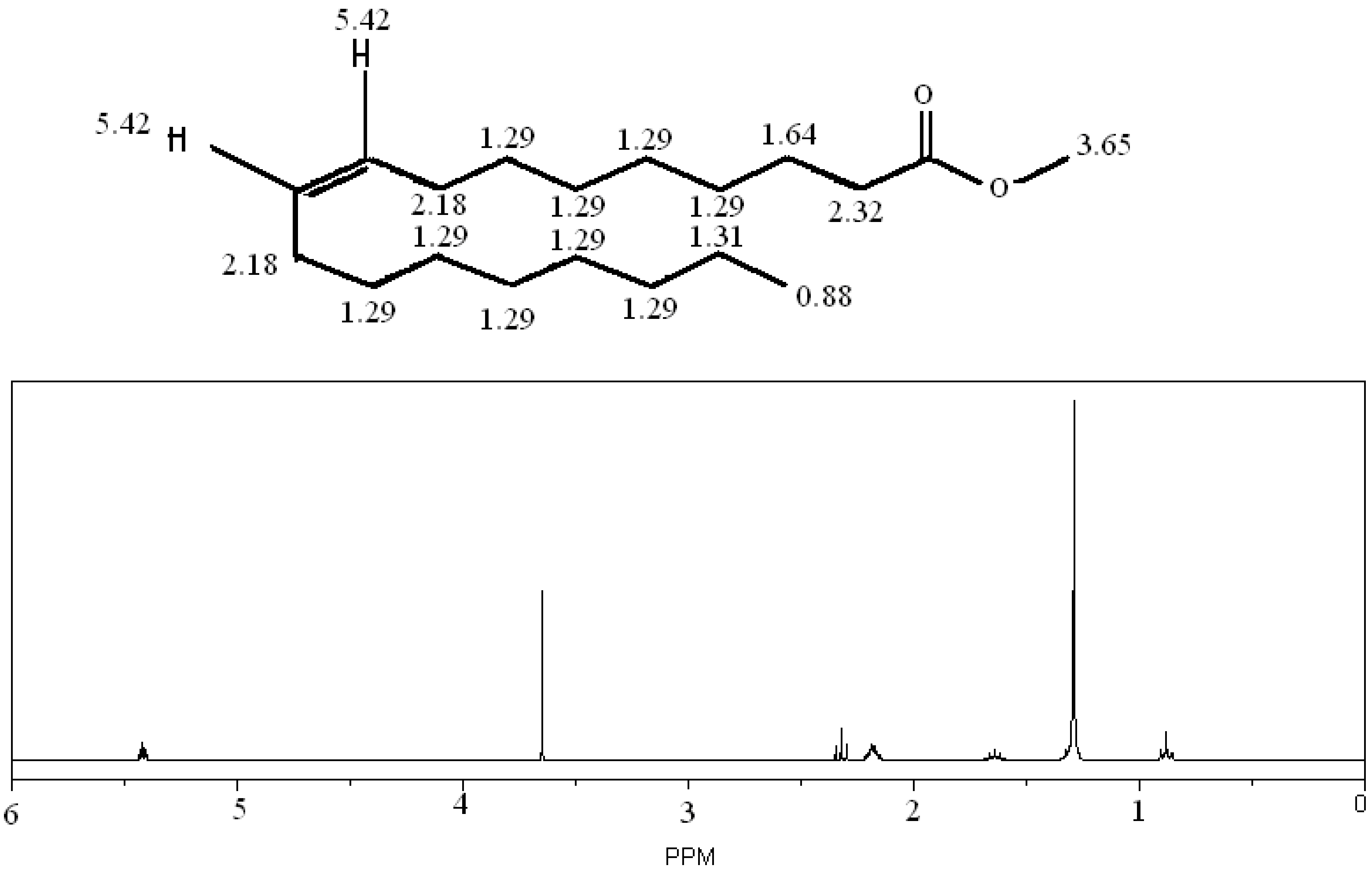


Figure A.7 ^{1}H NMR prediction of methyl oleate

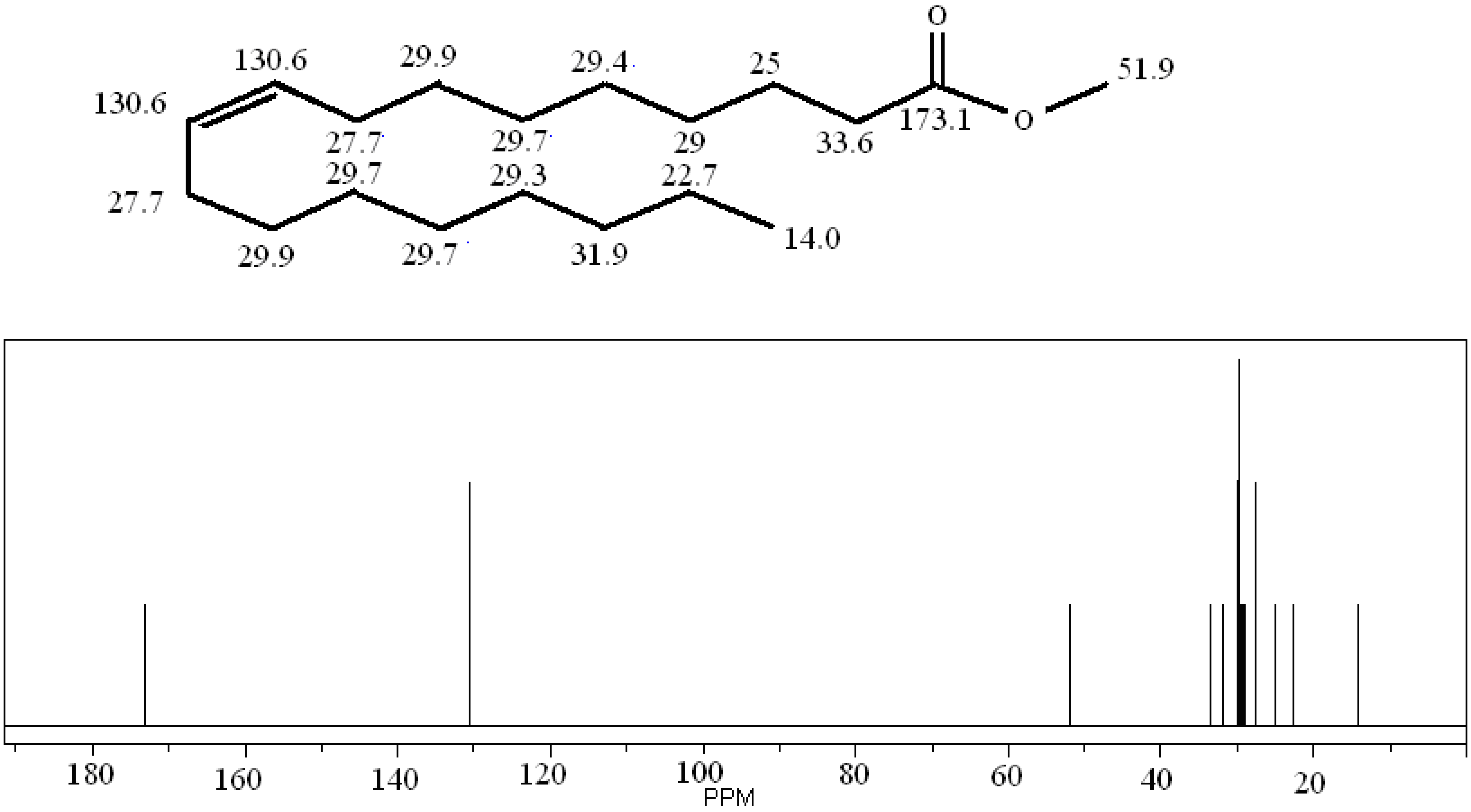


Figure A.8 ^{13}C NMR Prediction of methyl oleate

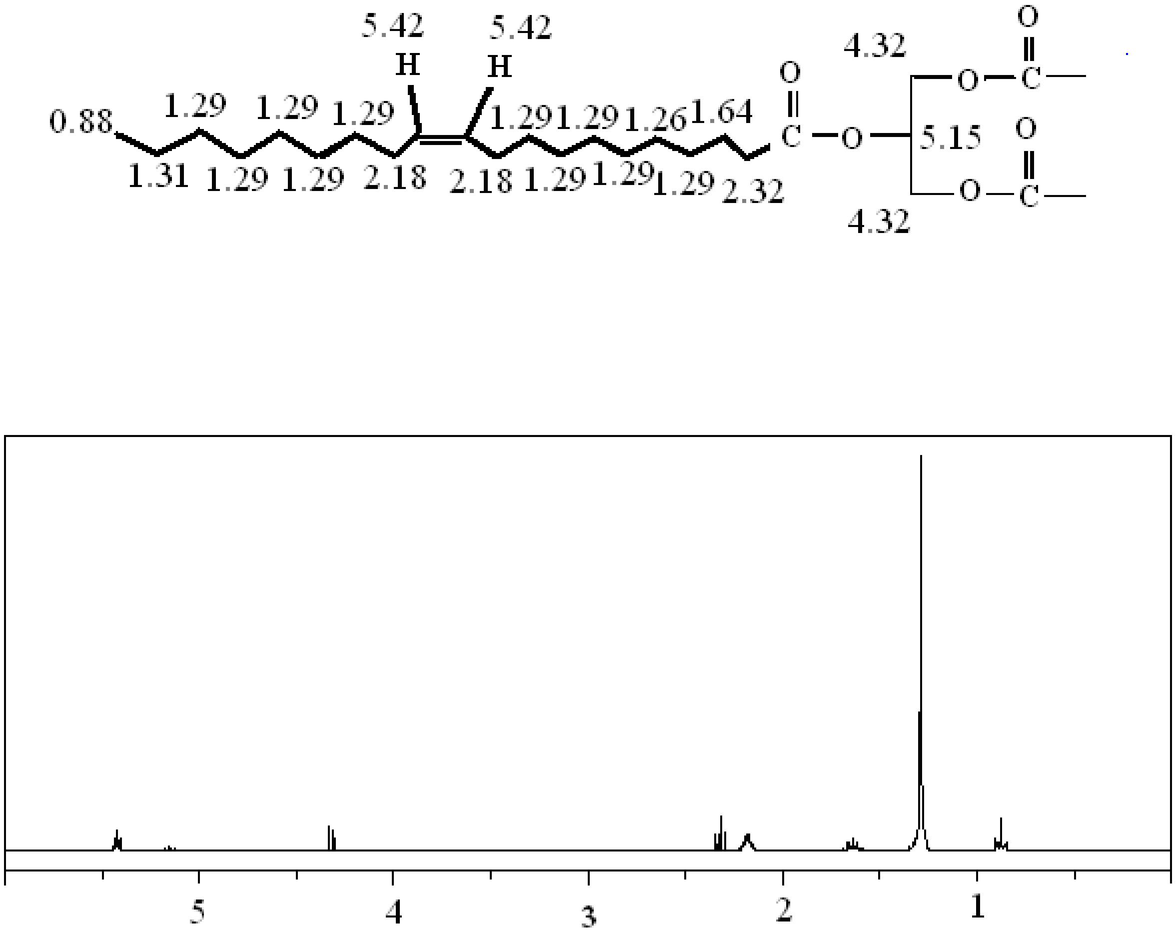


