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PREPARATION AND COPOLYMERIZATION OF SOYBEAN
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Major Professor's Signature

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PREPARATION AND COPOLYMERIZATION OF SOYBEAN OIL BASED MONOMERS

By

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ABSTRACT

PREPARATION AND COPOLYMERIZATION OF SOYBEAN OIL BASED MONOMERS

By

Samantha K. Friedlander

Society is pushing for a reduction in the use of petroleum-based materials. Soybean oil is a renewable, readily available, inexpensive resource that can be used in the production of novel polymers. By using allyl alcohol in the transesterification of soybean oil or fatty acid methyl ester (FAME) a terminal double bond can be added to the fatty acid chain. The methods for the conversion of soybean oil and FAME were investigated. The equilibrium kinetics for the transesterification of soybean oil was also determined. The terminal double bond that was added is then polymerized via free radical polymerization. A copolymer of the fatty acid allyl ester with styrene was produced with a random monomer configuration. A maximum of 30% ester was incorporated into the polymer.

ACKNOWLEDGMENTS

I would first like to thank my family for all of their support and help. My parents have had to listen to all of my exciting breakthroughs and all of the times when things didn't work out quite the way they were supposed to. My grandparents and aunt have been supportive of all of my endeavors, especially this one.

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CHAPTER 1

BACKGROUND

1.1 Why use alternative fuels?

The world has a dependence on fossil fuels; they are used in all of our daily activities; from driving a car to turning on the lights, most of the power that we use comes from a fossil fuel. The world used approximately 469.4 quadrillion BTU in 2006.[1] The energy use trend for the world and the top two energy-consuming nations, as of 2008, can be seen in figure 1.

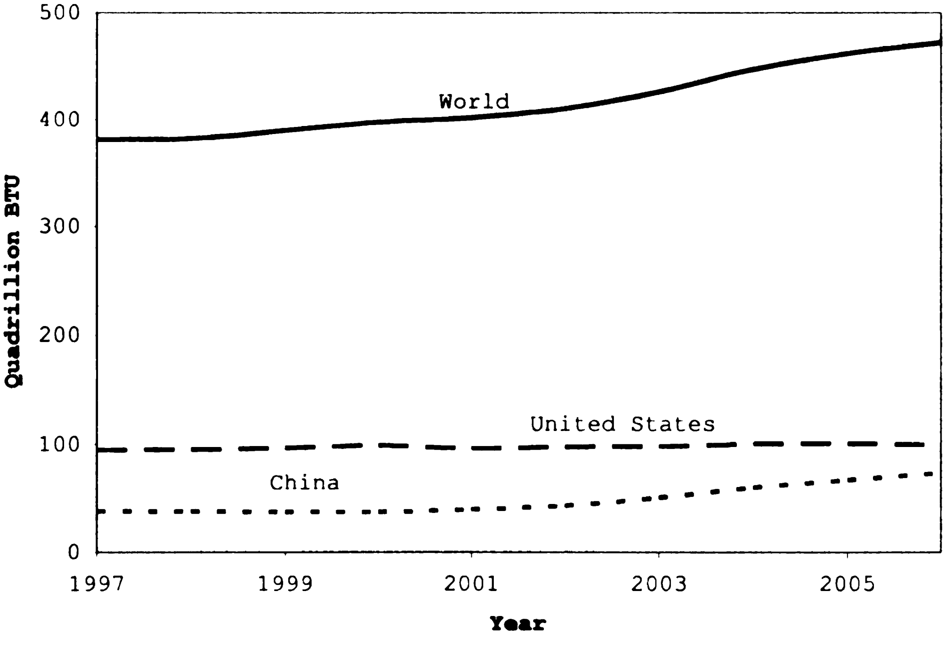


Figure 1: World Energy Consumption and Top Energy Consumers 1997-2006[1]

Although the United States energy use has remained relatively constant in the past decade, most of the energy was supplied by fossil fuels. Of the total energy used in 2008, approximately 7% was produced from renewable resources, and more than 80% was produced from fossil fuels, the remaining being from nuclear energy.[1]

There are four main sectors for energy use; transportation being the second major use of energy in the United States (the first is industrial usage), but only 3% of these fuels were from renewable resources (in 2008). The two main sources for renewable transportation fuel are ethanol and biodiesel.[1] So why use a renewable resource? There are many reasons for one to use an alternative fuel, such as biodiesel over the conventional petroleum diesel. One reason is for the reduction of our carbon footprint. The EPA's definition of a carbon footprint is "the amount of greenhouse gasses (GHG) that are emitted by one entity, such as a person…or company[2])." A measurement of one's carbon footprint will include both direct sources (such as driving a car) and indirect sources (a consequence of an activity, such as, purchasing electricity) and is reported in units of CO_2.[2] By using a renewable fuel like biodiesel, one's carbon footprint is reduced because the carbon is newly fixed carbon (soybeans for example) as opposed to carbon that was fixed millions of years ago (any fossil fuel).

Reducing GHG emissions is very important to the ecosystem; it is believed to be the cause of recent climate change. It's true that GHG's are important for life on Earth, as they keep the planet warmer than it would be without them. However, the massive influx of GHG's into the atmosphere is the cause of a rise in global temperature.[3] This rise in temperature is causing damage to the ecosystem, rising sea levels due to melting of ice caps and a change in rainfall patterns across the globe are just two examples of these effects.

A second and sometimes a more popular opinion for the conversion to biodiesel and other renewable resources is a reduction or elimination of the dependence on foreign oil. As seen in figure 2, the United States imports over half of the oil that is used in this country.[4] This dependence will only increase as the oil in this country is depleted.[4] It is also seen in figure 2, that the U.S. production of oil is decreasing every year.

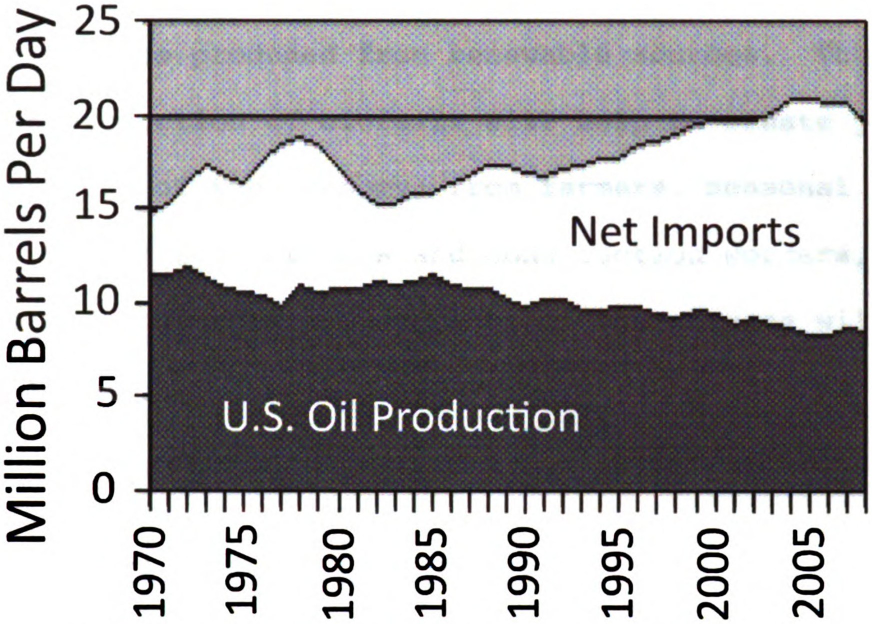


Figure 2: U.S. Petroleum Use 1970-2008[4]

As the need for oil grows, the dependence on foreign countries also grows. Of the top five oil producing countries (Saudi Arabia, Russia, United States, Iran and China) only two of the countries have the top proven oil reserves (Saudi Arabia, Canada, Iran, Iraq, Kuwait).[5] Unfortunately some of these oil rich countries have a history of political unrest and disagreements with the United States. If the United States can create a sustainable fuel source contained within its borders, it will not have to rely on other countries.

With the quest for a sustainable fuel, and the passage of the Energy Independence and Securities Act of 2007(EISA) another advantageous side effect can be found the creation of green jobs. The EISA requires that 36 billion gallons of motor fuel be produced from renewable sources. The increased production of biofuels will help to create jobs in all sectors of the economy; from farmers, seasonal workers, train/truck drivers and construction workers, to chemists and engineers all segments of the process will need employees.[6]

1.2 Biodiesel, what it is and how it is made

The term "biodiesel" was first used in a Chinese paper in 1988; however it was not used again until 1991.[7] Biodiesel refers to the fatty acid methyl esters produced from the transesterification of vegetable oils and animal fats (more specifically the triglycerides) and are also known as FAMEs. This reaction is shown in figure 3.

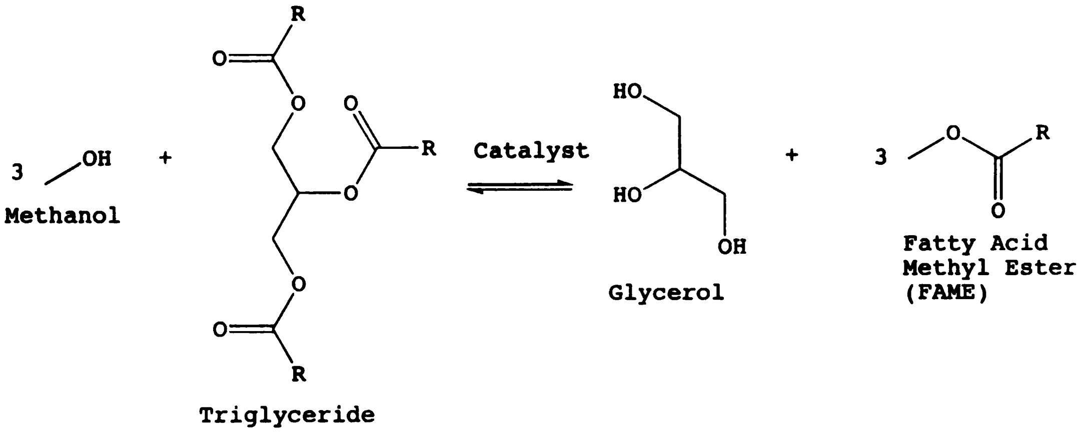


Figure 3: Transesterification of Triglyceride to FAMEs

The major chemical component in the oils produced from plant material and animal fats are triglycerides. Over 170 plants can be used for the production of biodiesel, the main plant oil used in the U.S. is soybean oil.[8]

A triglyceride, as seen in figure 4, consists of "3 fatty acid chains joined at a glycerol juncture"[9] (the glycerol shown in bold). The "R" on the fatty acid component of the triglyceride is a carbon chain containing 14 to 22 carbons and can contain 0 to 5 double bonds (depending on the source of the triglyceride)[10] Figure 5 shows the five esters found in soybean oil.

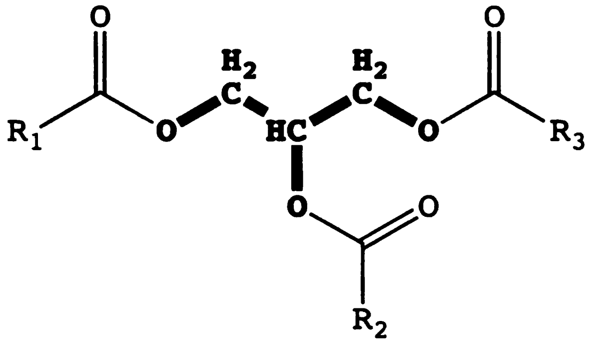


Figure 4: Triglyceride Components

In a typical triglyceride, the fatty acids contribute 94-96% of the total weight of the triglyceride.[11] The chemical and physical properties of the oil depend on the stereochemistry of the double bonds, the degree of unsaturation and the length of the chains.[12]

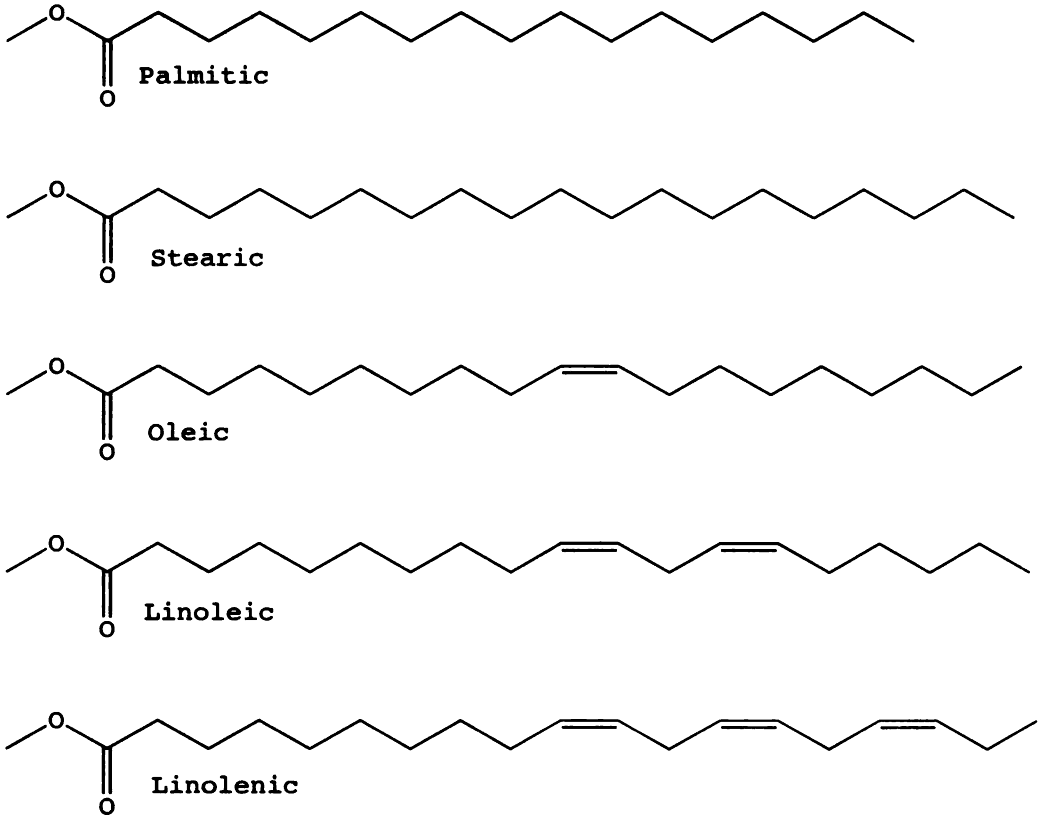


Figure 5: Fatty Acids in Soybean Oil After Transesterificaton

Longer carbon chains are found in the temperate crops (sunflower, soybean, and rapeseed oils) while shorter fatty acid chains are found in the tropical crops, such as coconut and palm oils.[13] The average degree of unsaturation (number of carbon-carbon double bonds) in the triglycerides can be characterized by the iodine value. This is the amount of iodine, in mg, that reacts with the double bonds in a 100g sample. There are three classifications of oils, drying oils (iodine value>130), semi-drying oils (100<

iodine value >130) and non-drying oils (iodine value <100).[11-13]

The total distribution of the fatty acids varies between types of crops and within each crop. Theses differences are based on growing conditions, season and purification.[11] Genetic engineering can be used to control the variation within each crop.[9]

The production of biodiesel begins with the production of soybean oil. The soybean (Glycine Max (L.) Merril) seed consists of 2 cotyledons, a seed hull and the hypocotyl or germ. The cotyledons make up 90% of the seed, and contain essentially all of the protein and oil.[14] This can be seen in table 1 along with the composition of each element of the seed.[14, 15]

Components	Yield (%)	Protein (%)	Lipid (%)	Ash (%)	Carbohydrates (%)
Cotyledon	90.3	42.8	22.8	5.0	29.4
Hull	7.3	8.8	1.0	4.3	85.9
Hypocotyl	2.4	40.8	11.4	4.4	43.4
Whole Soybean	100.0	40.3	21.0	4.9	33.9

Table 1: Composition of a Soybean Seed[14]

Given that the interest is in the oil and not the meal, a general overview of the oil extraction process will be discussed; the refining of the crude oil will be in more detail. After harvesting the soybean seeds, the production plant has two options for extraction of the oil; mechanical extraction and solvent extraction. In both processes the soybeans are dried, cleaned and flaked prior to extraction. In mechanical operations the flaked soybeans are fed into a screw press to squeeze out the oil.[14, 15] Less than 1% of the soybeans are processed by mechanical means,[14] due to the 4-5% oil left in the soy meal after extraction.[14, 15] In solvent extraction, the oil is extracted from the flaked seeds using hexane. The oil leaves the flakes and is dissolved in the hexane. After extraction the hexane is removed from the oil by flash evaporation, vacuum distillation or steam stripping.[14, 15] The crude oil then has the properties seen in table 2.