Figure A.9 ^{1}H NMR prediction of triolein

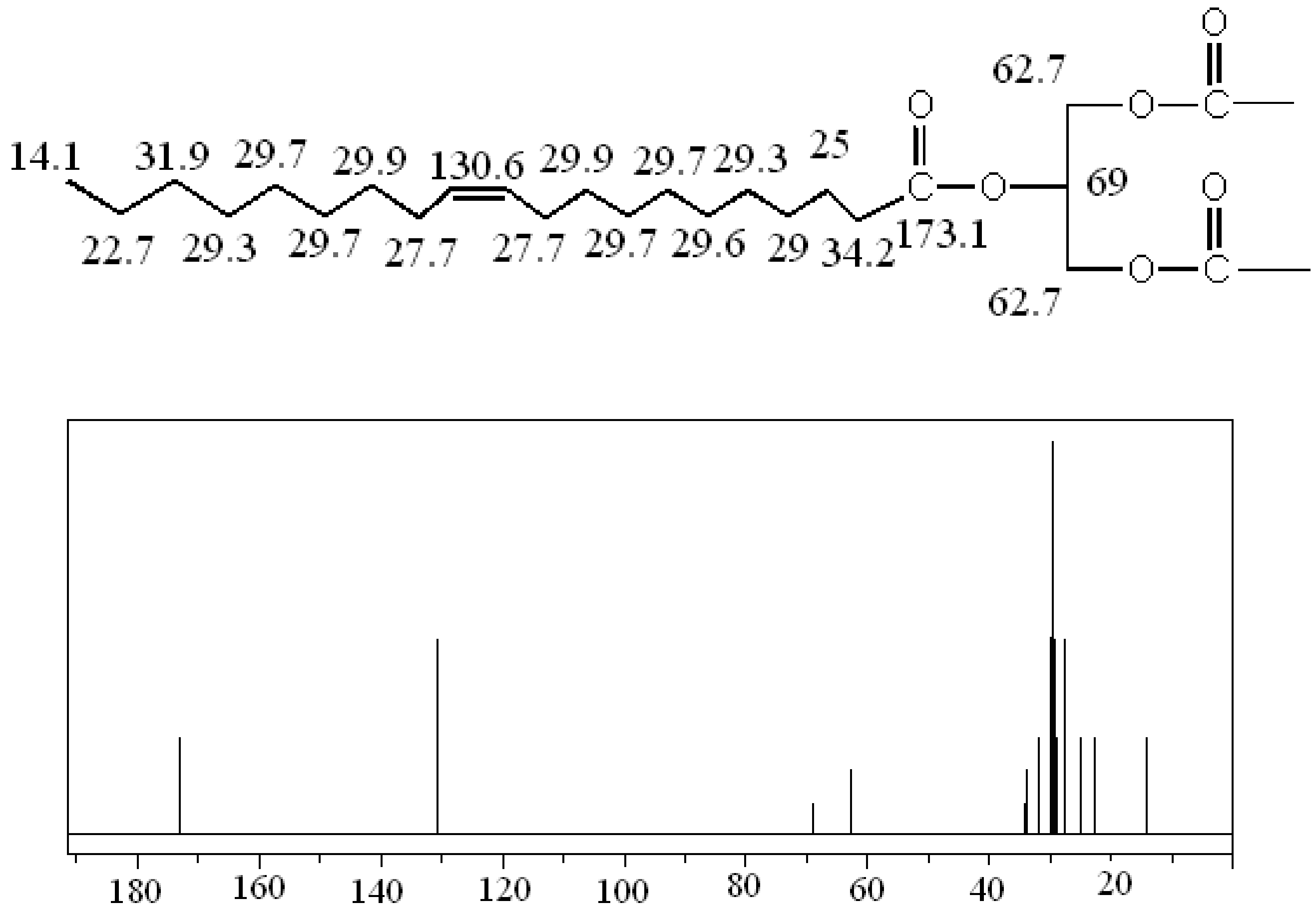


Figure A.10 ^{13}C NMR prediction of triolein

APPENDIX B

CHAPTER 4 NMR SPECTRA AND PREDICTION

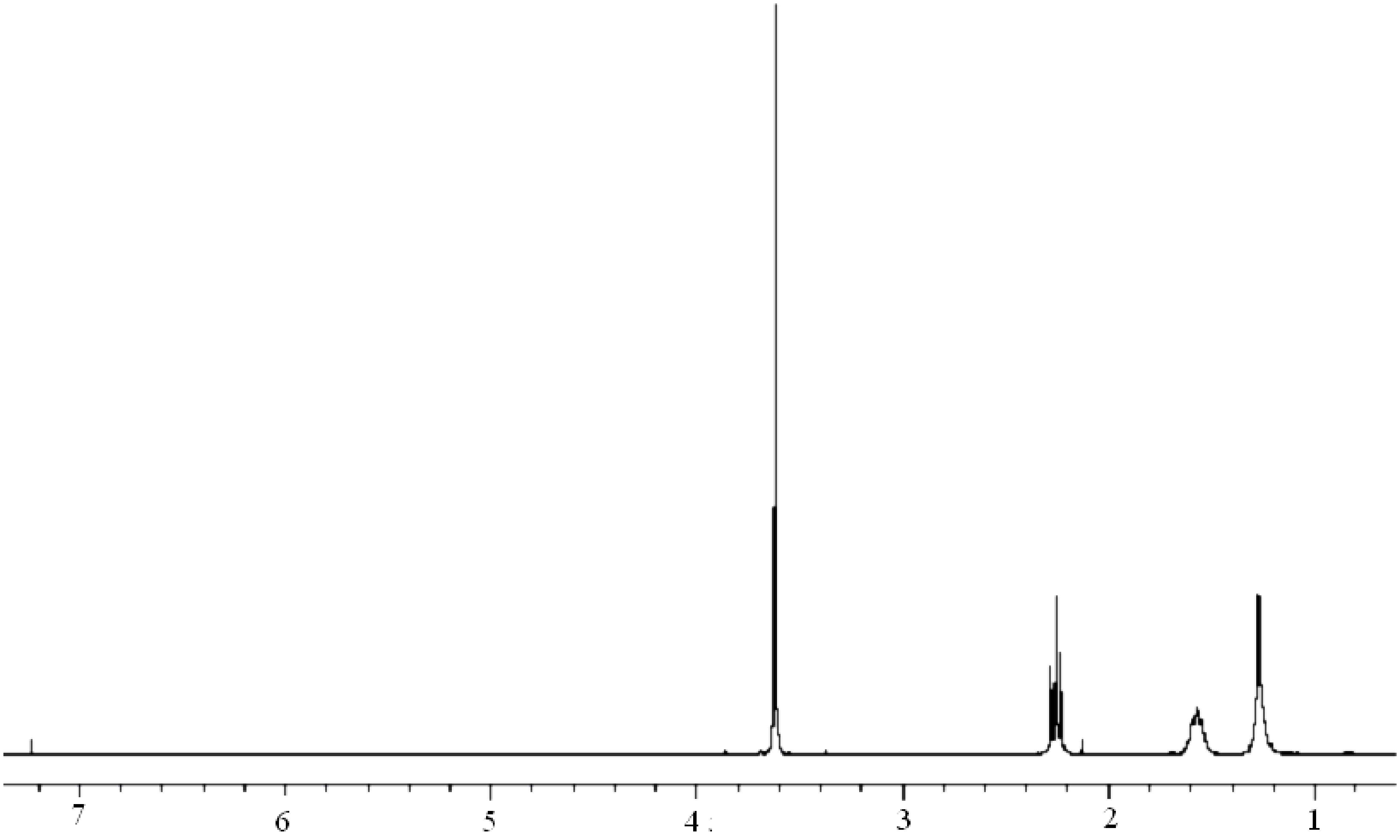


Figure B.1 ^{1}H NMR spectrum of dimethyl azelate

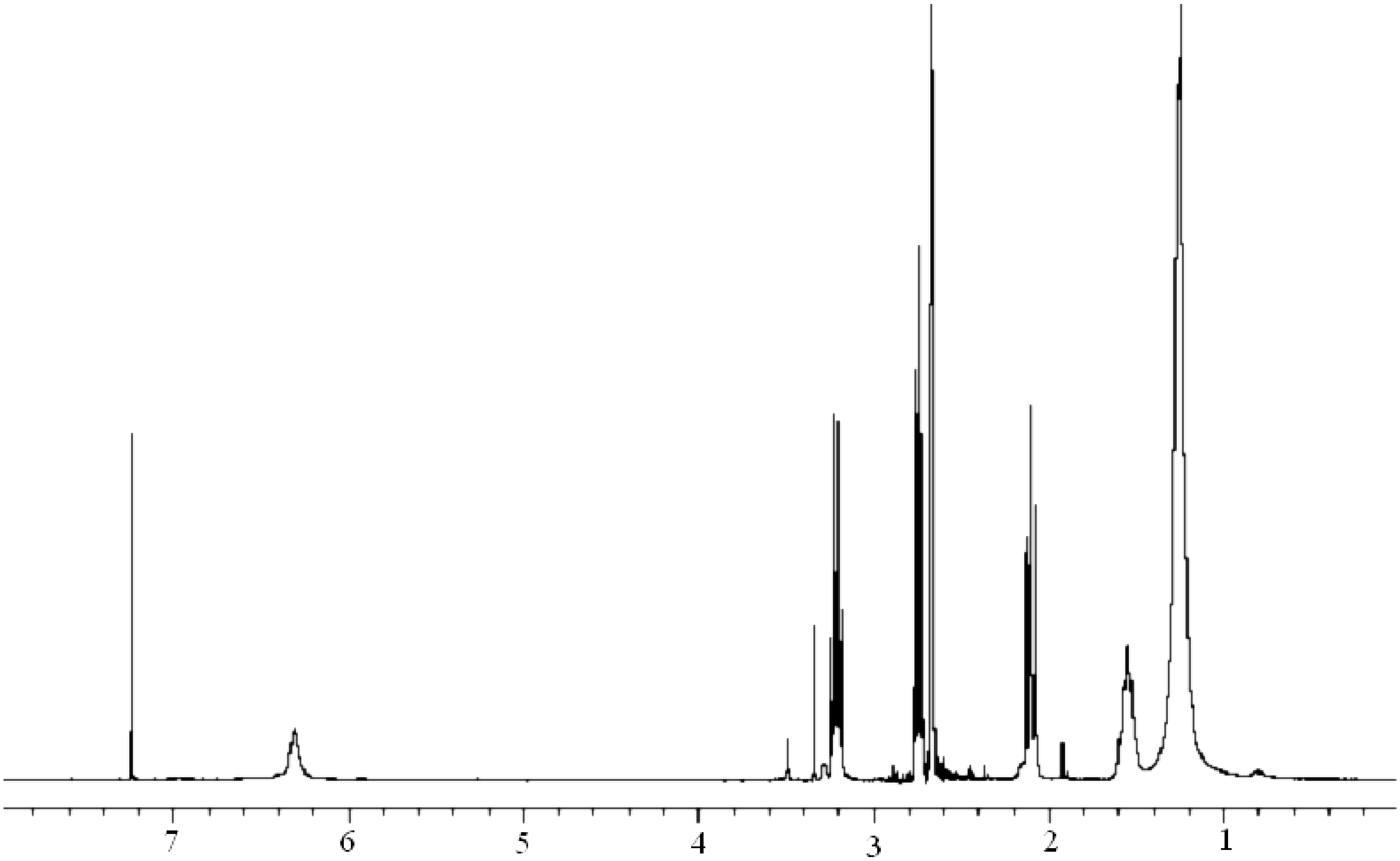


Figure B.2 ^{1}H NMR spectrum of amidation product

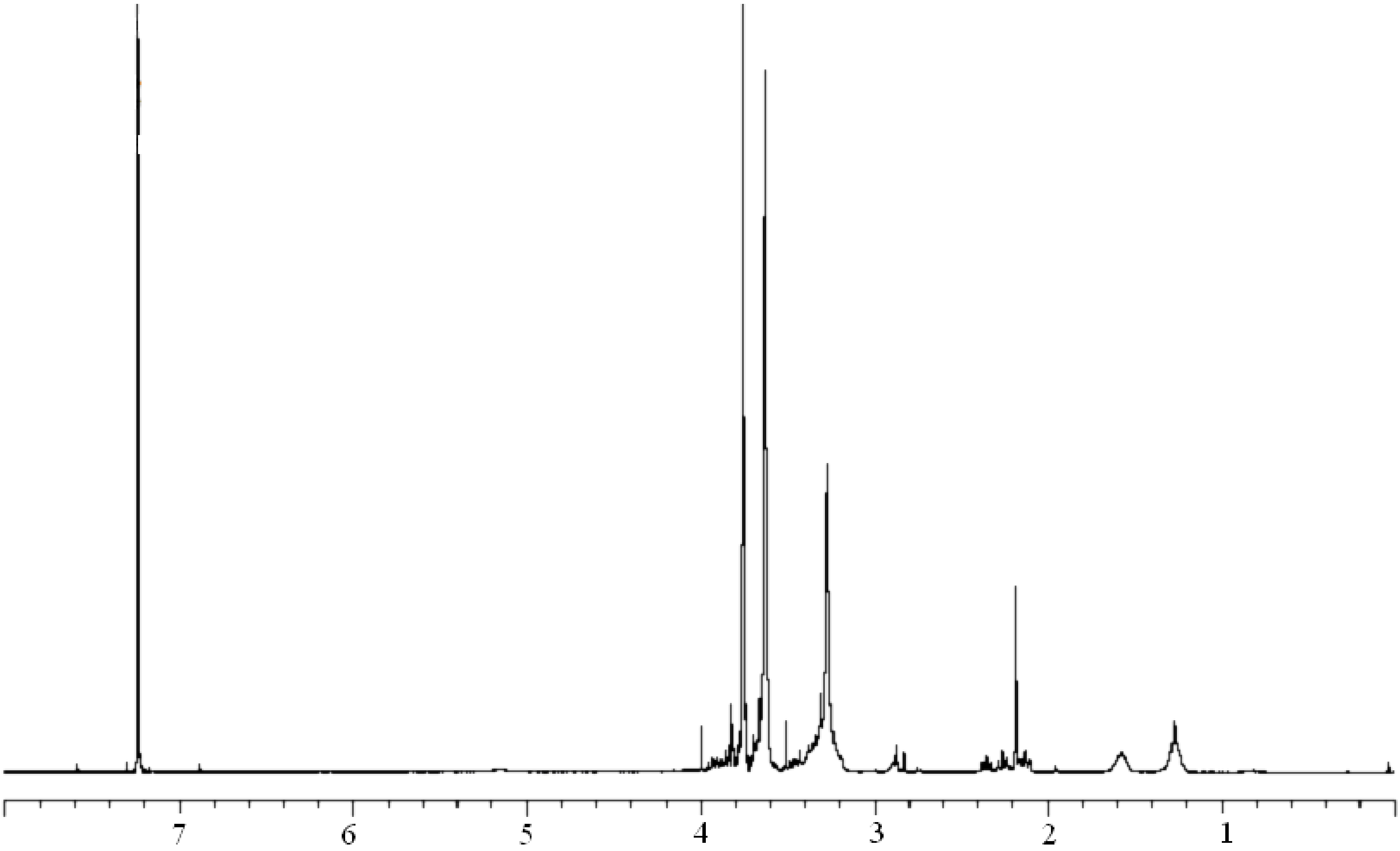


Figure B.3 ^{1}H NMR spectrum of carbamate

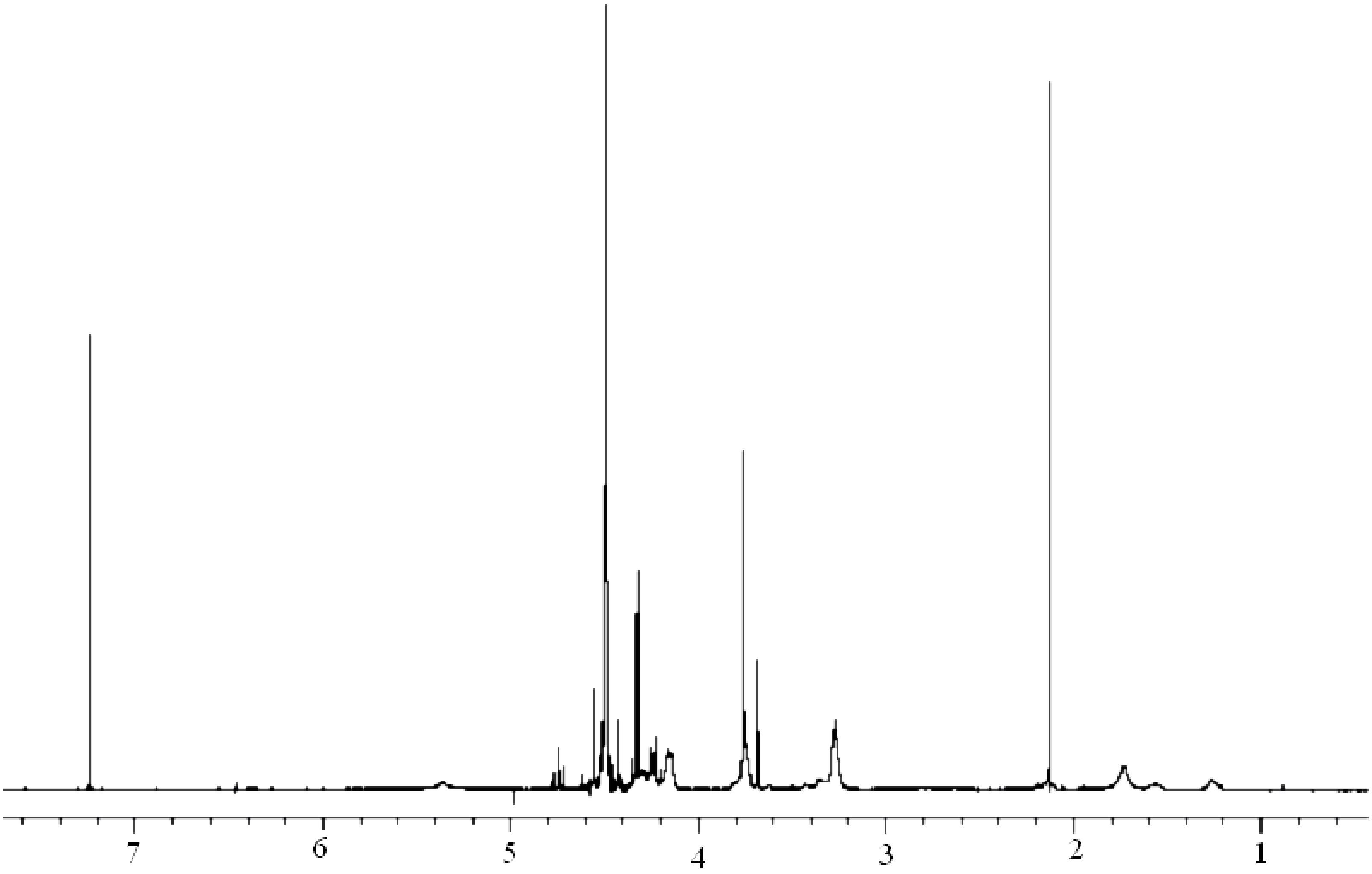