	Crude Oil (%)	Refined Oil (%)
Triglycerides	95-97	0.99
Phospholipids	1.5-2.5	0.003-0.045
Unsaponifibles	1.6	0.3
Free Fatty Acids	0.3-0.7	<0.05

Table 2: Composition of Crude and Refined Soybean Oil[14]

There are four steps to the refining of soybean oil, degumming, removal of free fatty acids, bleaching and deodorization. The degumming stage of the process removes the phospholipids and is generally carried out in the extraction plant. A dilute phosphoric acid solution is mixed with the oil to form gums; these gums then precipitate and are removed by centrifugation. By removing the phospholipids first a reduction in the oil loss is seen in the following phases. The oil free phospholipids are cleaned and sold as a byproduct known as soybean lecithin.[14, 15]

There are two methods for the removal of free fatty acids, a chemical and a physical process. The chemical process involves neutralization with an alkali to form a soap that is soluble in water. This soap stock is removed in a centrifuge and the oil is washed and dried and ready for the next step. In physical refining, the fatty acids are removed by steam distillation (this process also achieves deodorization).[14, 15]

Bleaching and deodorization are two relatively simple processes. Activated carbon is added to remove most of the carotenoid pigments and chlorophyll in the oil. The carbon is then removed by filtration and the oil is deodorized by steam distillation under high vacuum and temperature. The final composition of the processed oil is shown in table 2. 14, 15

The production of biodiesel can begin using crude, degummed, or completely refined oil, although the processing changes slightly. The biodiesel reaction, seen previously in figure 3 is a catalyzed reaction. The catalyst can be an acid, base or an enzyme (lipase catalyzed). In industry, the base reaction is primarily used; this is due to the slow reaction speed of both the acid and enzyme catalyst (as well as the cost of the enzyme).[16, 17, 18] The base reaction is 4000 times faster than the acid reaction (when using the same amount of catalyst).[18]

The three main factors that affect the yield of the production of biodiesel are the time, temperature and amount of mixing. Given enough time the reaction will go to completion at room temperature.[18] This time, however, is to long to make large scale production efficient. Murugesan et al found that the most efficient reaction temperature was between 60°C and 80°C, higher and lower temperatures will give a lower yield. They also found that a mixing speed of 360 rpm gives the best yield, any higher mixing speed produces no increase in yield, although a lower speed will decrease yield.[18]

There are two methods that can be used in the production of biodiesel in industry (batch and continuous operations).[17] In the batch reactor the residence times are longer, usually 20 minutes to 1 hour. The continuous operation is a series of plug flow reactors, with a separator between each tank to remove the glycerol that is produced in each tank to drive the reaction foreword.[17] The residence time in each reactor is 6-10 minutes.

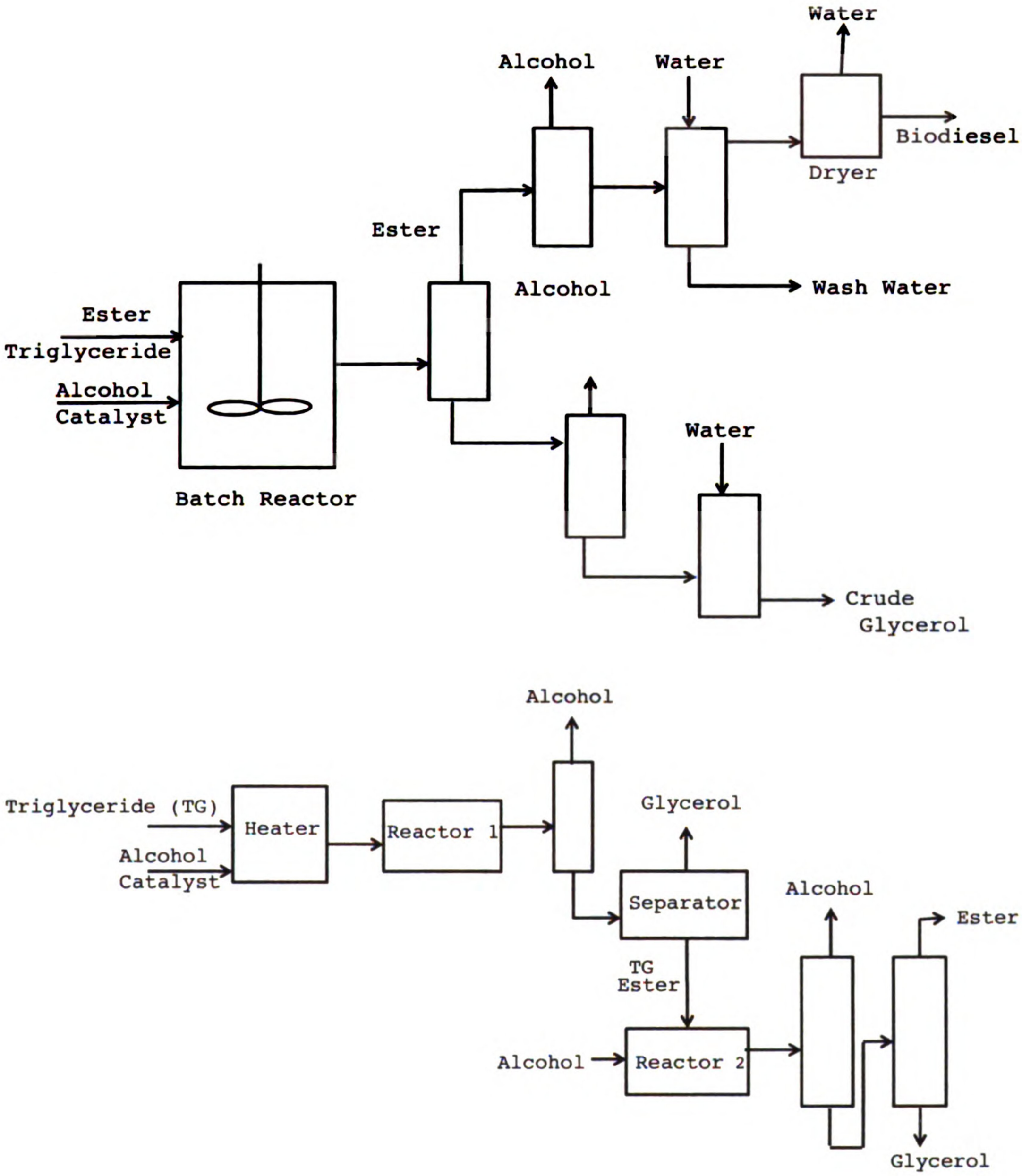


Figure 6: Process Flow Diagrams for Batch (Top) and Continuous (Bottom) Biodiesel Production[17]

After both the continuous and batch reaction the glycerol and excess alcohol are removed and the base is neutralized. A flow diagram of both the batch and continuous processes are seen in figure 6.

The carbon chains produced from transesterification are chemically similar to the ones found in petroleum diesel (which are 10-15 carbon atom chains)[19] and only have 10% less energy than petroleum diesel.[20] As previously stated there are many other oils that can be used for the production of biodiesel, table 3 shows the composition of soy oil as well as other oils with similar composition.

Vegetable Oil	14:0	16:0	18:0	18:1	18:2	18:3	22:1
Sunflower	--	3.5-7.6	1.3-6.5	14-43	44-74	--	--
Soybean	--	2.3-13.3	2.4-6	17.7-30.8	49-57.1	2-10.5	--
Cottonseed	.6-1.5	21.3-26.4	2.1-5	14.7-21.7	46.7-58.2	--	--
Rapeseed	0-1.5	1-6	.5-3.5	8-60	9.5-23	1-13	5-56
Canola	--	1.2-6	1-2.5	52-66.9	16.1-31	6.4-14.1	--
Corn	0-.3	7-16.5	1-3.3	20-43	39-62.5	.5-13.5	--
Peanut	0-.5	6-14	1.9-6	36.4-67.1	13-43	--	--

Table 3:Composistion of Soybean Oil and Similar Oils[16]

The two major differences between conventional diesel and biodiesel are the internal double bonds and the oxygen atoms found in the biodiesel chains. Petroleum diesel is strictly straight chain and single bonds.[19] These two differences produce advantages and disadvantages for the biodiesel over the conventional diesel.

The oxygen in biodiesel leads to more complete combustion, and therefore lower carbon monoxide and particulate emissions. Being a bio-based fuel, its biodegradation is faster than that of conventional diesel and it also has higher lubricity and flash point.[19] There is an increase in nitrogen oxide (NO_x) emissions in biodiesel due to a higher combustion temperature.[19] The second difference, the internal double bonds in the biodiesel, leads to a higher oxidation rate.[19]

Although there are many advantages of biodiesel over conventional diesel, one of the main limitations for using biodiesel is the high cloud point and pour point temperature associated with biodiesel.[19, 21, 24-28]

1.3 Cloud Point and Pour Point of Biodiesel

As previously mentioned one important concern with the adoption of biodiesel into wide use is its high cloud point (CP) and pour point (PP). This makes the use of biodiesel difficult during the winter months in many states. The ASTM definition for CP is "the temperature at which the smallest observable cluster of wax crystals appears upon cooling[22]." This temperature is different from the PP due to the fact that the biodiesel can still flow and be used; the PP is "the lowest point at which movement of the specimen is observed[23]." The CP can still be a problem though; the small crystals that form can clog the fuel filter and fuel lines.

There are several commercial additives are known to improve the properties of petroleum diesel. These additives, however, only affect the PP of biodiesel, not the CP, even when the amount used is more than the recommended amount.[24] When four commercial additives were used on biodiesel from four different sources (soybean methyl ester, mustard methyl ester, mustard ethyl ester and used oil methyl ester) the CP of each of the methyl esters was not "statictically significant," the ethyl ester showed a different result.[24] The ethyl ester was slightly more effective, an average reduction of 3°C.[24] This difference is thought to be related to the end methyl group's distance from the carboxylic group. In the methyl ester the methyl group has a slight polarity due to the carboxylic group, this causes the crystals to easily form due to the polar attractions. In the ethyl ester, the end methyl group is farther from the carboxylic group, so there is less of a polar effect on it, meaning it is less likely that there will be any polar attraction.[24]

The PP of the biodiesel was lowered by the commercial additives by approximately 3-7°C in the methyl ester and by 19°C for the ethyl ester.[24]

A common commercial additive used for reducing the CP and PP of petroleum based diesel fuel is a polymer. There are various copolymers that are known to be effective. One of these consists of a maleic anhydride alpha-olefin copolymer (alpha olefins are carbon chains with a double bond in the alpha, or end position)[29] , another is a propionate/vinyl branched carboxylate terpolymer.[30] These polymers can work in two ways, the first interrupts the formation of wax crystals in the diesel fuel which limits the size of the crystals produced and the second acts as a nucleating agent which creates smaller crystals. Both of these methods reduce the CP and the PP of the diesel fuel.[29, 30]

Simply blending biodiesel with conventional diesel will lower the CP and PP. Rushang and Pegg found that there is a correlation between both these temperatures (CP and PP) and the amount of biodiesel in the blend, by volume.[25] An equation can be calculated that will predict these properties of the fuel, although each batch of biodiesel will have different properties so these equations are not universal.

The commercial additives mentioned previously will also work on blends, where they have the most effect. The PP could be depressed up to 36°C using the conventional additives in a 5 to 20% blend.[24] The problem with using blends to reduce the PP and CP of biodiesel is that most of the wanted renewable fuel effects are gone. Some of the effects can be appreciated, but not to the full extent.

It has also been found that using different alcohols in the transesterification will change the properties of the fuel. If the alcohol is branched such as isopropyl and 2-butyl alcohol the CP and PP can be reduced more than using straight chain alcohols.[26] Lee et al found that using these two alcohols reduced the CP by 7°C and 10°C respectively. This became even lower when low saturated oil is used.[26] The drawback to using these branched alcohols is in the cost. These alcohols are more expensive, have a lower yield and an increase in impurities in the final product.[26]

"Winterizing" of biodiesel has also been considered for lowering the cold flow properties of biodiesel. The wintering process is when the biodiesel is cooled until crystals begin to form (the crystallization onset temperature T_{CO}). At this point, the crystals are filtered and the process is repeated until the intended CP is reached.[27] This removes the saturated esters from the biodiesel. When regular soybean oil is used, this process becomes lengthy (11 steps, each step being a cooling and filtering of the liquid) to reach a T_{CO} of -7.1°C.[27] This process was found to be shorter if one of two things was done. The first was using a hexane solvent on the soybean oil, the second to use a variety of soybean that has low saturates. When either of these were employed, the CP was reduced to 3 steps, however the yield for the low saturates was better (86%) than the soybean oil and solvent (77%).[27] This method does reduce both the PP and the CP for the biodiesel, but problems still remain in the storage or transportation of the saturates. Since the saturated portion of the fuel cannot be used in the winter months in the north they either need to be stored until warmer weather or transported to warmer locations. Both the storage and transportation will lead to an increase in costs.[27]

Finally there are researchers who have used blend of biodiesel with ethanol to improve these properties, and have been successful. Park et al and Torres-Jimenez et al have found that the addition of ethanol will decrease the PP and CP. By using a blend of 15% ethanol the CP can be decreased by 3°C and the PP by the same amount.[21] There are two advantages to using ethanol; the first is the entire fuel could potentially be renewable (if the ethanol is from fermentation),[28] the second being a reduction in viscosity, which would bring the viscosity of biodiesel closer the viscosity of petroleum diesel.[21, 28]

The disadvantage to doing this is a change in the flash point. With only a 5% addition of ethanol the flash point drastically decreases, to near the flash point of ethanol, which is well below the required flash point standards for biodiesel. This would mean that an additive is needed to increase the flash point.[21] A second disadvantage is the affinity for ethanol and biodiesel to absorb water. The storage and transportation could become difficult if barriers from the atmosphere are needed to prevent the absorption of water from the humidity in the air.[21]

There are many methods for reducing the CP and PP of biodiesel, most of which are additives, but a few change the chemical structure of the biodiesel itself. They all have their advantages and their disadvantages. There is no perfect method.

CHAPTER 2
BIOBASED MONOMERS

2.1 Literature Review

2.1.1 Introduction

There is an increase in the demand for renewable resources in every industry. This includes the production of polymers and the monomers from which they are produced. Currently almost all polymers are produced from fossil fuel sources;[31] the most used is naphtha-a distillation fraction of crude oil and natural gas.[32] The production of polymers consumes approximately 7% of the world's fossil fuels.[13] Another reason for decreasing the use of petroleum based monomers and polymer is biodegradability. Petroleum based polymers do not easily biodegrade, meaning there are few (or no) microbes that will break them down. However, there are many biobased polyesters, plastics and inks that have proven to be biodegradable.[33-37] In addition to the potential biodegradability, other advantages for production of monomers and polymers from renewable resources are their low cost, ease of availability, and the availability of the feedstock in large quantities.[11, 31]

Currently there are biopolymers produced from polysaccharides[13, 32, 38] (starch and cellulose), lipids[13, 32,

[38] (plant and animal triglycerides), polyphenols,[38] sugars,[13] proteins[13, 38] and natural rubbers[13]. One of the first industrially produced biobased polymers was linoleum, developed in 1864 by F. Walton, the main component being linseed oil.[12] Vegetable oils and animal fats, like linseed oil, have been used in the production of coatings,[10, 13, 39, 40] plasticizers,[10, 39, 40] lubricants,[10, 13, 39, 40] inks,[37, 39, 40] paints,[13, 39, 40] and agrochemicals[10, 39, 40].

2.1.2 Triglycerides

The previous chapter discussed the use of triglycerides in the production of biodiesel and the structure of the triglyceride. The same oils seen in Table 3 can also be used in the production of monomers. Other oils are only used in the production of monomers or for direct polymerization; this is due to the added functional groups on these triglycerides. These include Tung[10, 30], Lesquerella Gracilis[30], Veronia[30] and Castor oils.[10, 30] These oils contain natural epoxy, hydroxyl groups and conjugated double bonds. Others are known to have triple bonds and ether functions.[11] These natural functional groups allow these oils to be directly polymerized.

2.1.3 Triglyceride Based Monomers

There are many paths that can be taken to produce a monomer using the triglyceride. These pathways, shown in Figure 7a and 7b, are modifications made to the initial triglyceride. The first of these is to functionalize the internal double bonds of the fatty acid portion of the triglyceride

These functional groups are commonly epoxy groups,[10-12, 31, 32, 40, 41] hydroxyl groups,[31, 32, 42-47] and maleates[9, 40] (paths 5-8 and 11).