Figure B.4 ^{1}H NMR spectrum of polyurethane from carbamate

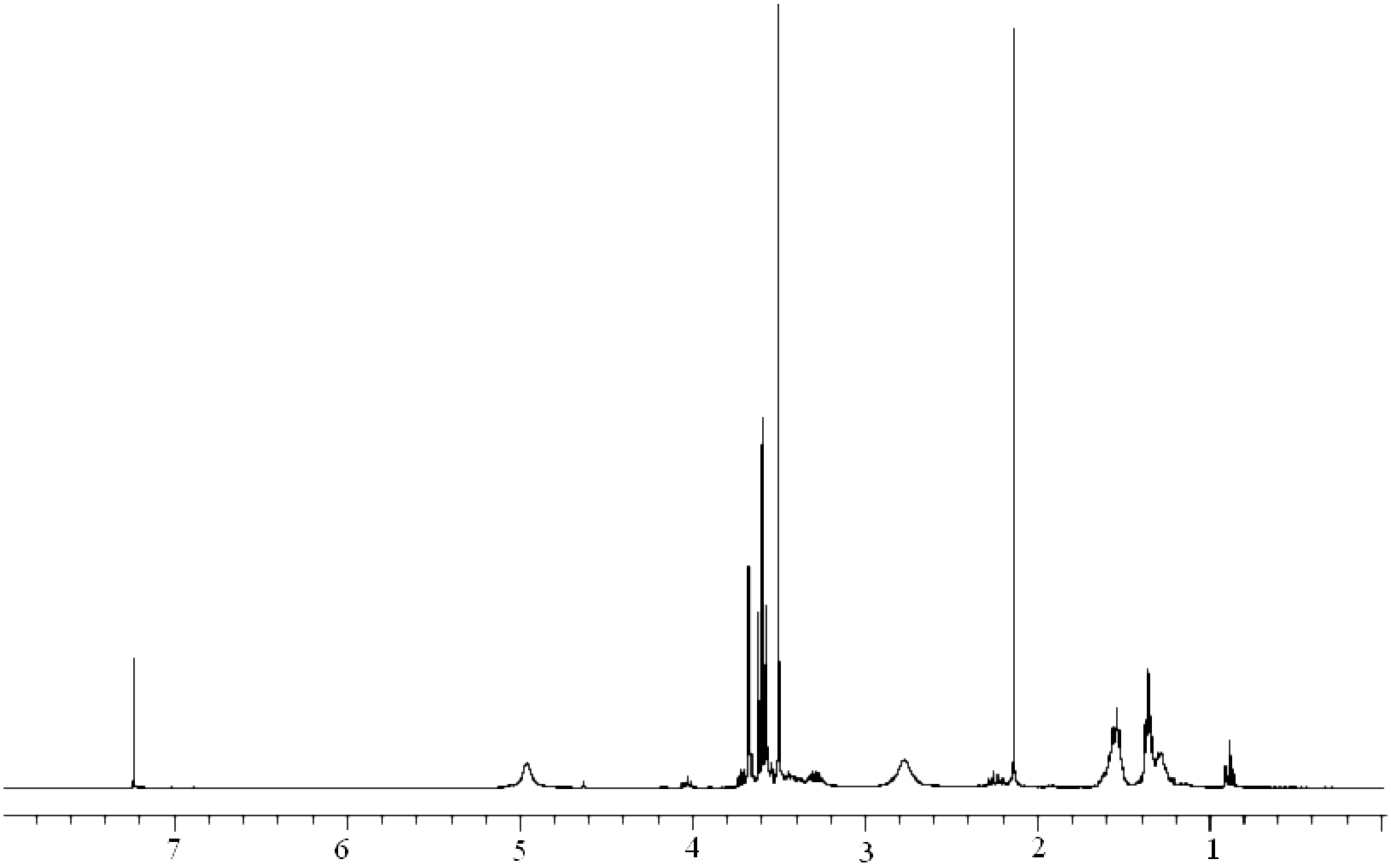
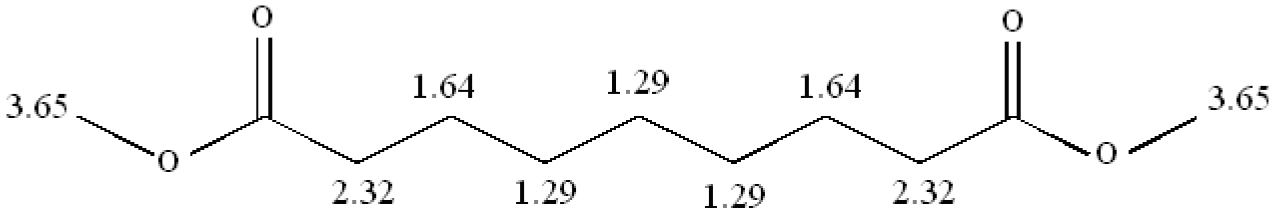


Figure B.5 ^{1}H NMR spectrum of polyurethane synthesized with ethylene carbonate



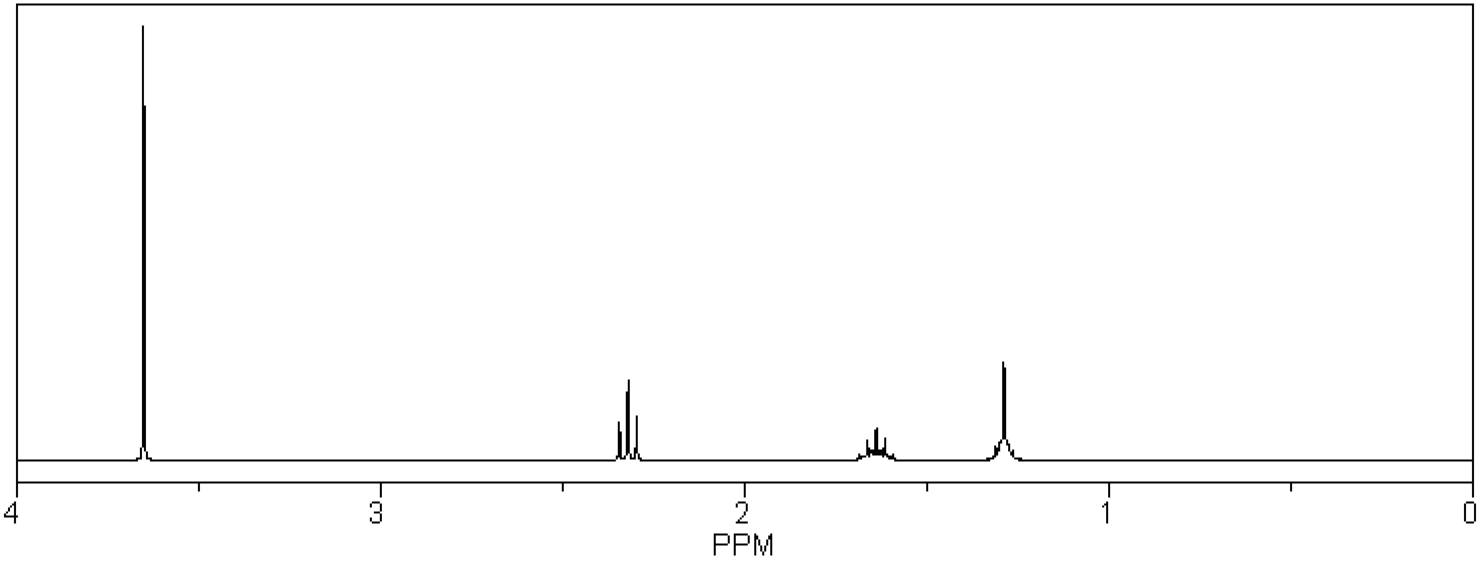


Figure B.6 ^{1}H NMR spectrum of dimethyl azelate prediction

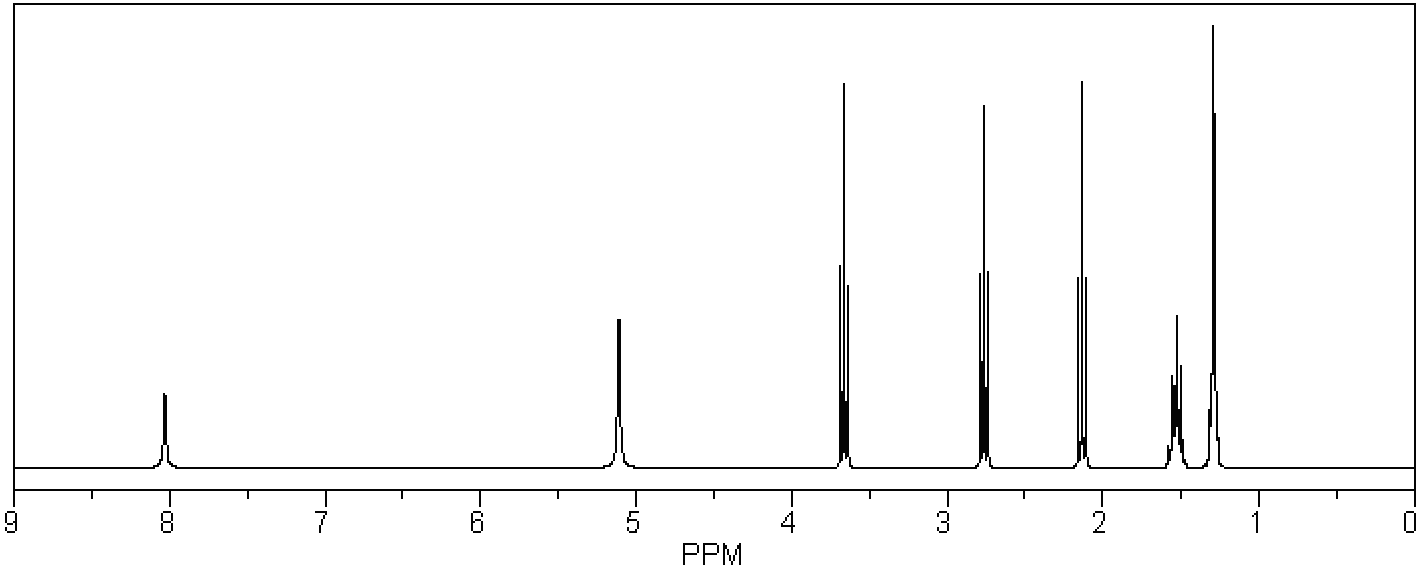


Figure B.7 ^{1}H NMR spectrum prediction of amidated dimethyl azelate

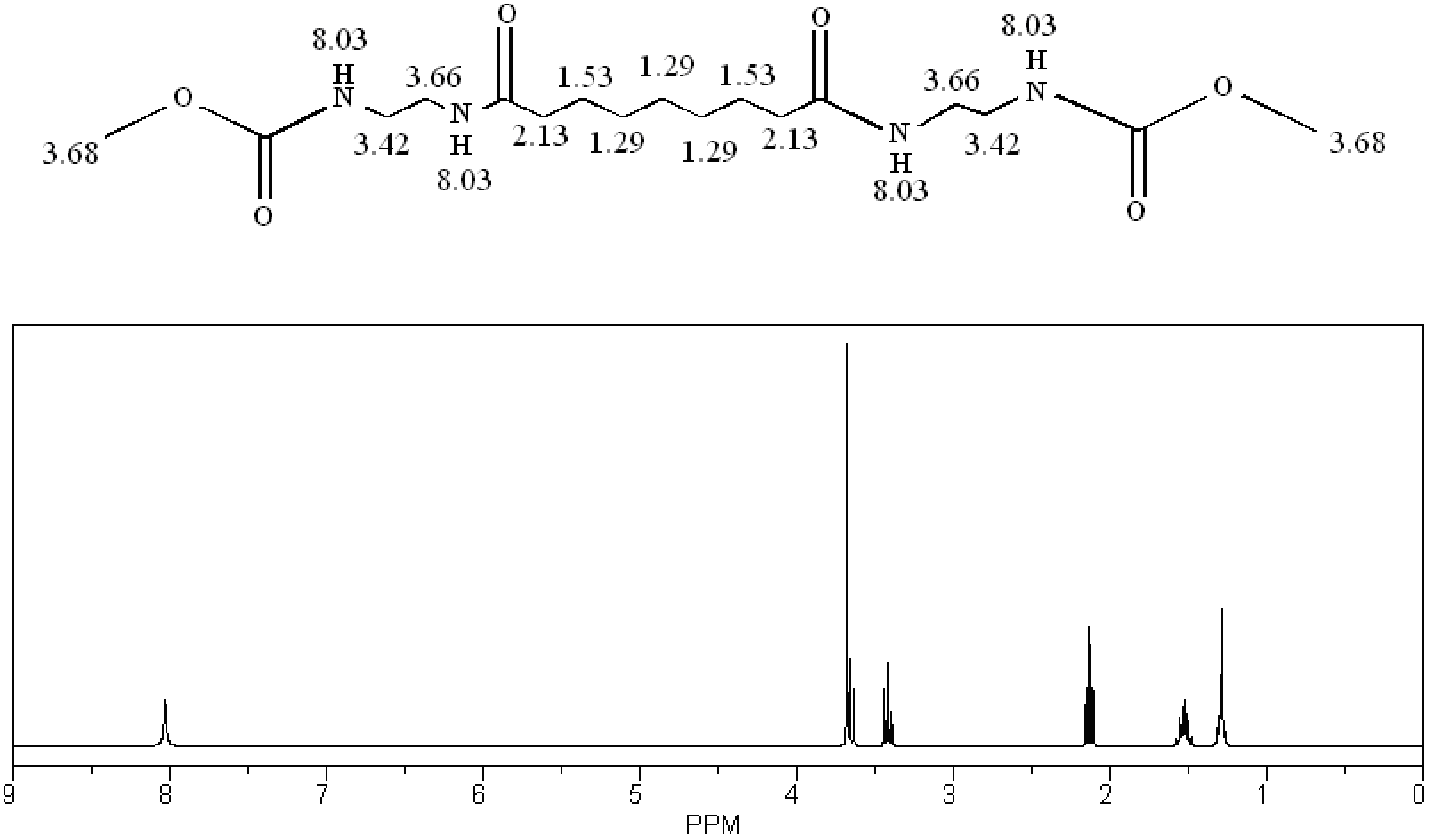


Figure B.8 ^{1}H NMR spectrum prediction of carbamate

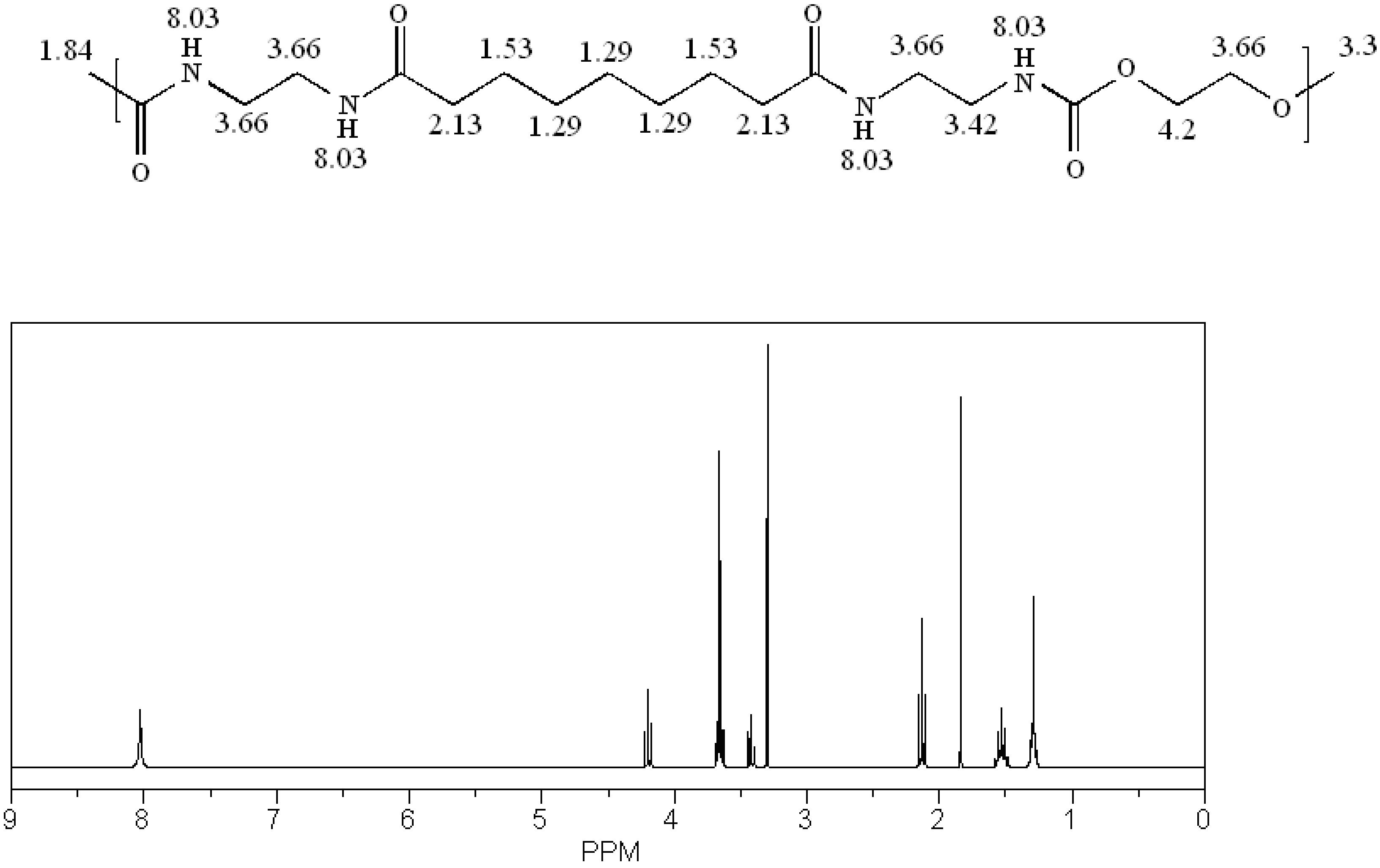


Figure B.9 ^{1}H NMR prediction spectrum of polyurethane

APPENDIX C

CHARACTERIZATION TECHNIQUES

This section describes the background to techniques used to analyze the end products quantitatively and qualitatively in this thesis experimentation. Unless specified, the details discussed in this section are applicable for all the analyses conducted.