Epoxy groups are generally produced by the reaction of the triglyceride with molecular oxygen, hydrogen peroxide or via a chemo-enzymatic reaction[12]. *In situ* epoxidation of soybean oils has been studied extensively; this process uses a two-phase system to safely achieve epoxidation.[41] Epoxidation processes using peroxides and peracids have been known to form mixtures, which will explode upon heating, the *in situ* process avoids this by allowing low concentrations of the peracid to form, resulting in a safer process[41].

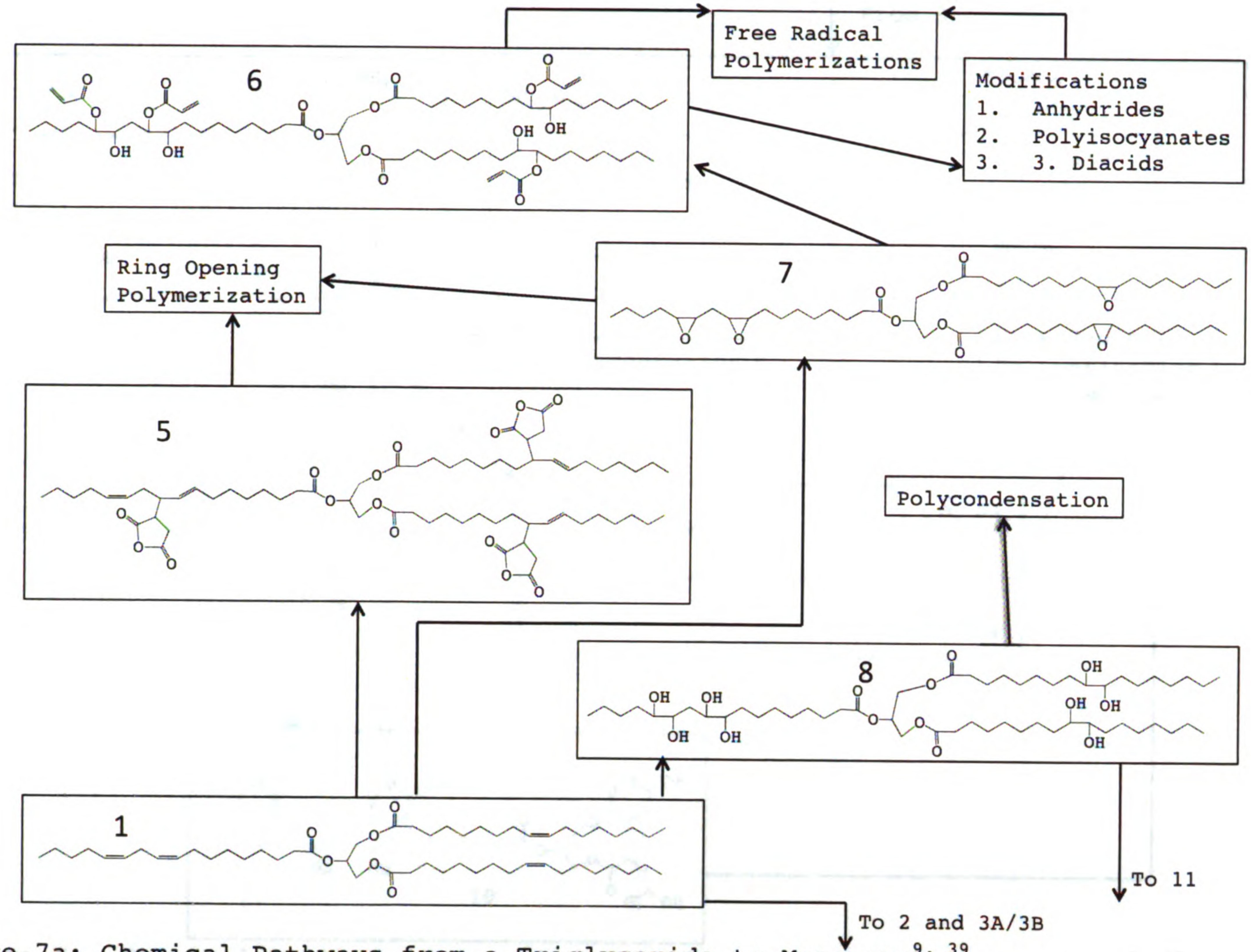


Figure 7a: Chemical Pathways from a Triglyceride to Monomers[9, 39]

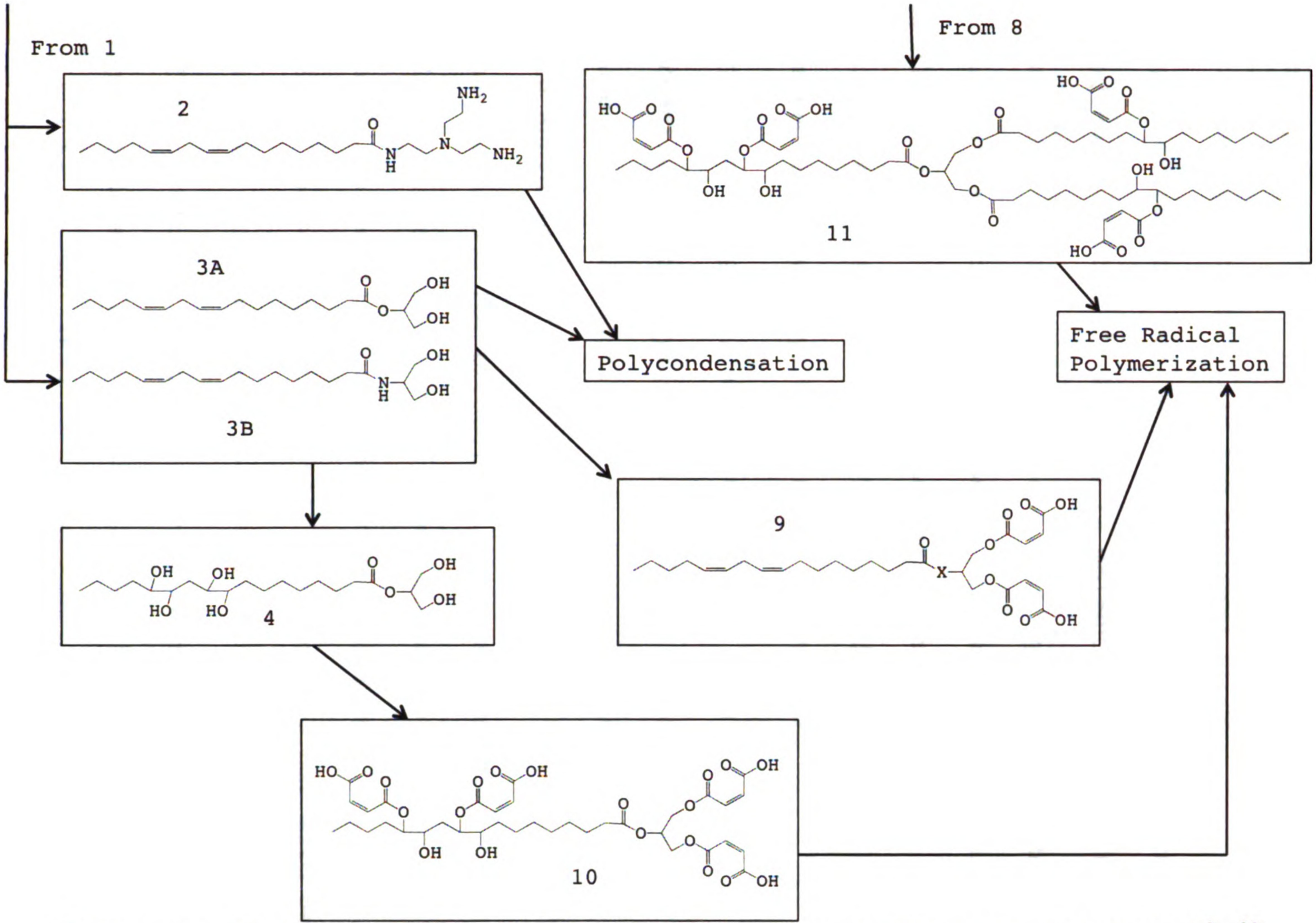


Figure 7a: Chemical Pathways from a Triglyceride to Monomers (Continued)[9, 39]

The epoxidized oils can be used in polymerization or they can be converted into hydroxyl groups via alcoholisis of the epoxy group.[32, 43, 45] The oxirane ring will open in an acidic environment to yield the hydroxyl group.[47] Halogenated polyols can be achieved using hydrochloric acid or hydrobromic acid.[46] Polyols (a molecule with more than one hydroxyl group) can be produces using another method as well. This method uses the double bond and converts it to an aldehyde in a process called hydroformulation with carbon dioxide and hydrogen. The aldehyde is then converted to a hydroxyl group using a catalyst.[32, 44, 45] Using the epoxy group, acrylates[9, 13, 40, 48] can be added by the reaction with acrylic acid. Maleate esters are also produced from the reaction of the hydroxyl groups with maleic anhydride.[9, 12, 40]

The second method for producing a monomer from a triglyceride is production of a monoglyceride through a glycerolisis reaction or amidation reaction (path2 2, 3A and 3B). The monoglycerides that are produced can also be maleated to produce maleate half esters (path 9).[9, 40]

The final method is to do both types of reaction, produce a monoglyceride and functionalize the double bond (path 4). This can be accomplished using two methods. The first, starts with a functionalized triglyceride then glycerolisis is performed. The second begins with a monoglyceride and functionalizing of the double bonds is done second. These functionalized monoglyceride can also be reacted with maleic anhydride if necessary (path 10).[9, 40, 49-51]

There is a second method for producing the maleated monoglycerides. Performing alcoholisis of the triglyceride with pentaerythritol produces a monoglyceride and an oil pentaerythritol glyceride, which can be reacted with maleic anhydride.[52, 53]

2.1.4 Monomers from Fatty Acids

The internal double bonds of the unmodified triglyceride do not easily polymerize because of their location. This is the reason for modification of these double bonds. This is also true for the fatty acid. Modification of the fatty acid is necessary to achieve polymerization because the double bonds are internal and cannot undergo free radical polymerization.

One other method to produce a polymerizable monomer out of the triglyceride is the production of a fatty acid with a terminal double bond (although the internal double bonds of a fatty acid can be epoxidized[54-56] or hydroxylted[44, 47] as seen in the previous section).

One method for the preparation of an allyl ester uses a Finkelstein transposistion.[57, 58] This method uses no allyl alcohol and uses glycerol (a byproduct from biodiesel production) as a feedstock.

Another reaction that can be used is the esterification of the fatty acid (Figure 8). This method is generally used on a single species of fatty acid[56, 59-61]however it has been used on the fatty acids of soybean oils and linseed oils[62]. The reaction that occurs uses an acid catalyst to produce water, the water is azetropically removed with excess allyl alcohol until water is no longer produced.

Figure 8: Esterification of the Fatty Acid Using an Acid Catalyst

The second method of production of allyl esters is the transesterification of the methyl ester-producing methanol as a byproduct (Figure 9). This reaction is also known as alcoholisis and is generally not used due to low yields. When alcohols such as methallyl and crotyl alcohol are used the yields are significantly lower than the esterification method[60].

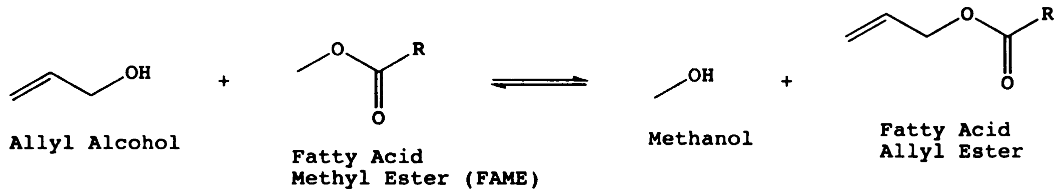


Figure 9: Transesterification of Methyl Ester with Methanol as a Byproduct

Finally the direct transesterification of any vegetable oil triglyceride can be used to produce allyl esters (Figure 10). This reaction is the same reaction that produces biodiesel using allyl alcohol in the place of methanol. This method has been shown to have high yields[54, 56]

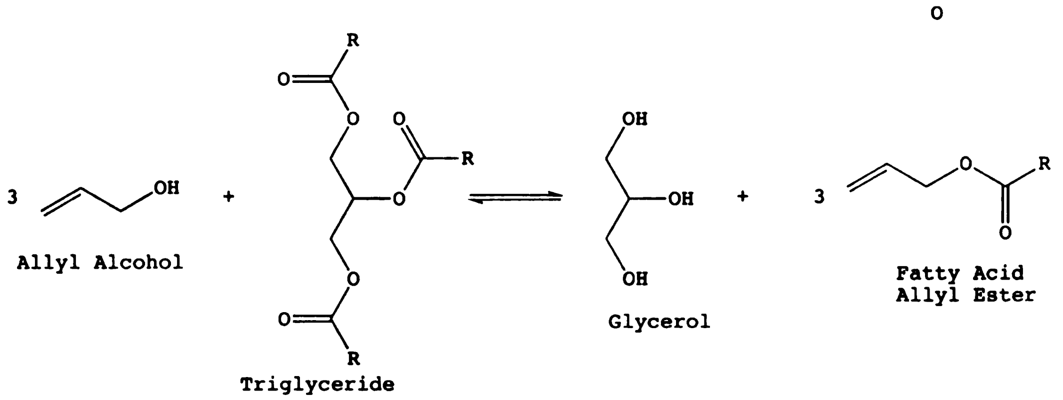


Figure 10: Transesterification of the Triglyceride to Produce Allyl Esters

2.2 Transesterification of Soybean Oil

2.2.1 Materials

Low saturated RBD (refined, bleached and deodorized) soybean oil was obtained from Zeeland Farm Services in Zeeland, Michigan and the allyl alcohol was purchased from Fisher Scientific. Both the allyl alcohol and the soybean oil were stored at room temperature in a dark location to prevent the oxidation of the double bond in both. All other chemicals were obtained from reliable resources and were used as received.

2.2.2 Experimental procedure

Approximately .5g potassium hydroxide (KOH) was dissolved in 50g (.86 mol) allyl alcohol to which 50g (.06 mol) soybean oil was added. Prior to the addition of soybean oil to the allyl alcohol the alcohol and soybean oil were heated to 90°C. The oil and alcohol were mixed in a 150mL three-necked batch reactor equipped with a reflux condenser, magnetic stir bar and stopper for 1.5 hours at a reflux temperature of 105°C. After cooling a stoichometric amount of concentrated hydrochloric acid was added. The neutralized reaction mixture was then transferred to a separating funnel. The glycerol product and the salt formed by neutralization were allowed to settle out of the ester layer. After the salt and glycerol were removed, the ester layer was washed with distilled water to remove any residual salt, glycerol and some of the excess allyl alcohol. Any remaining unreacted allyl alcohol was removed under vacuum.

2.2.3 Characterization

Fourrier Transform Infrared Spectroscopy (FTIR) spectra were obtained using a Perkins and Elmer instruments, spectrum one FTIR spectrometer. All FTIR spectra were normalized, this was done by dividing the difference between absorbance and the minimum absorbance in the spectrum by the difference between the maximum absorbance and the minimum absorbance. Nuclear Magnetic Resonance (H-NMR) spectra were obtained of the esters in $CDCL_3$ using a Varian Inova-300 spectrometer operating at 300.103MHz. Gas Chromatography (GC) analysis was done using a HP 5890 series II equipped with a Supelco PTA-5 column (30m x 0.25mm with a film thickness of 1μm). HPLC grade dichloromethane was used as the solvent and methyl undeconate was used as an internal standard. Finally, iodine values were calculated using ASTM method D1959-97[63]. The Wij's solution was purchased from Sigma-Aldrich corp. and carbon tetra chloride was used as the solvent.

2.2.4 Results

The normalized FTIR spectra for both the starting soybean oil and the allyl ester product can be seen in Figures 11a and 11b. At first glance, the two spectra look similar however; there are differences that show a change in the material.

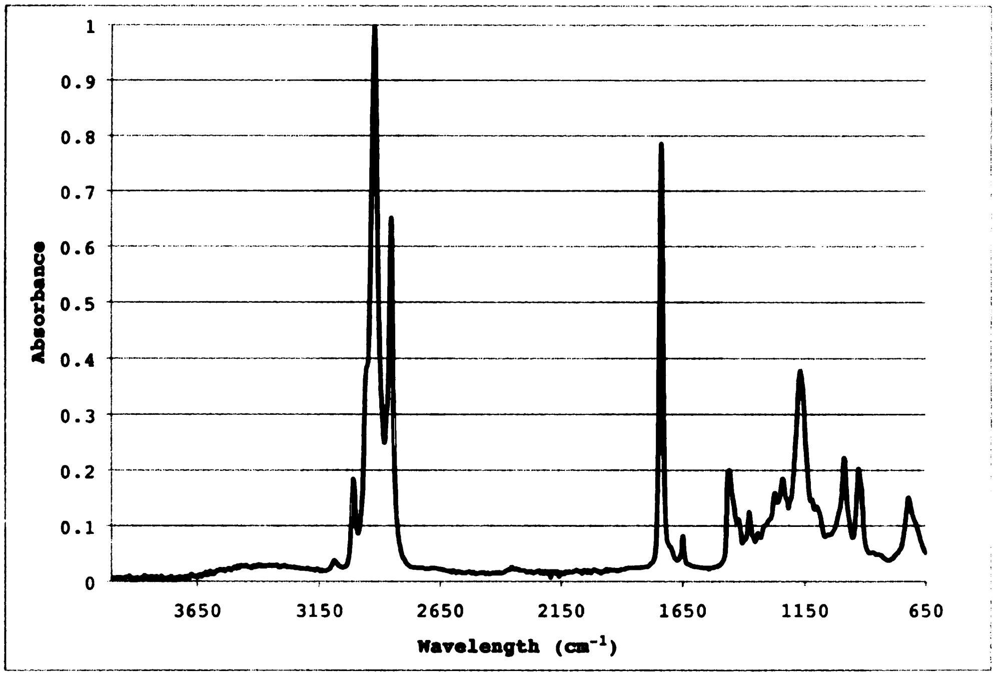


Figure 11a: FTIR Spectrum of the Allyl Ester

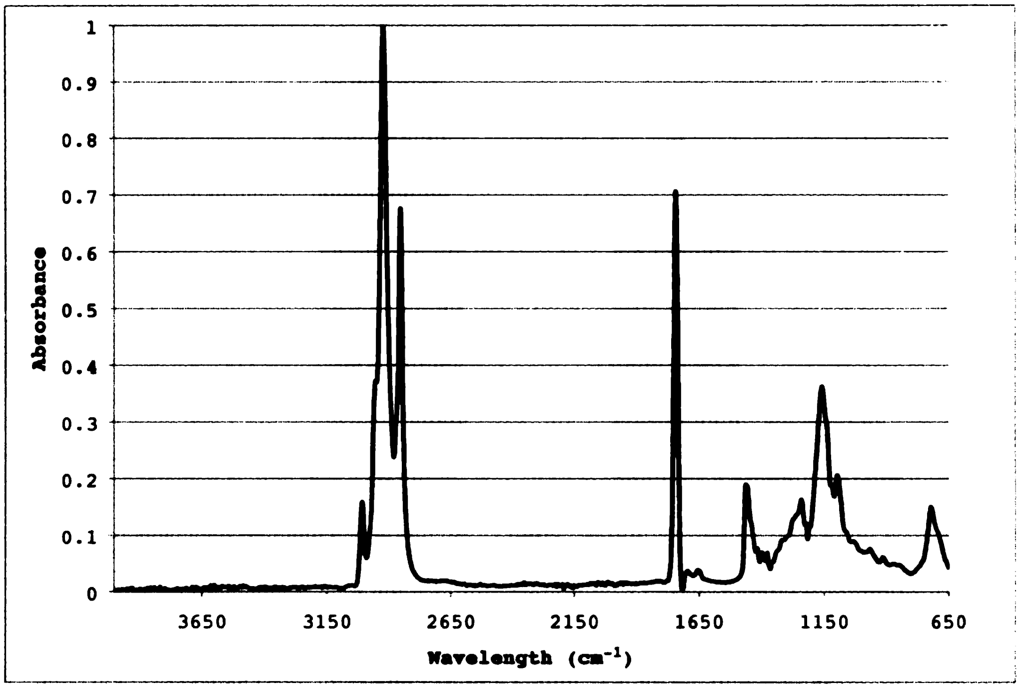


Figure 11b: FTIR Spectrum of Soybean Oil

The first of these is the peak from 2990cm^{-1} to 3050cm^{-1}, the peak characteristic of the =C-H stretching. This is more clearly shown in Figure 12, which shows there is a change in the amount of absorbance. The soybean oil has smaller total absorbance than the allyl ester peak (meaning there is a smaller area under the curve for the soybean oil compared to the allyl ester).

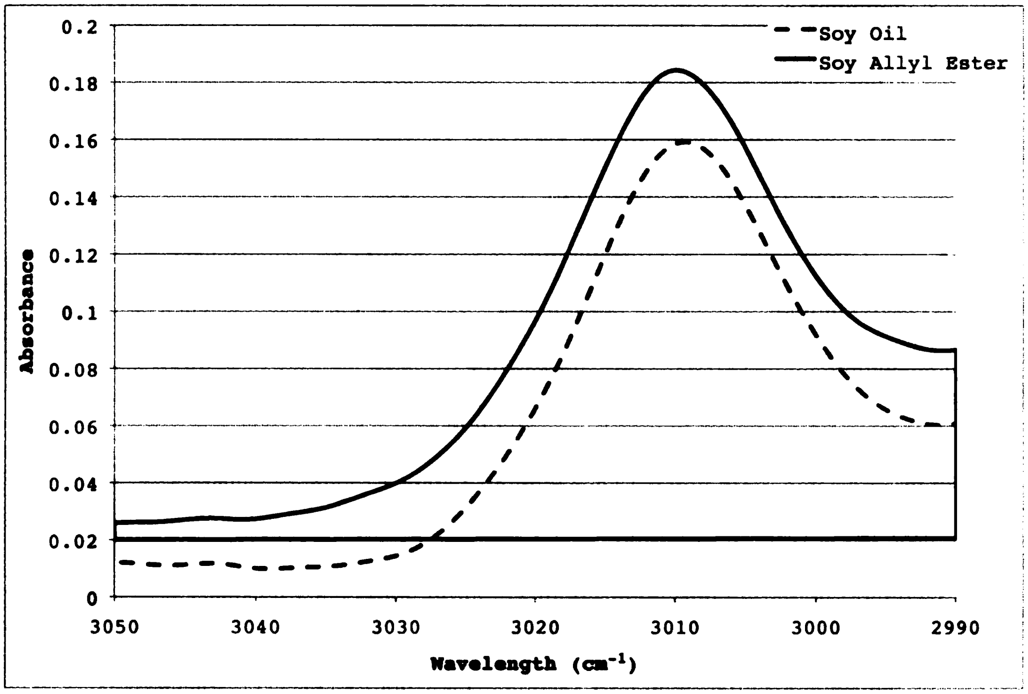


Figure 12: Peak Characteristic of =C-H Stretch

Since the peak intensity directly correlates to the number of double bonds in the sample, this shows that the allyl ester sample has a larger number of double bonds. The second important peak is characteristic of the ester (C=O stretching). This peak, from 1690cm^{-1} to 1790cm^{-1} (see Figure 13), shows a shift of the maximum absorbance from 1744cm^{-1} to 1739cm^{-1}. This shift is an indication of the change in the chemical groups next to the C=O. Any groups near the C=O alter the wavelength that this group will absorb at. So the change from the glycerol backbone to the allyl group shifted the absorbed wavelength.

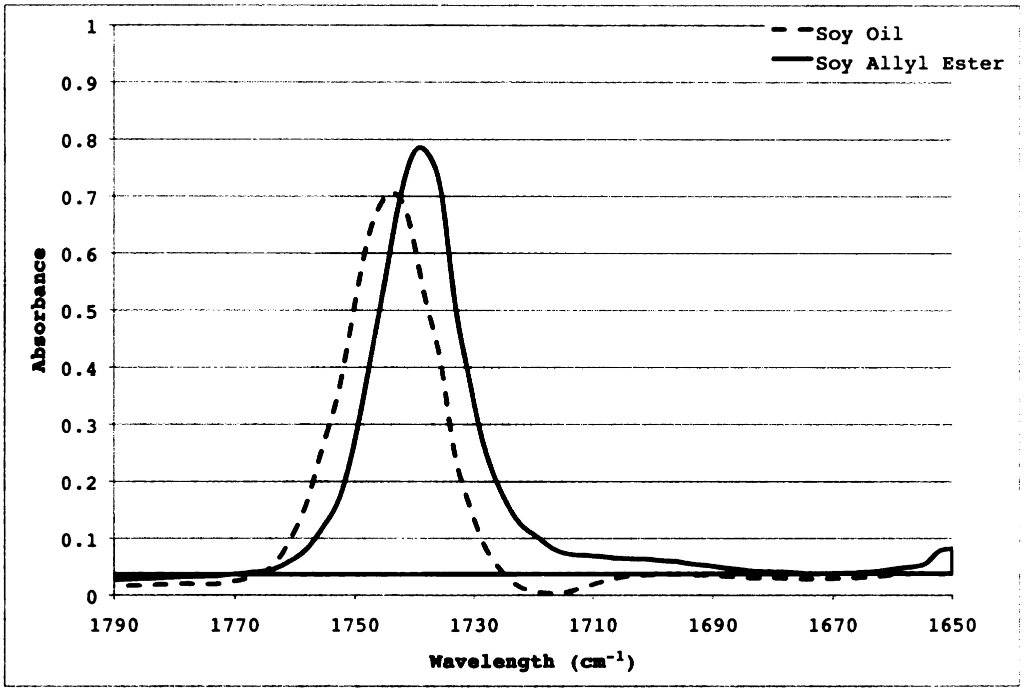


Figure 13: Peak Characteristic of C=O Stretch

The iodine values, seen in Table 4, confirm the increase in double bonds. By using a theoretical value of 216.00, (see appendix 1 for calculations) a percent conversion of 83.72% is found.

Sample	Average	Standard Deviation
Soybean Oil	142.1	4.93
Allyl Ester from Soybean Oil	204.54	2.96

Table 4: Iodine Values for Soybean Oil and Allyl Ester Product

The H-HMR spectra also indicate the changes that occur when the triglyceride is transesterified. The first H-NMR spectrum, seen in Figures 14, is the spectrum for the soybean oil. Peaks A, B and, C are the three most important peaks. These peaks correspond to the protons in the glycerol backbone of the triglyceride where A and C (at 4.1ppm and 4.3ppm) are the protons on the two and carbons and B (5.2ppm) is the proton on the middle carbon.

When this is compared to the allyl ester spectra, the peaks A B, and C are no longer present. This would indicate that there is no longer glycerol present. The new peaks D and E at 5.9ppm and 5.2 ppm are the indication of the terminal group on the ester. Peak F, at 4.5ppm, is indicative of the methylene protons in the allyl portion of the ester. These three peaks (D, E, and F) indicate that the allyl groups had been added to the ester chain. The remaining peaks at 5.3-5.4ppm and below 3.0ppm are the protons in the fatty acid chain and do not change when the ester is produced since they do not take place in the reaction.

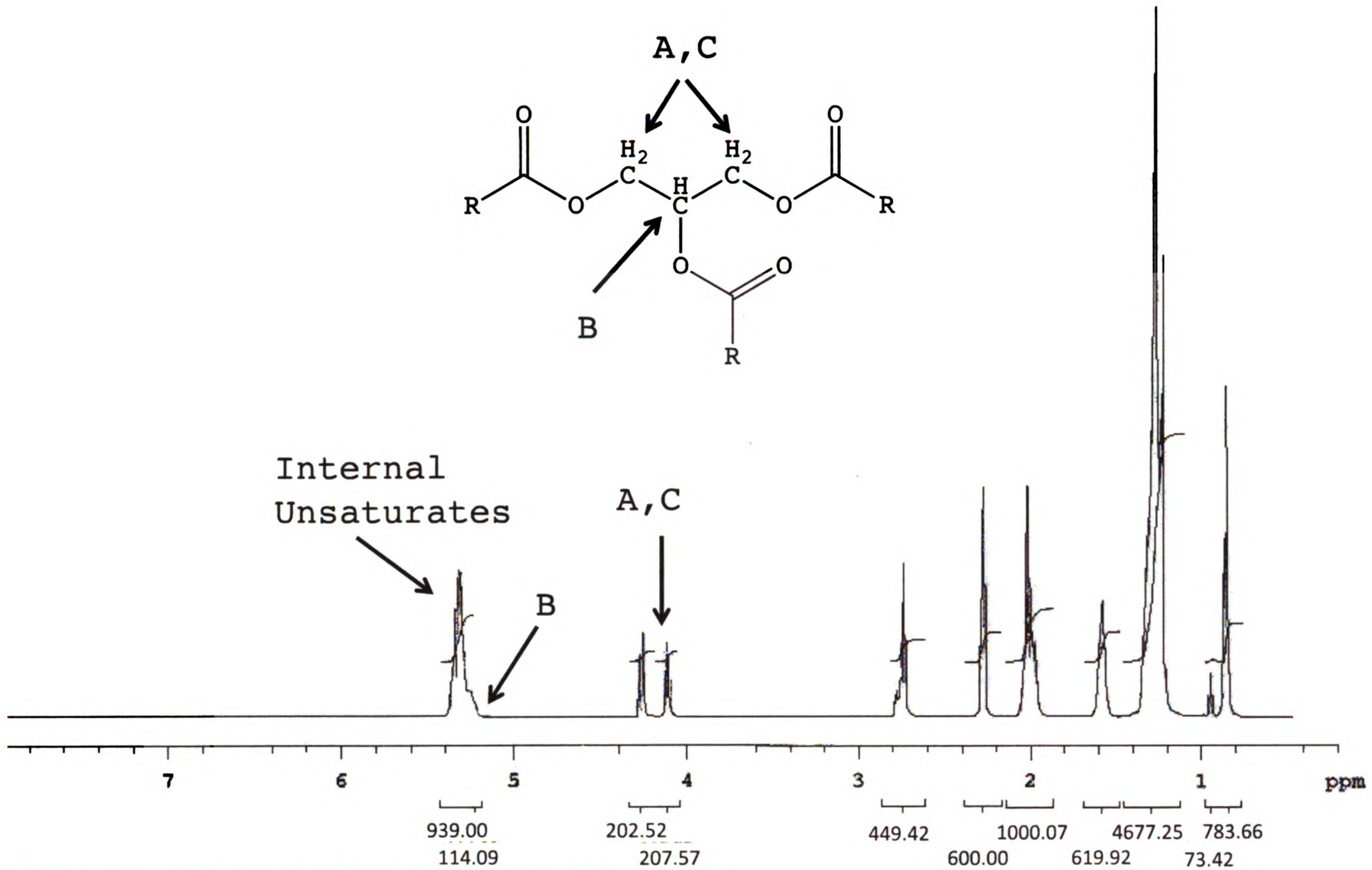


Figure 14: H-NMR Spectrum of Soybean Oil

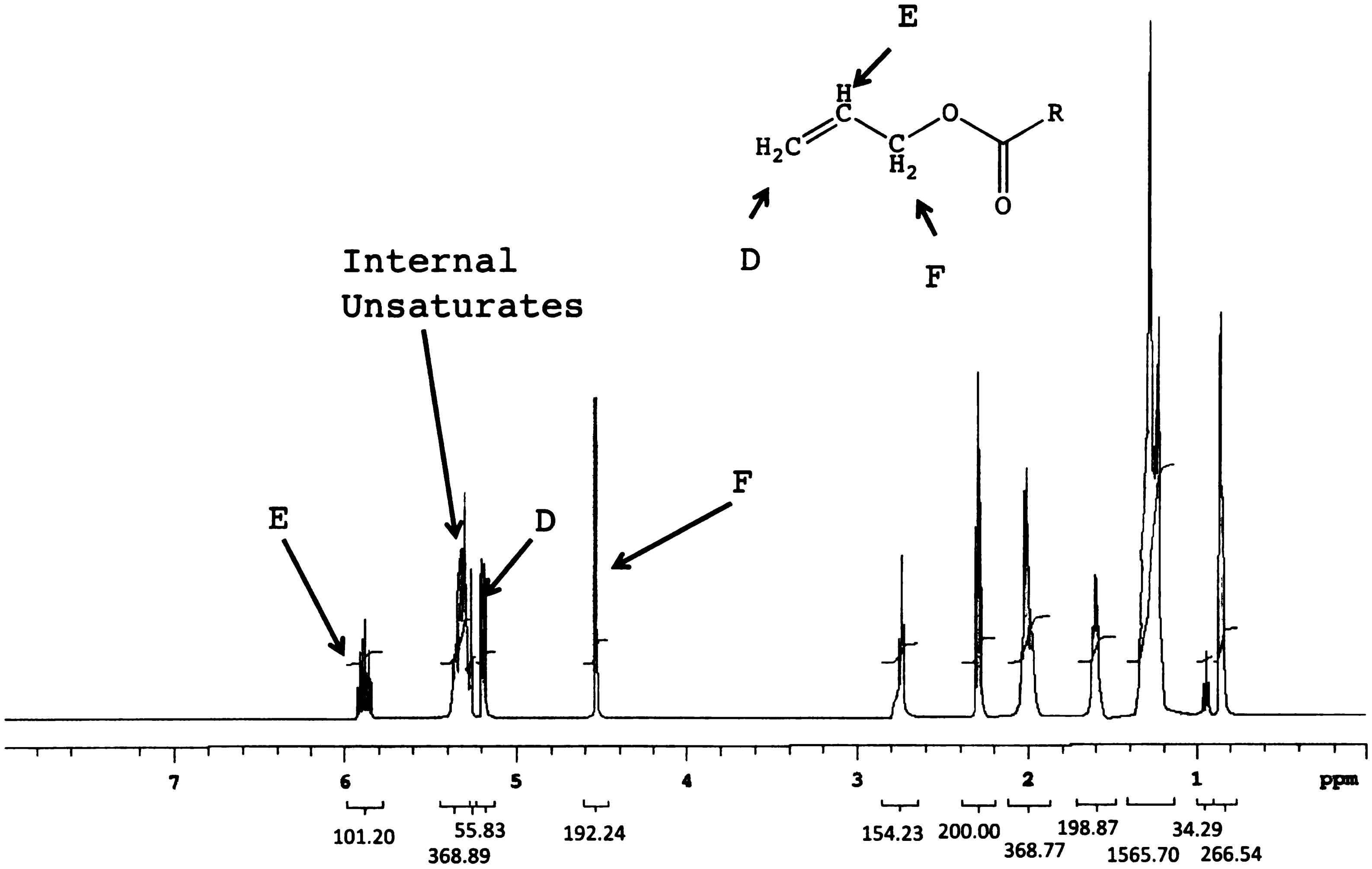


Figure 15: H-NMR Spectrum of Allyl Ester from Soybean Oil

Gas Chromatography was used to analyze the allyl ester. This data, along with the data from a methyl ester produced from the same soybean oil can be seen in Table 5. As this Table shows, the residence times for the allyl product are slightly longer than that of the methyl ester. This longer residence time can be attributed to the additional molecular mass of the allyl ester