C.1 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR, a single beam system, is a common analytical technique, which utilizes infrared (IR) radiation to determine the different functional groups in each compound. IR radiation falls between wavelengths of 0.78-40 μm.[1] When the IR radiation contacts molecules, the functional chemical group absorbs the radiation and produces a unique vibration mode (stretch, bend and contract). The intensity of absorption is detected by infrared spectroscopy. The spectrum produced from this method gives unique absorption results. The correlation between the wavelength positions of chemical compounds can be used to identify functional group content. A major advantage of FTIR is the possibility of multiple scans of the sample to increase the signal to noise ratio (S/N).[1] All the spectra provided in this thesis were scanned with 16 scans.

Attenuated total reflection (ATR) was used for analysis of all the spectra provided in this thesis. ATR-IR utilizes a high refractive index crystal, which allows IR absorption measurement of non-transparent materials. Good contact with the top surface of the ATR crystal and the sample allows the infrared penetration into the sample and reflection within the crystal several times.

C.2 Hydroxyl Value

Hydroxyl value is an important characteristic of polyols that is expressed as milligram (mg) of potassium hydroxide (KOH) per one gram of sample.[2] This number represents the amount of terminal hydroxyl groups available per gram of polyol, which is required to determine the amount of isocyanate needed in order to adjust the molecular weight of the polyurethane formed. A titrimetric method based on ASTM standard D1957 was used to determine this value.[3] The hydroxyl group is reacted with an organic anhydride, such as acetic anhydride to form acetic acid. The unreacted anhydride is hydrolyzed with water at the end of the reaction and the acetic acid produced is neutralized by a known normality of potassium hydroxide. The detailed reaction can be seen in Figure C.1 below.

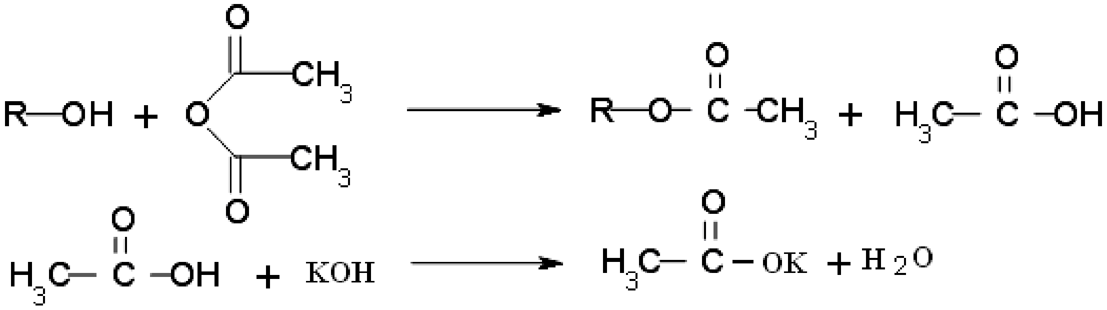


Figure C.1 Hydroxyl Value Reactions

The volume of potassium hydroxide needed to neutralize the mixture can be calculated as the hydroxyl group content of each compound. Free acid present in the sample will also produce some hydroxyl number during the titration, but can be corrected during the calculation of the final hydroxyl number. A blank is also prepared to measure the amount of KOH required without any sample present. The titrations were conducted potentiometrically due to the dark color of the product solution after acetylation. The formula used for hydroxyl value (H.V.) calculation can be seen in C-1 below, where B is the KOH needed to titrate the blank (ml), S is the sample used for hydroxyl titration (g), A is the KOH needed for acid value titration (ml), C is the sample used for acid value titration (g), V is the KOH needed for hydroxyl sample titration (ml) and N is the normality of the KOH used for both acid and hydroxyl value titrations.

$$H.V. = \frac{B + (\frac{SA}{C}) - V}{S} \times N \times 56.1 \qquad \text{C-1}$$

C.3 Acid Value

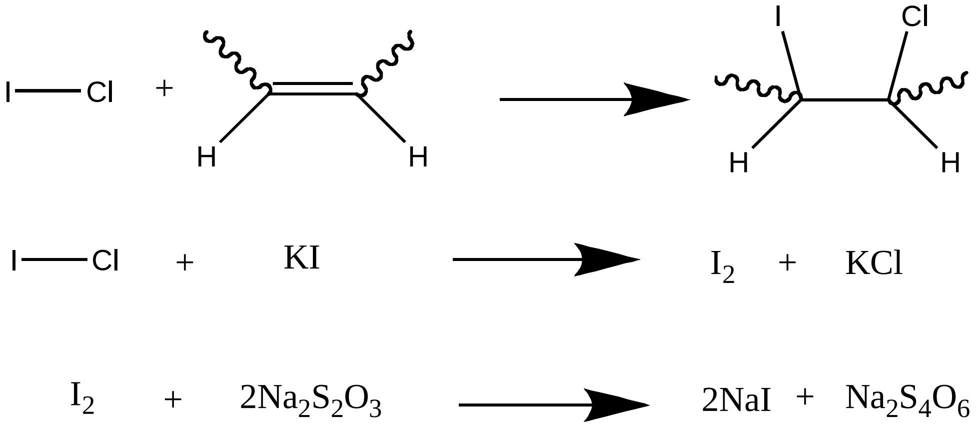
This method is used to measure the amount of free acid in the sample. Acid value is defined as the amount of potassium hydroxide (KOH) in milligrams required to neutralize the acidity of one gram of sample.[4] The sample is dissolved and titrated with potassium hydroxide solution. Phenolphthalein is used as the end-point indicator. The solution of 0.1N KOH was used for this color titration, to achieve a more precise end point. The formula to calculate acid value (A.V) can be seen in C-2 below, where S is the volume of KOH needed for titration of the specimen (ml), B is the volume of KOH needed for titration of the blank (ml), N is the normality of the KOH used, and W is the specimen weight (g).

$$A.V. = \frac{(S - B) \times N \times 56.1}{W} \qquad \text{C-2}$$

Acid value also is used as a correction factor in determining the hydroxyl value. Reactivity, shelf life, and hydrolytic stability of polyols can be affected by the acid value.[5]

C.4 Iodine value

The iodine value method is used to determine the degree of unsaturation, which represent the carbon-carbon double bond content. The iodine value is defined as centigrams of iodine (I_2) per gram of sample.[6] The preferred solvent is carbon tetrachloride (CCl_4); however its toxicity and carcinogenicity have led to substitution with cyclohexane. The sample is dissolved in cyclohexane, then mixed with iodine monochloride (ICl) solution (Wijs Solution). The Wijs solution is light, temperature and moisture sensitive. Therefore titration of the sample and the blank has to be done at the same conditions, and relatively at the same time. Transfer of reagent to the sample flask should be done away from bright light and away from the heat source. After addition of the reagent, the solutions are kept in the dark for one hour for the reaction to take place. The potassium iodide solutions are added after one hour of reaction, and then the solutions are titrated with sodium thiosulfate ($Na_2S_2O_3$). The reaction of iodine value titration can be seen in Figure C.2 below.



$$I-Cl + KI \longrightarrow I_2 + KCl$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