Residence Time	Component	Percentage in Methyl Ester	Percentage in Allyl Ester
15.21	Methyl Palmitiate	4.27	
16.19	Allyl Palmitate		2.44
16.44	Methyl Unsaturates	88.91	
16.56	Methyl Stearate	6.81	
17.60	Allyl Unsaturates		87.62
17.67	Allyl Sterate		9.93

Table 5: Retention Times and Percentage of Components in Allyl Ester and Methyl Ester Produced from Soybean Oil

2.3 Transesterification of Fatty Acid Methyl Esters (FAMEs)

2.3.1 Materials

The materials used for these reactions are the same as the previous section.

2.3.2 Experimental procedure

Approximately 1g KOH was dissolved in 50g (.86 mol) of allyl alcohol, 50g (.18 mol) of methyl ester was then added after the KOH was completely dissolved. The reaction vessel (a three-necked batch reactor) was equipped with a dean stark trap/condenser a magnetic stirrer and a thermometer. The reaction mixture was heated (maximum temperature of 105°C) until approximately 20mL of alcohol (a mixture of methanol and allyl alcohol due to the azetrope) was collected in the dean-stark trap. The reaction was allowed to cool slightly and 20mL of allyl alcohol was then added to the esters to ensure an excess of allyl alcohol is maintained. The removal and addition of alcohol was repeated four times.

2.3.3 Characterization

The same characterization techniques and equipment were used on the allyl ester produced from methyl esters as the allyl ester produced from soybean oil.

2.3.4 Results

The normalized FTIR spectra for both the allyl ester and the methyl esters that it was produced from are in Figures 16a and 16b. These spectra have even more similarities than that of the soybean oil and its allyl ester product.

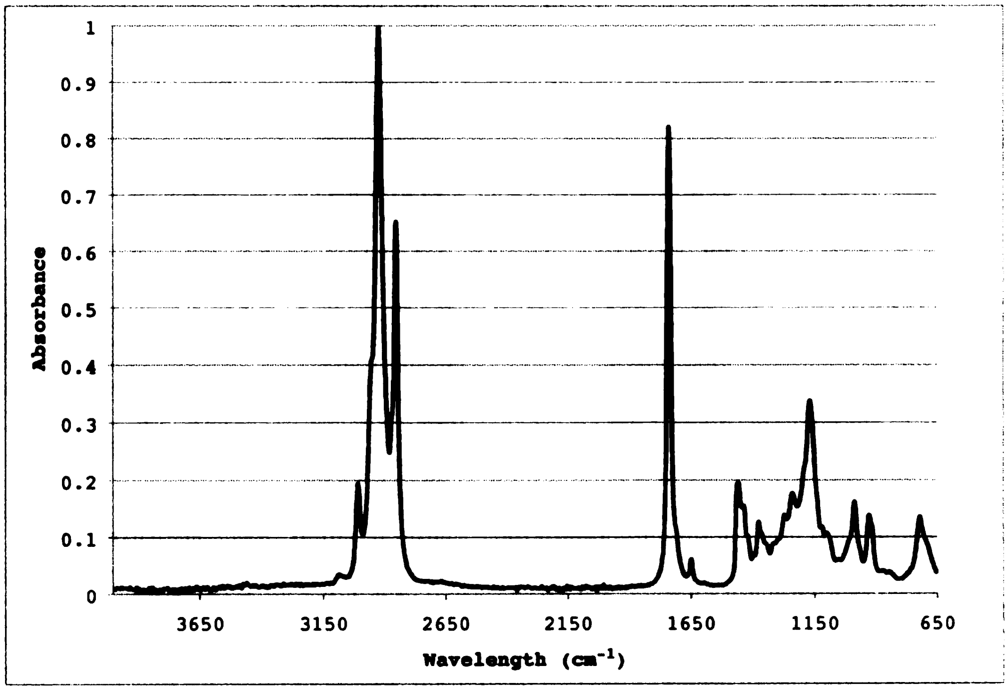


Figure 16a: FTIR Spectrum of Allyl Ester from Methyl Ester

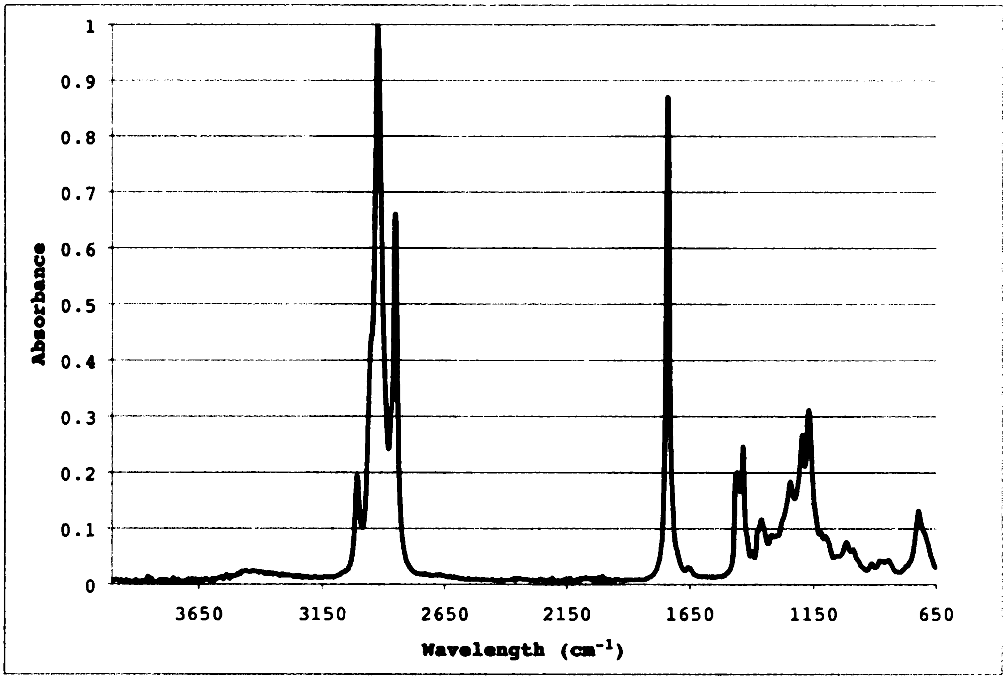


Figure 16b: FTIR Spectrum of Methyl Ester

One of the main differences, like the soybean allyl ester is the C=O peak (wavelengths 1690cm^{-1} to 1790cm^{-1}). This peak shows the same type of shift as the ester produced from soybean oil, from 1742cm^{-1} to 1740cm^{-1}, Figure 17. The peak associated with the =C-H stretching (2990cm^{-1} to 3050cm^{-1}, Figure 18), does not show any change in the amount of absorbance. As mentioned, the absorbance is proportional to the number of double bonds in the sample. This would suggest that there is no change in the number of double bonds and therefore no addition of the allyl group to the ester. This conclusion, however, is not supported by the iodine values calculated.

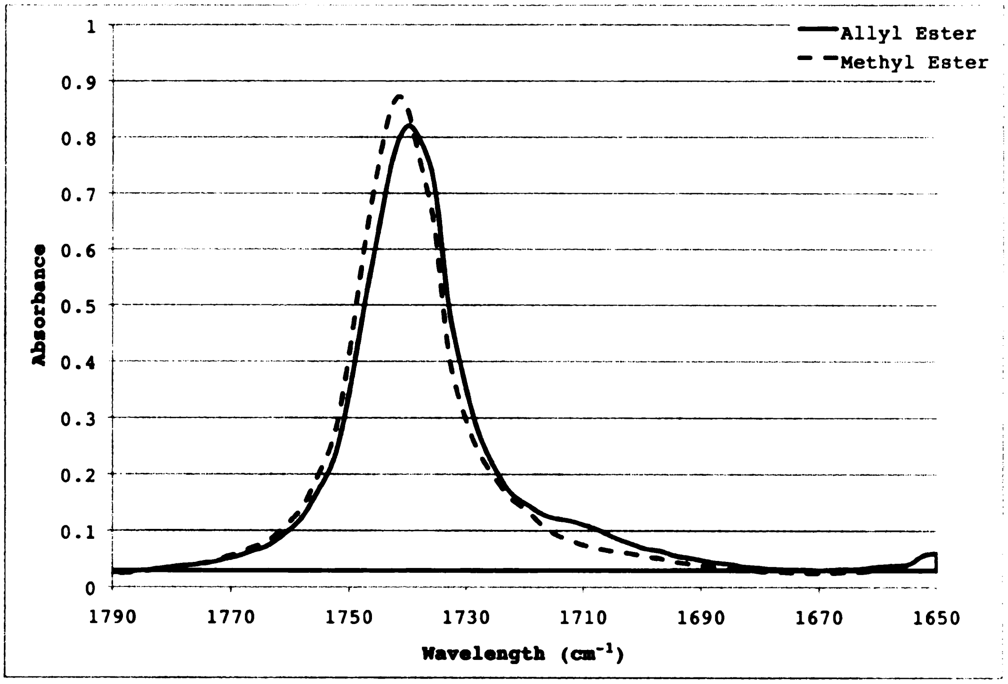


Figure 17: Peak Associated With C=O Stretch

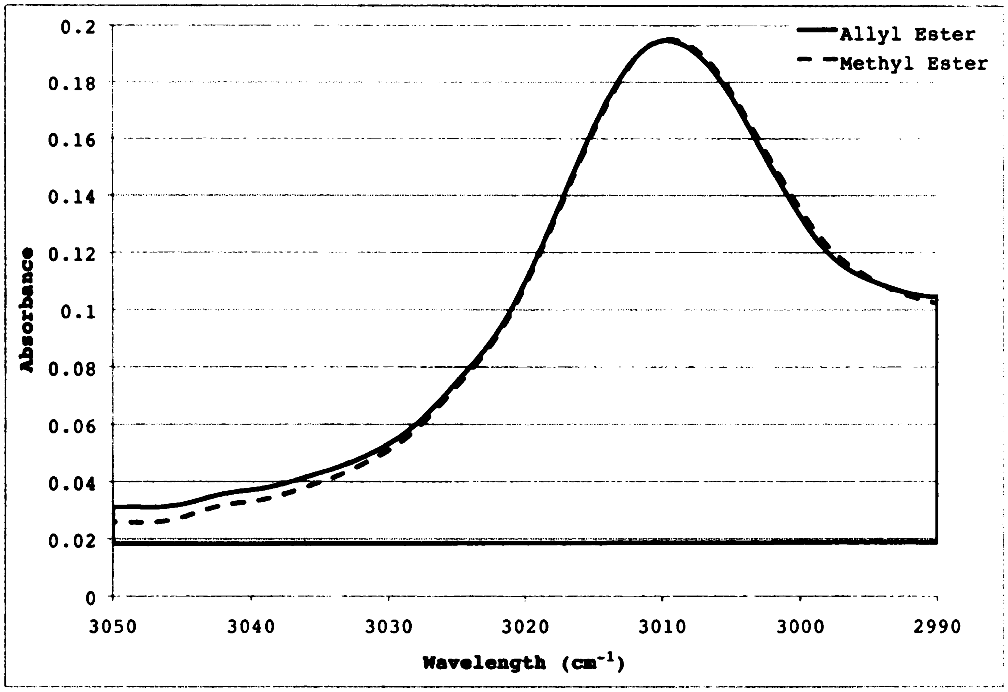


Figure 18: Peak Associated With =C-H Stretch

The iodine values 141.93 and 188.57 were calculated for the methyl ester and the allyl ester respectively (Table 6). This is one conformation that there is an addition of the allyl group to the ester, since there is an increase in the number of double bonds. Using the same theoretical value for one hundred percent conversion (216.00), a conversion of 62.16% is found for this reaction.

Sample	Average	Standard Deviation
Methyl Ester	141.93	2.95
Allyl Ester	188.57	3.74

Table 6: Average Iodine Values for Allyl Ester and the Methyl Ester Used to Produced It

The GC analysis also confirms conversion to the allyl ester. The residence times and area percents for the final allyl ester product are seen in Table 7 (the results shown are after the final removal of allyl alcohol). As this data reinforces the conclusion that there is not complete conversion, since there is still methyl ester in the product even though the allyl alcohol was maintained in excess and methanol was removed during the reaction (Pure methyl ester residence times can be seen in Table 5).

Residence Time	Component	Percentage in Reaction mixture
15.21	Methyl Palmitiate	1.79
16.19	Allyl Palmitate	2.74
16.44	Methyl Unsaturates	30.41
16.56	Methyl Stearate	3.74
17.60	Allyl Unsaturates	48.89
17.67	Allyl Sterate	1.88

Table 7: Retention Times and Percentage of Components in Allyl Ester and Methyl Ester Produced from Methyl Ester

Finally the H-NMR spectra also (Figures 19 and 20) confirm the conversion of the methyl ester to the allyl ester and that there is not complete conversion of the methyl ester. The peak, labeled H, is indicative of the protons of the methyl group. Since this peak is present in both spectra it can be concluded that the product is a mixture of esters. The three peaks, K, L and M indicate the protons attached to the three carbons in the allyl group that is added to the ester. The C=C at 5.2ppm and 5.9ppm and the methylene group at 5.2ppm. The remaining peaks at 5.3-5.4ppm and below 3.0ppm are the protons on the remaining fatty acid chain.

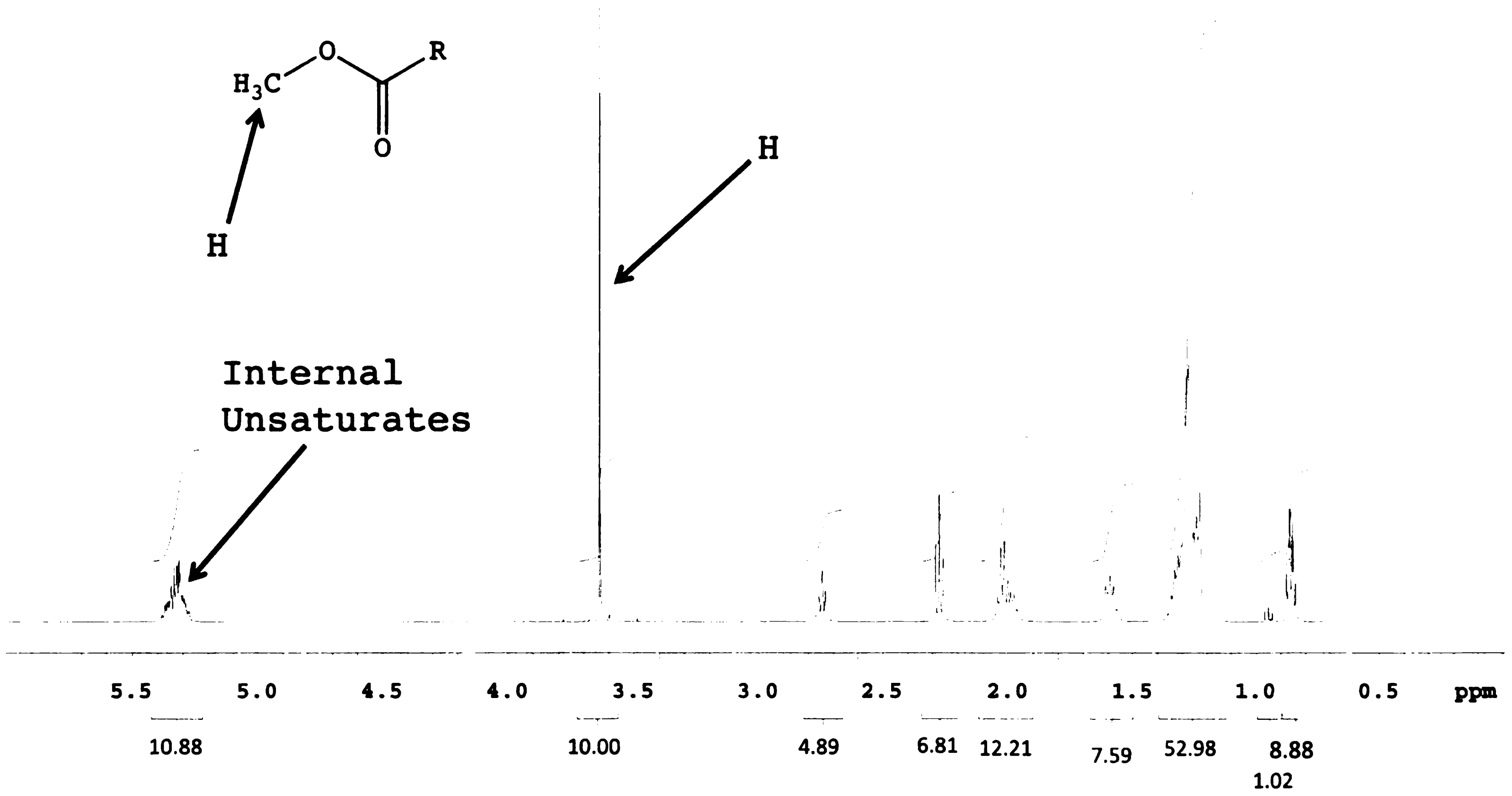


Figure 19: H-NMR Spectrum for Methyl Ester

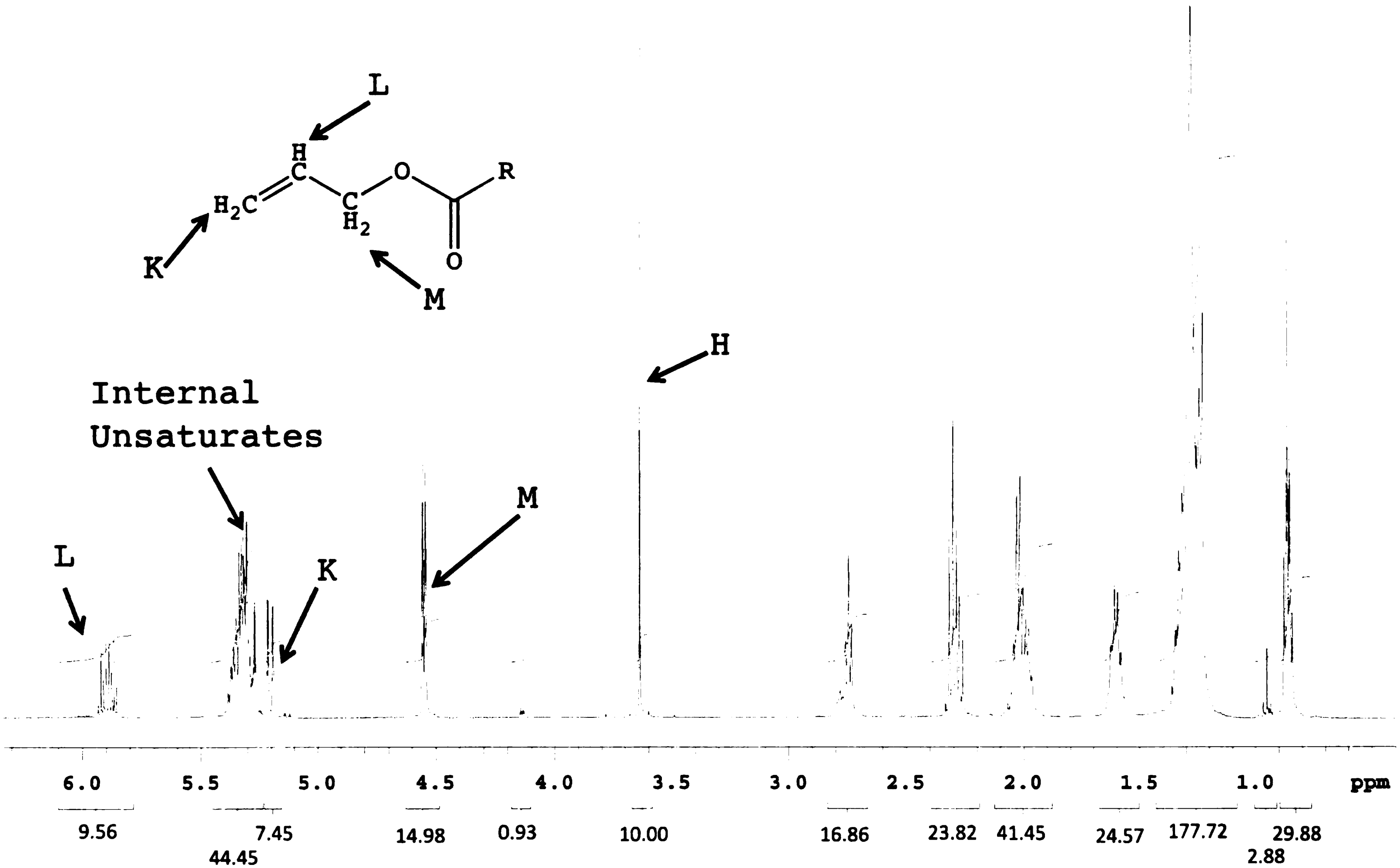


Figure 20: H-NMR Spectrum For Allyl Ester Produced from Methyl Ester

2.4 Discussion of the two methods of production

The data discussed previously indicates that there is a reaction of both the soybean oil and the methyl ester, but do both methods produce the same product? The data suggests that they do. The first confirmation is in the GC analysis of each product. The residence times for the product from both methods are the same. This indicates that the two products must be similar since they elute at the same time under the same conditions. The second confirmation is the shift of the ester peak in the FTIR spectra. The maximum of the peaks shifted to approximately the same place (1740cm^{-1} vs. 1739cm^{-1}). Finally, both product H-NMR spectra have peaks at 4.5ppm (methylene protons), 5.2ppm and 5.9ppm (terminal double bond protons). Since the peaks fall at the same location, it can be concluded that there is the same material is in both product.

As shown there are two methods for producing the allyl ester from soybean oil, direct transesterification and transesterification of the methyl ester. The direct transesterification seems to be the more efficient method of production. The conversion of the soybean oil is significantly higher than the methyl ester conversion.

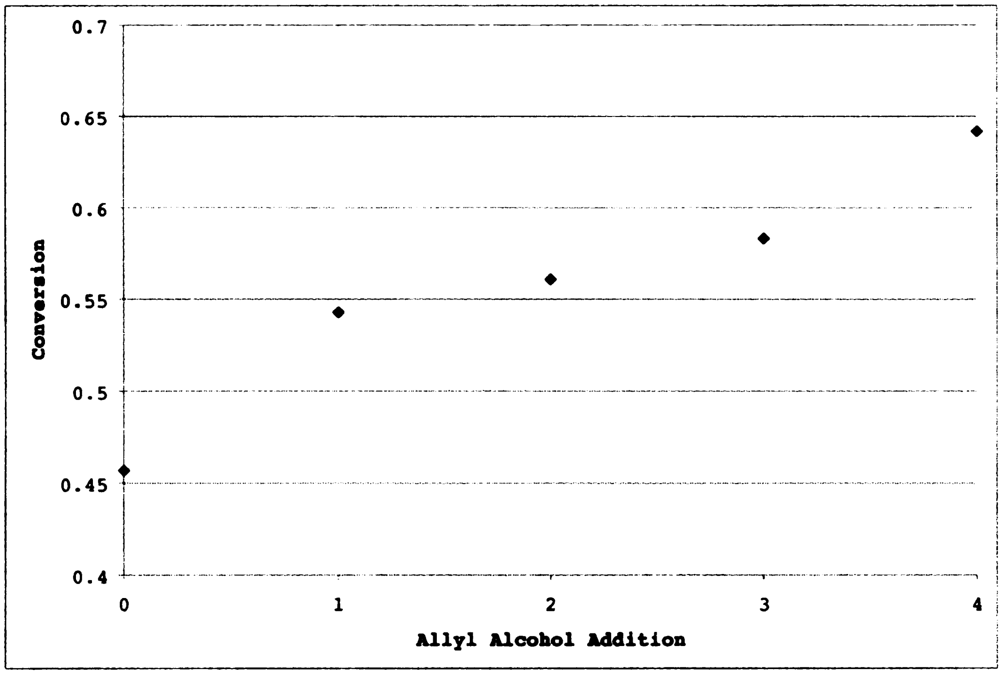


Figure 21: Conversion of Methyl Ester to Allyl Ester with the Removal and Addition of Alcohol

Although it may be possible for the methyl ester reaction to reach the same conversion as the soybean oil reaction the soybean oil uses less allyl alcohol. Figure 21 shows with each addition and subsequent removal of alcohol the conversion increases, but this process will use more allyl alcohol as well as time and energy than the soybean oil process.

2.5 Kinetics of transesterification

2.5.1 Experimental Equipment

Reaction for kinetic data was carried out in a 250mL three-necked batch reactor, where the total volume of reactants was 140g. The reactor was equipped with a reflux condenser, magnetic stirrer, and a stopper to remove samples. The temperature of the reactor was maintained at 105°C.

The set of equilibrium reactions were carried out in Erlenmeyer flasks. A magnetic stirrer was used for stirring the chemicals.

2.5.2 Experimental Conditions

The experiments were planned to determine the reaction rate constants, effect of the catalyst concentration, and the temperature on reaction rate. The first experiment was carried out over 1 hour using potassium hydroxide as the catalyst at atmospheric pressure with a 6:1 molar ratio of allyl alcohol: soy oil.

Experiments were also conducted changing the potassium hydroxide concentration (0.25, 0.5, 0.75, 1, and 1.25 wt % of soy oil), and the mol ratios (1:2.4, 1:3, 1:3:6, 1:4.2, 1:4.8) for 6 hours.

2.5.3 Experimental Procedure

Experiment A: The reactor was initially charged with the amount of soybean oil, heated to 90°C. The potassium hydroxide was dissolved in the allyl alcohol and also heated to 90°C. Once both reached the temperature, the allyl alcohol solution was added to the stirred reactor. The reaction was timed as soon as the potassium hydroxide/allyl alcohol solution was added to the reactor, and it continued for 1 hour. During the reaction, samples of 1mL were taken at the following reaction times: 1, 2, 3, 4, 5, 7, 9, 11, 13, 15, 17, 19, 30, 40, 50 and 60 minutes. The samples were quenched immediately by cooling in 4mL of water that had been cooled in an ice bath and were then centrifuged to remove glycerol and water. For capillary gas chromatography, the known amount sample and internal standard was mixed and diluted with approximately 1mL of dichloromethane and then analyzed.

Experiment B: Various molar ratios (soybean oil: allyl alcohol) with different potassium hydroxide concentrations as described earlier were used for the reactions and samples were analyzed as described above.

2.5.4 Characterization

To ascertain the change in the reaction product composition over time samples were analyzed by capillary gas chromatography, which allowed for the simultaneous quantification of fatty acid methyl esters. The analyses were performed on a Hewlett-Packard 5890 series II chromatograph connected to a Hewlett-Packard 3396SA integrator, using a Supelco pta-5 30m X 0.25mm column with a film thickness of 1μm and FID detector. Methyl Undeconate was used as the internal standard. The glycerol concentration was determined, through the material balance of the reaction, from the previously calculated concentrations and the initial concentrations of triglyceride and allyl alcohol.

2.5.5 Results and Discussion

The mechanism for the given reaction is shown in Figure 22.

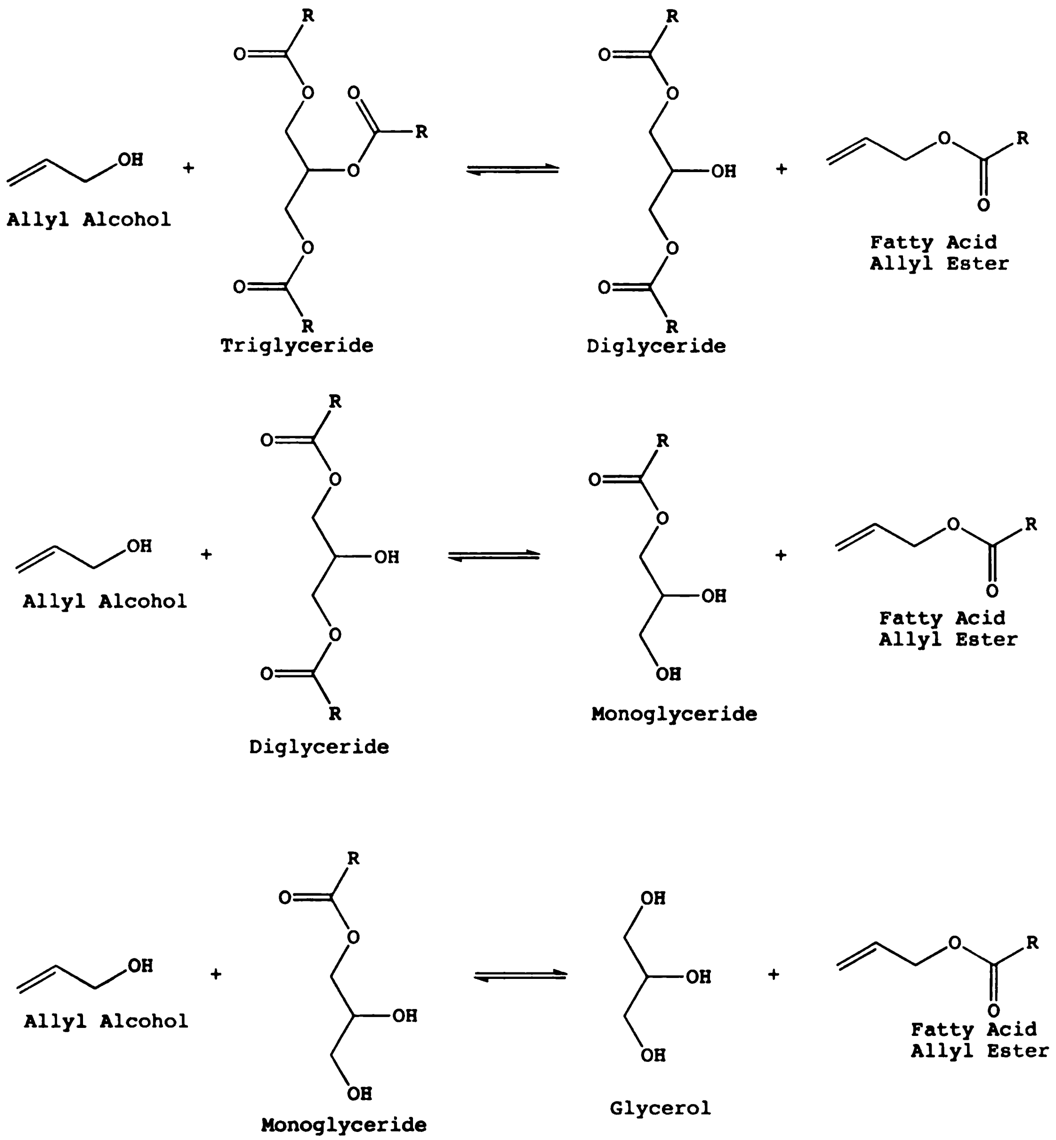


Figure 22: Step-wise Reaction for Allyl Ester Production from Soybean Oil

For calculation purposes this reaction is considered as one step (Figure 23).