Figure C.2 Iodine Value Titration Reaction

The iodine (I_2) is produced by reaction of potassium iodide and unreacted Wijs solution. Therefore, a blank solution is required to determine the Wijs solution reaction with the specimen tested. The formula used to calculate iodine value (I.V.) can be seen in C-3 below, where B is the sodium thiosulfate required for blank titration (ml), V is the sodium thiosulfate required for the specimen titration (ml), N is the normality of the sodium thiosulfate, and S is the weight of the specimen used (g).

$$I.V. = \frac{(B - V) \times N \times 12.69}{S} \qquad \text{C-3}$$

C.5 Amine Value

In a substance there are three amine possibilities: primary, secondary and tertiary amines. The total amine value is the number of milligrams of potassium hydroxide equivalent to the total basicity in one gram of sample.[7] The method involves dissolving the sample in isopropyl alcohol and titrating against standardized hydrochloric acid (HCl) solution. Bromophenol blue indicator solution is used to determine the end point. The formula used to calculate the total amine value can be seen in C-4, where V is the HCl required to titrate the specimen (ml), N is the normality of the HCl used, and S is the weight of the specimen used (g).

$$\text{Total amine value } = \frac{V \times N \times 56.1}{S} \qquad \text{C-4}$$

C.6 Saponification Value

The saponification value is the amount of alkali required to saponify 1 gram of sample, this number is expressed as miligrams of potassium hydroxide per gram of sample.[8] The ester content in this reaction is hydrolyzed with known KOH solution, and the excess of KOH is then back-titrated with standardized sulfuric acid or hydrochloric acid. Hydrochloric acid was used to measure the saponification value in this thesis analysis. A blank is required in this method to know the acid required to neutralize the original KOH solution before reaction with any sample. This number will be used to calculate the KOH consumed during the saponification reaction. The reaction of this saponification value titration can be seen below (Figure C.3)

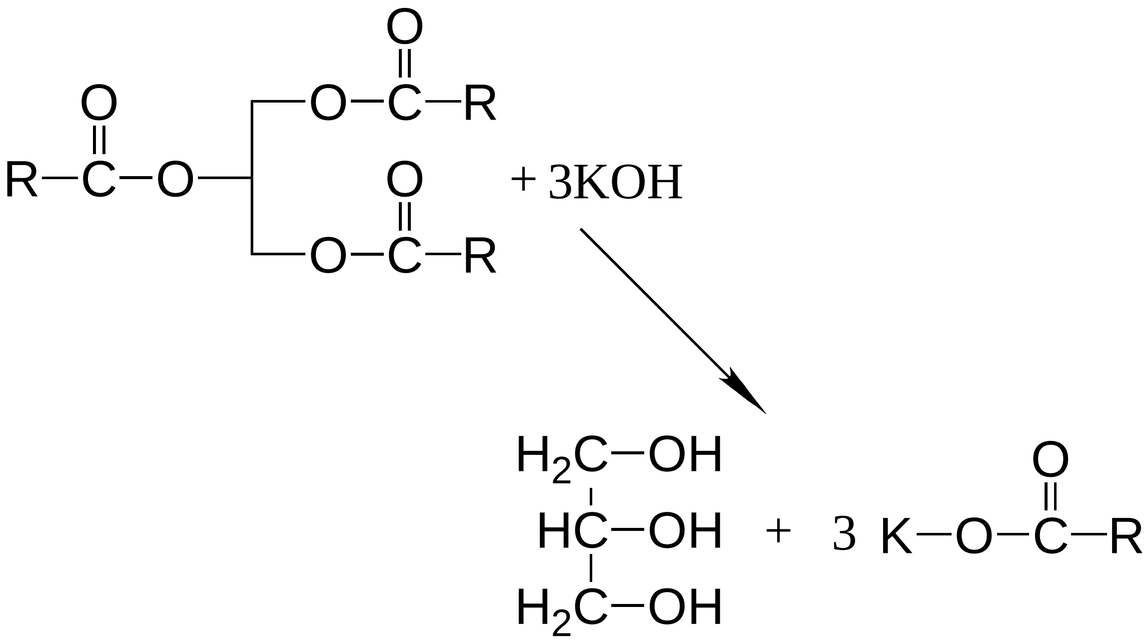


Figure C.3 Saponification reaction

The hydrolysis reaction goes to completion. One alkali is required for each equivalent ester. Therefore this method can be used to quantitatively measure the ester content. Saponification value (S.V) is calculated with the formula in C-5, where B is the HCl required to titrate the blank (ml), V is the HCl required to titrate the specimen, N is the normality of the HCl used and S is the weight of the specimen (g).

$$S.V. = \frac{(B-V)\times N}{S} \times 56.1 \qquad \text{C-5}$$

C.7 Gas Chromatography (GC)

Gas chromatography (GC) is a chromatography method used to separate a mixture of volatile compounds into its components.[1] The separation occurs inside a chromatography column that is filled with packing material (the stationary phase). The moving phase, which carries the compounds to be analyzed, is gas in this type of chromatography. Inert gas is usually used to avoid interaction with the stationary phase and the sample. Helium is used in the GC that was used to analyze samples in this project work.

The dilute sample is injected into the gas stream. It is vaporized immediately after injection. The vapor is then carried by the carrier gas (mobile phase) to be separated. After the separation process, the components are detected by a detector system. Different compounds will have specific retention times, thus enabling compound identification. The retention time of a particular compound is dependent on the column, the mobile phase flow rate and the heating rate. Therefore, a constant gas flow rate is important in order to obtain a constant retention time.[1]

Gas chromatography can be used as both a qualitative and a quantitative analysis method. Qualitatively GC can detect what components or impurities are present in an unidentified substance. Quantitatively, the area under the peak is proportional to the molecular concentration present. GC can also be paired with mass spectrometry (MS) or FTIR in order to enable direct identification.

C.8 Nuclear Magnetic Resonance (NMR) Spectroscopy

Nuclear magnetic resonance (NMR) is a powerful analytical method that can be used to determine molecular structure.[1] Magnetic nuclei that can be measured with NMR are hydrogen (^{1}H), fluorine-19 (^{19}F), phosphorus-31 (^{31}P), and carbon-13 (^{13}C) isotopes. Proton and carbon-13 NMR were used mainly in this thesis. Hydrogen atom is present as ^{1}H (proton NMR) and ^{2}H (deuterium NMR) in NMR spectrometers. Deuterium molecules are known as lock substances that are very stable and mostly used as solvents.[9] The common solvents that are used in NMR analyses are deuterated chloroform ($CDCl_3$), water (D_2O), Dimethyl Sulfoxide-d_6, tetrahydrofuran-d_8, and acetone-d_6, which all contain deuterium (^2H). The signal that shows in NMR spectra depends on the strength of external magnetic field and radiofrequency (RF) radiation. The interaction between RF radiation and nuclei causes absorptions that re-radiate during the acquisition time and generate an NMR signal.[1] All signals gathered from NMR are assigned to the corresponding protons. A prediction program (ChemDraw) is used to help with this proton assignment. Quantitative analysis can be done with NMR. The intensity of NMR resonance (area under the curve) is proportional to the molar concentration of sample.

The NMR spectra for carbon-13 can be done with compounds that contain methyl, methylene, methane and quarternary carbon.[9] The most common carbon isotope is ^{12}C that has no spin, and ^{13}C is only present at about 1.1% of total carbon. Therefore a higher concentration of sample is required to get the NMR spectra compared to proton NMR. One of the differences of carbon NMR compared to proton NMR is that the carbon NMR signal is not proportional to the number of atoms.

C.9 Differential Scanning Calorimetry (DSC)

DSC is a thermal analysis instrument that measures the amount of heat the sample absorbs under isothermal conditions. DSC provides important information on the properties of the polymer tested, such as degree of crystallinity, glass transition temperature (T_g), melting temperature (T_m), and cystallization temperature (T_c).[1] DSC uses of two pans, a reference pan and a sample pan; both pans are heated at the same rate. Aluminum pans were used for both sample and reference pans. The amount of heat absorbed by the sample pan is compared to the reference pan, and a graph of heat flow vs. temperature is generated from the process. The response can be endothermic or exothermic. The changes in heat flow provide information about physical and chemical changes during the heating process.

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