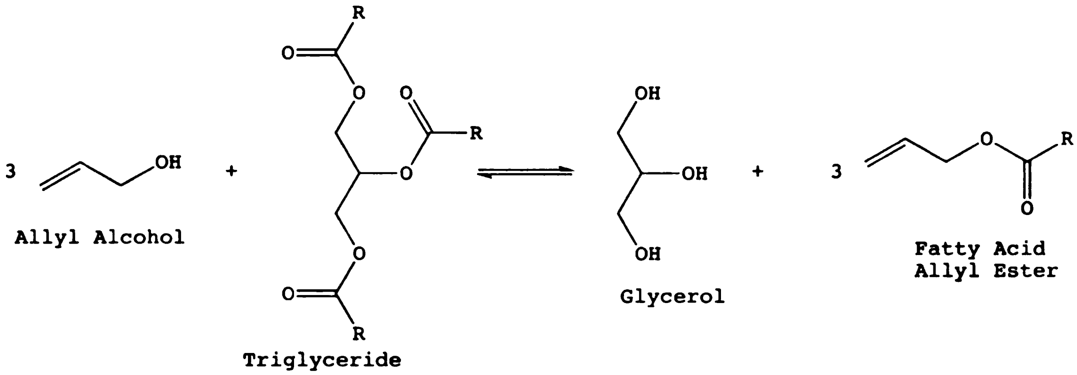


Figure 23: Reaction Scheme Used for Equilibrium Kinetics

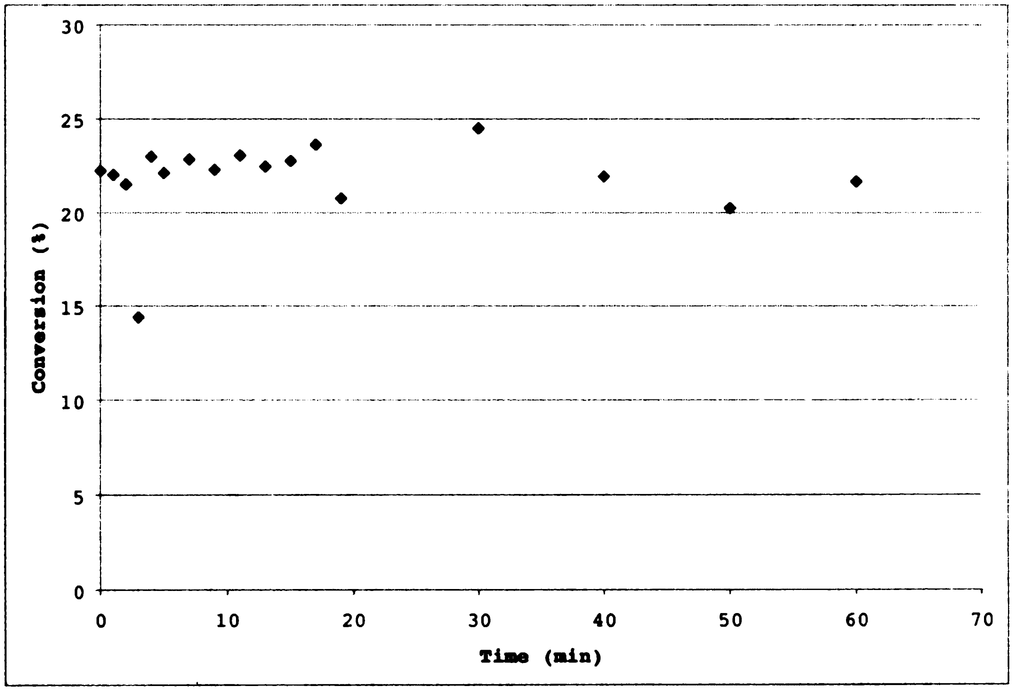


Figure 24: Percent Soybean Oil Conversion with Respect to Time

Figure 24 shows that for a given mole ratio of soybean oil, allyl alcohol, and catalyst concentration, the conversion of soybean oil does not change with respect to time. Also the conversion is not 100% at a mole ratio higher than theoretical. This means both the reactants and products are present in the system in a definite amount. So the system can be considered reversible. Equilibrium had been reached as soon as the samples were mixed. An important fact for this system is both of the reactants are miscible. At given potassium hydroxide concentration, the reaction is not kinetically controlled but mass transfer controlled. As both the reactants are miscible, only the mixing time is the time required to reach the equilibrium.

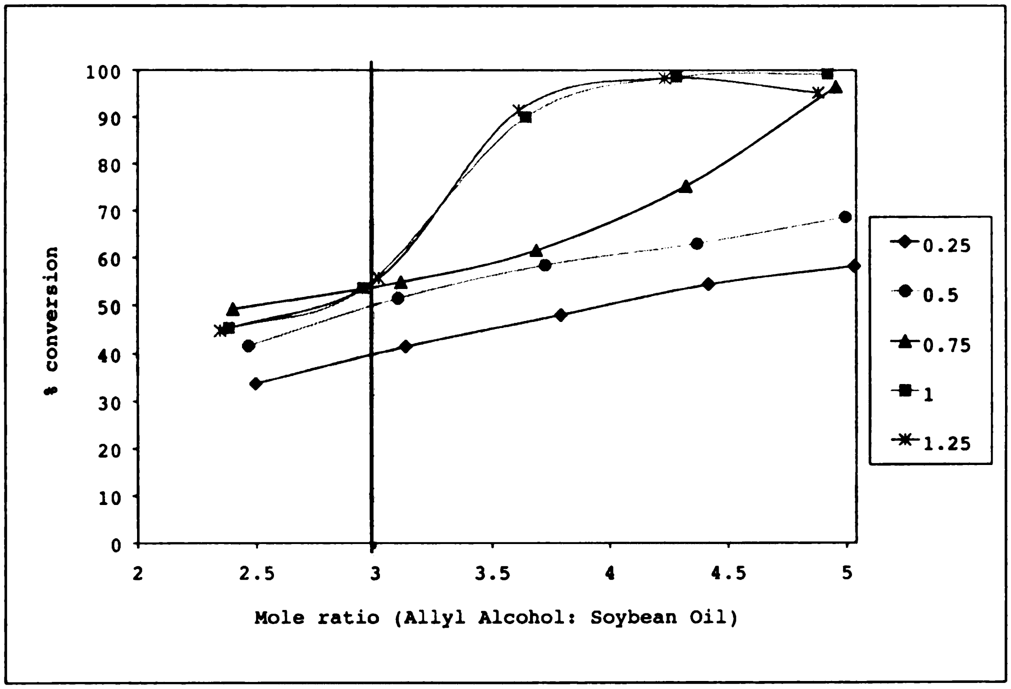


Figure 25: Effect of the Catalyst Concentration on Conversion

Figure 25 shows the effect of potassium hydroxide concentration for various molar ratios of soybean oil and allyl alcohol. Potassium hydroxide, as per the literature[62], was considered as a catalyst for the transesterification. If it is considered a catalyst, then the conversion for the same reactant mole ratios with different potassium hydroxide loading should remain constant. But Figure 25 shows increased conversion with increase in the potassium hydroxide loading. The theoretical mole ratio of the reactants is 1:3 (soy oil: allyl alcohol). The effect is more pronounced at higher than theoretical mole ratios. Based on the data available the equilibrium constant is calculated (see appendix 2 for calculation method). The equilibrium constant changes with respect to the mole ratios of soy oil and allyl alcohol as well as potassium hydroxide. The range of the equilibrium constant calculated is 0.68 to 1974.89. In this case the number of moles of reactants and products are same so the equilibrium constant has no units. Table 8 shows the equilibrium constant (K) for various soy oil, allyl alcohol and sodium hydroxide composition.

Mole ratio (Soy oil: allyl alcohol)	Percent Potassium hydroxide (Based on soy oil)	Percent soy oil conversion	Equilibrium constant (K)
2.50	0.25	33.75	0.68
3.13		41.55	1.23
3.79		48.06	1.11
4.42		54.43	0.89
5.03		58.26	0.98
2.46	0.50	41.72	8.72
3.10		51.55	9.86
3.72		58.48	7.11
4.37		63.02	5.32
4.99		68.65	4.43
2.40	0.75	49.28	19.59
3.11		54.90	15.15
3.69		61.57	11.80
4.32		75.23	26.65
4.95		96.52	179.64
2.38	1.00	45.33	42.74
2.95		53.61	33.89
3.64		89.99	503.95
4.28		98.55	1714.78
4.92		99.18	1105.43
2.35	1.25	44.83	56.84
3.02		55.71	49.91
3.61		91.39	818.19
4.23		98.27	1974.90
4.88		95.25	152.90

Table 8: Equilibrium Constant for Various Concentrations

CHAPTER THREE

COPOLYMERIZATION OF MONOMERS

3.1 Literature Review

3.1.1 Modified Triglycerides

As discussed previously, there are many modifications that can be made to a triglyceride (some natural triglycerides have the same modifications) in order to produce a monomer to be used in polymerization. Epoxidized oils have been used to improve the processing of PVC (Polyvinyl chloride). It acts as both a stabilizer and a plasticizer.[9, 11, 32, 40] This is not the only use for epoxidized oils; they have been used in the production of UV cureible[10-12] and thermosetting coatings[55]. Some of these systems have been known to be biodegradable[33] and have moderate glass transition temperatures (Tg) and thermal properties.[12] The acrylated epoxidized oils have been used to produce pressure sensitive adhesives[48] and polymers with a high Tg and a high modulus.[9, 40]

Hydroxylated oils and polyols are generally used in the production of polyurethanes.[31, 42, 43, 45, 46] The polyurethanes

are produced using a condensation reaction with an isocyanate.[43] Polyurethanes from vegetable oil polyols can have properties ranging from a hard rubber to a rigid plastic; some are also rigid to soft foams.[31]
The maleates soybean oil monoglycerides have also been used to make polymer resins by copolymerizing them with styrene[41] and by maleation mixtures of the monoglyceride and neopentyl glycol then copolymerizing the resulting mixture with styrene.[9, 40, 50] The cured thermoset copolymer of the maleate with styrene was a clear rigid solid with a slight yellow hue.[51] With the addition of the neopentyl glycol the Tg of the resulting thermoset was increased, where as the tensile strength and modulus decreased over previous polymer.[50]

3.1.2 Unmodified Triglycerides

One method for polymerizing triglycerides without modification to the double bonds is by using a cationic initiator. These initiators are usually Lewis acids or protonic acids.[13, 38, 39] The most common copolymers produced are a triglyceride with divinylbenzene or a divinylbenzene/styrene mixture.[38, 39, 64, 65] Cationic polymerization is possible due to the stability of the intermediate carbocation (a positively charged ion of carbon) of the internal double bonds.[38] By this method high molecular weight polymers could be produced because the triglyceride itself has a high molecular weight and since each of the fatty acids of the triglyceride can react (meaning it is multifunctional) longer chains can be produced.[13, 38] Conjugation of the internal double bonds (which is natural in some oils[66] and can be produced by a catalyzed reaction[67]) produces a higher molecular weight. Its intermediate carbocation is more stable than that of the nonconjugated double bonds.[38, 46] The copolymers produced from triglycerides, divinylbenzene and styrene have been found to be soft rubbers to hard thermosets depending on the reaction conditions.[13, 38, 39] Many of these polymers were found to be good damping materials[13, 38, 39, 68, 69] and have shape memory.[13, 38, 65, 68] When the reaction was completed with dicyclopentadiene as the comonomer tough and ductile materials to very soft materials were the result.[13,70]

3.1.3 Fatty Acid polymerization

Allyl esters are polymerized via free radical polymerization. The three typical process; initiation, propagation and termination; all occur during these polymerizations.[71] Chain transfer, also a normal process in free radical systems, occurs in the polymerization of allyl systems. However, in the allyl systems the chain transfer leads to a termination of not only the growing chain, but the chain reaction itself.[59, 60, 71, 72] The radical produced in the degradative chain transfer is very stable; it is stabilized by the resonance and is therefore less active – essentially terminated.[71] This is why many allyl polymerizations are characterized by little polymerization and low molecular weights.[59, 60, 71, 72]

A method for reducing the degradative chain transfer in an allyl polymerizations has been described by Shigetomi et al. This method retards the degradative chain transfer by inhibiting the "abstraction of the allylic hydrogen[72]." This means that it would prevent the chain transfer to a stable resonance. By adding an electron-attracting group (such as an ester) to the allyl compound, the electron density of the double bond in the allyl group will be affected and assist in retarding the degradative chain transfer.[72]

Copolymerizations of some allyl undecanoates with styrene, methyl acrylates, and vinyl chloride have been attempted.

The polymerizations with styrene and methyl acrylates had very little of the ester intergraded in to the polymer matrix. The vinyl chloride was the exception, the allyl ester readily polymerized with it.[73]

When allyl esters of long chain fatty acids were polymerized (soybean,[59] cottonseed,[55] and palm esters[56] as well as other long chain esters[60]) little of the esters were able to homopolymerize. If sufficient initiator was used to achieve high yields, the polymers geled.[56] Gan et al. found that if the fatty acid was epoxidized before polymerization the yield could be increased. The oxirane group did not participate in the polymerization and remains intact[56]. The copolymerization of the long chain fatty acid esters with diallyl pthalate yielded materials ranging from tough to soft colorless.[60]

3.2 Polymerization

3.2.1 Monomer synthesis

The biobased monomer (allyl ester) used in the copolymerization was produced by transesterification of soybean oil. Please refer to the chapter 2 for this procedure.

3.2.2 Polymer Synthesis

Approximately 6g of monomer was mixed with .2g 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane (trade name Luperox 101). The ratio of allyl ester to styrene used in each sample can be seen in Table 9.

Vial #	Styrene (g)	Styrene (M) MW=104	Allyl Ester (g)	Allyl Ester (M) MW~325	Molar ratio Styrene/ Ester
1	5.041	0.04847	1.001	0.003080	100: 6.4
2	4.000	0.03846	2.008	0.006178	100:16.1
3	3.074	0.02956	3.005	0.009246	100:31.3
4	2.014	0.01937	4.001	0.012317	100:63.6

Table 9: Ratios of Allyl Ester to Monomer in the Feed

20mL syntelation vials were used to prepare each polymer sample. After the monomer and initiator were added to the vial, the vial was flushed with nitrogen to remove the oxygen in the vial. Each vial was then stoppered with cotton and heated in an oil bath at 140°C with constant mixing for five hours. Once the samples were cool, 10mL of toluene was added to each sample. This dissolved both the polymer formed and the unreacted monomer. The polymer was then precipitated in methanol by drop wise addition. The solid polymer was then filtered using a Büchner funnel and dried overnight in the oven. After drying the polymer was dissolved in 10mL of toluene and precipitated, filtered and dried a second time using the same methods to ensure the removal of unreacted monomer.

3.2.3 Materials

The low saturate soybean oil was obtained from Zeeland Farm Services, Zeeland Michigan, and the allyl alcohol was purchased from Fisher Scientific. All other materials used were obtained from reliable sources. Prior to usage the styrene and the 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane was stored in the refridgerator to prevent any autopolymerization (styrene) and degradation (initiator). The styrene was rotovapped under vacuum to remove the inhibitor (4-tert-butylcatechol) prior to mixing with the allyl ester monomer.

3.2.4 Characterization

The polymer product was characterized using Gel Permeation Chromatography (GPC), Thermogravimetric Analysis (TGA), Differential Scanning Caliometry (DSC) and Nuclear Magnetic Resonance (H-NMR). GPC samples were prepared by dissolving a 20mg sample into tetrahydrofuran. 100μL of each sample was injected into the column. The GPC was equipped with Waters icocratic pumps, a Waters 717 autosampler and a Waters 2414 refractive index. Waters breeze software was used to collect and analyze the data. TGA was performed using a TA Instruments TGA Q500 in a Nitrogen atmosphere. The samples were heated in a platinum pan to 500°C from room temperature at a rate of 10°C/min, until the sample was completely degraded. A TA Instruments DCS Q2000 with auto sampler was used for obtaining the DSC spectra. The samples were prepared using a standard aluminum pan; each sample was cooled to -10°C where it was allowed to equilibrate. The samples were then heated to 130°C at a rate of 10°C/min in a nitrogen atmosphere. H-NMR was performed using a Varian Inova-300 operating at 300.103 MHz.

3.2.5 Results

The molecular weight of the polymers formed were found to be relatively low and is dependent on the monomer ratio. Both the number average molecular weight (Mn) and the weight average molecular weight (Mw) are proportional to the amount of styrene monomer. The Mn (Figure 26) increases linearly with increasing styrene concentration in the monomer mixture. The Mw also increases but has a much faster rate of increase. This difference in rate gives a broad molecular weight distribution.

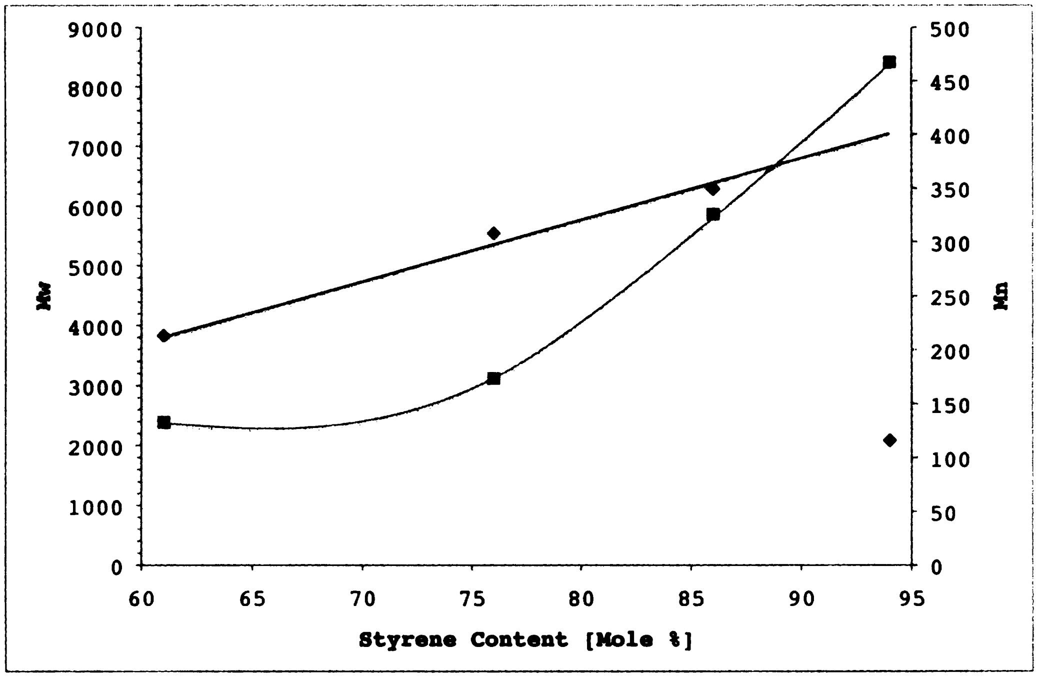


Figure 26: Molecular Weight as a Function of Monomer Feed

The broad molecular weight distribution could be an effect of chain transfer to the internal double bond of the allyl ester. This chain transfer will lead to termination of the chain growth and a broad distribution would result.

The TGA (Figure 27) confirms that both the styrene and the allyl ester are found in the polymer. This is seen in the two degradation peeks, the first at approximately 190°C and the second at approximately 400°C. These two peaks would correlate to the allyl ester and styrene respectively (TGA traces for samples 2-4 can be seen in Appendix 3).

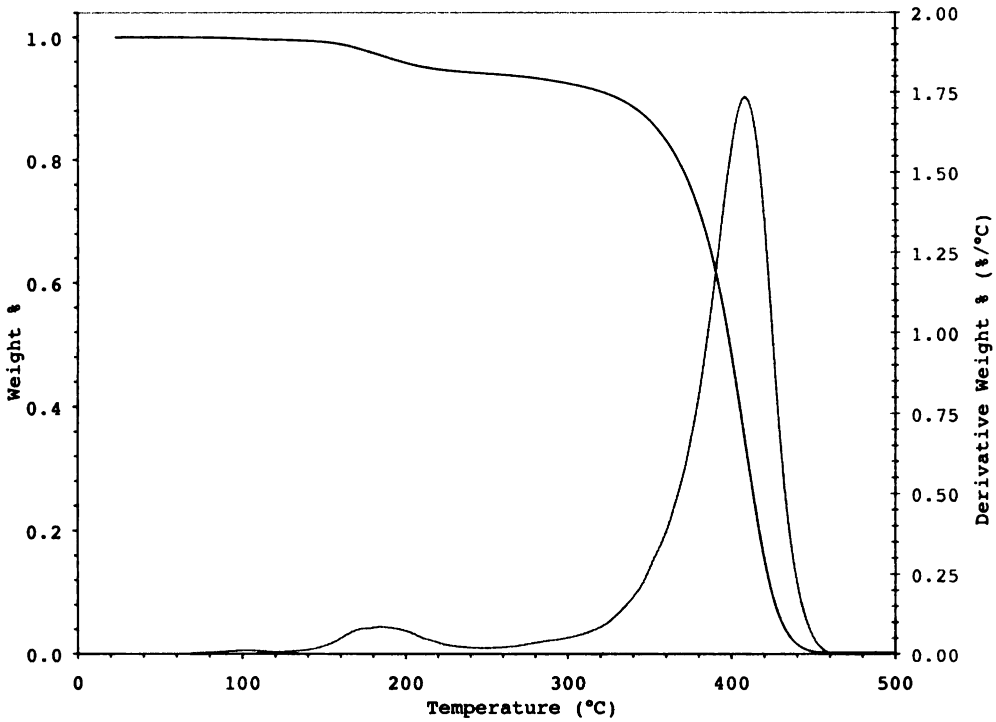


Figure 27: TGA of Styrene/Allyl Ester Polymer (Sample 1)

The DSC curve (Figure 28) confirms a random copolymer was produced. There is only one Tg (glass transition temperature) shown between 40°C and 60°C. This is indicative of a random copolymer, a graft or block copolymer would show the two individual Tg's for the homopolymers that are within the copolymer. Since the Tg of styrene is approximately 366°C (in air)[74], and is not seen in the curve, the configuration of the monomers can only be random.

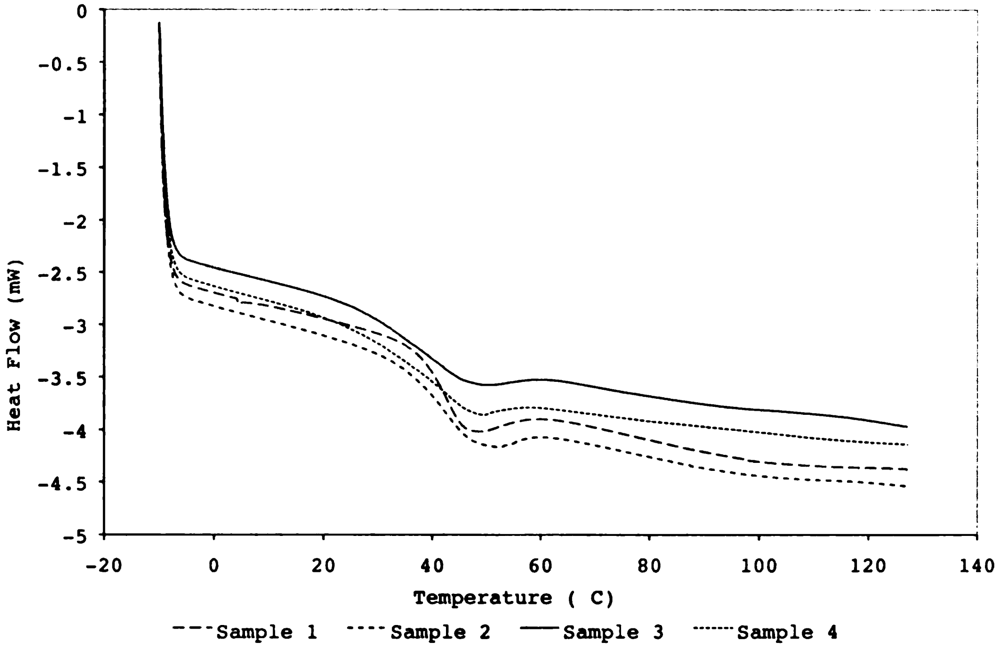
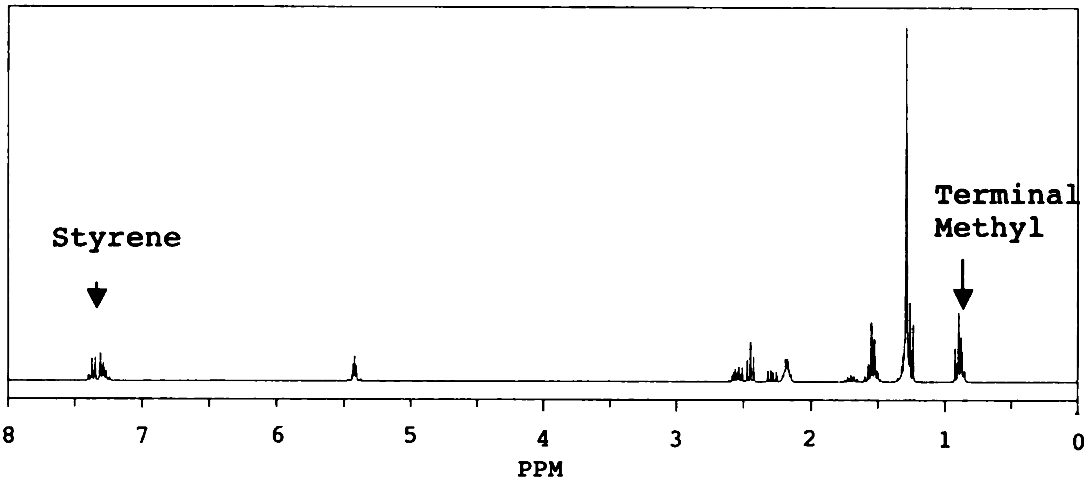


Figure 28: DSC Traces of the Four Copolymer Samples

The H-NMR spectra are used to determine the amount of allyl ester that has been incorporated into the copolymer. Figure 29 is a simulated H-NMR spectrum (actual spectra can be found in Appendix 4), along with the structure of the copolymer. This simulation was used to determine the sets of peaks that relate to the two monomers used to produce the polymer. In this case the proton attached to the benzene ring in the styrene (at 7.2ppm) and the terminal methyl group in the ester chain (at .9ppm).



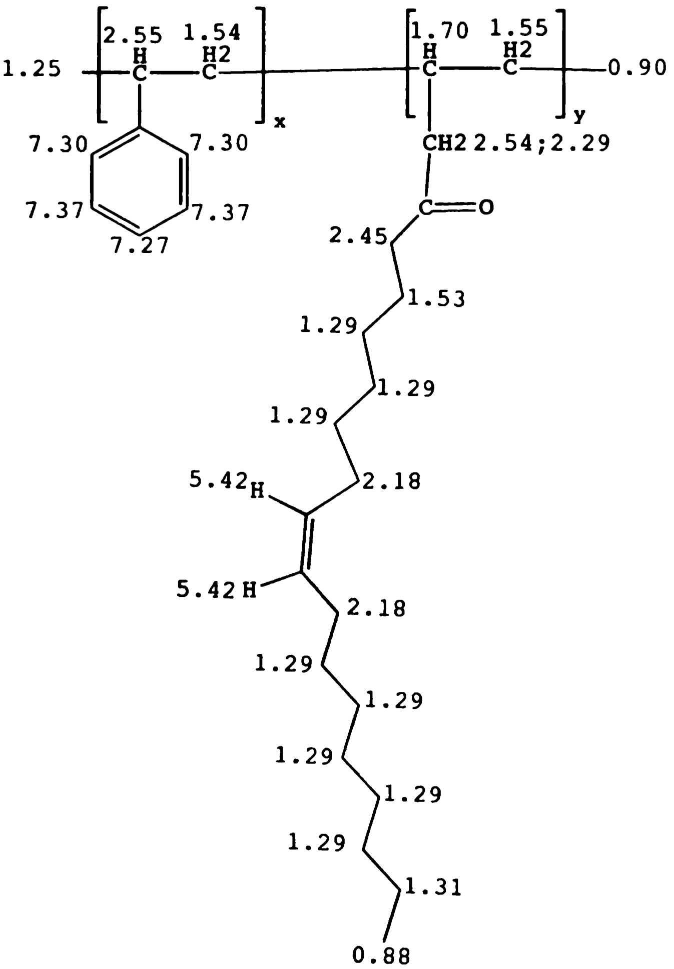


Figure 29: Simulated H-NMR and Copolymer Structure

The heights of these two peaks correlate to the number of protons in the sample that will correspond to each of the structures. By using the number of hydrogen's found in each structure (5 for the ring in styrene and 3 in the methyl group) the total number of each structure and the ratio between them can be found, and consequently the ratio of styrene to ester in the copolymer. The heights of these two peaks and the resulting ratios are seen in Table 10.

Vial#	Styrene @7.2 ppm		Ester @ 0.9 ppm		Ratio Styrene/Ester
	Peak Height	5H	Peak Height	3H	
1	2587	517	137	46	100 : 9
2	2006	401	186	62	100 : 15
3	3202	640	580	193	100 : 30
4	3049	610	567	189	100 : 31

Table 10: H-NMR Peak Heights of the Copolymers and the Resulting Monomer Ratios in the Copolymer

When the copolymer composition and the initial monomer feed are compared (Figure 30) there is an initial increase in allyl ester in the polymer with increasing allyl ester in the monomer feed. However, there is a maximum allyl ester that can be incorporated into the copolymer.

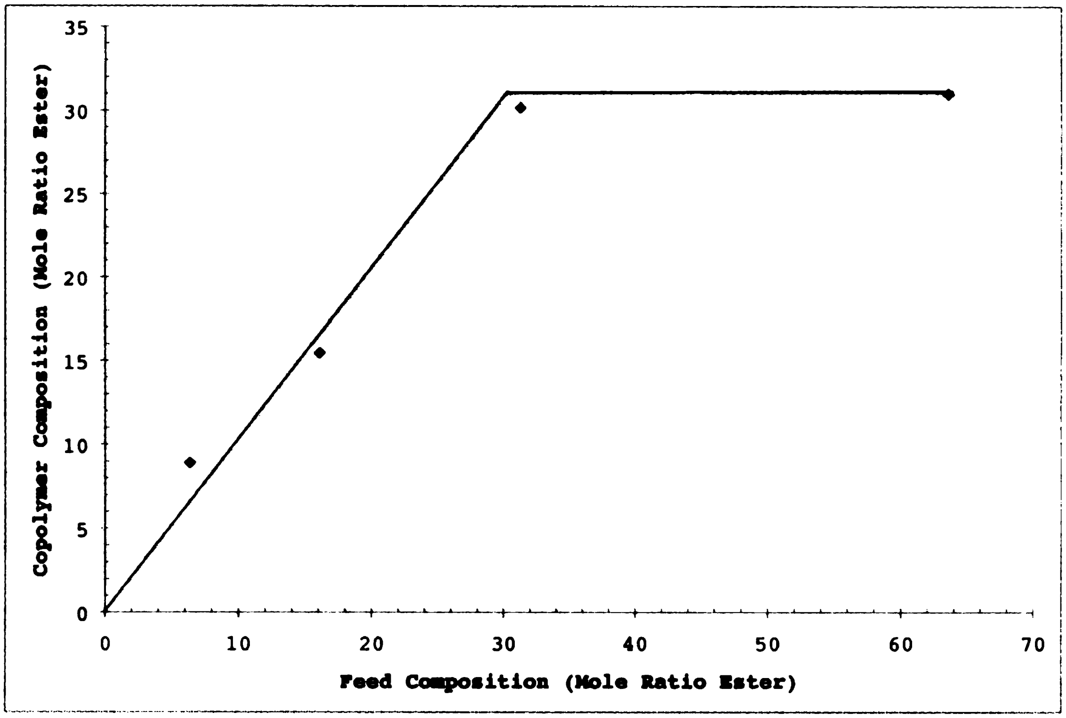


Figure 30: Composition of Allyl Ester in the Monomer Feed and the Resulting Copolymer

This maximum of 30% allyl ester is most likely due to the long chains of the ester. These chains would interfere with the ester homopolymerizing, and therefore a need for styrene monomers to separate the esters when they are polymerized. This is in agreement with Gan et al. the allyl ester of palm oil did not homopolymerized to any appreciable extent.

CHAPTER 4

CONCLUSIONS

4.1 Review of Work and Results

Allyl Esters from soybean oil were produced using two different methods, transesterification of the triglycerides and transesterification of the methyl ester that was produced from the triglyceride. Both of these methods produced the desired product (as proven by GC, FTIR and H-NMR), however not to the same extent. The conversion of the soybean oil was significantly higher than the methyl ester, and although it may be possible to achieve similar conversion the process would not be more efficient than the production from soybean oil.

The kinetics of the transesterificaton of soybean oil was also investigated. The equilibrium constants were calculated for various allyl alcohol/soybean oil/potassium hydroxide ratios. The reactions using the same reactant concentrations but different potassium hydroxide concentrations produced different equilibrium conversions. The allyl esters were also copolymerized via free radical polymerization with styrene. The polymers produced were found to have increasing molecular weight with increasing styrene concentration. By using TGA and DSC, the polymers were found to have both monomers integrated into the polymer matrix and a random copolymerization was achieved. The maximum ratio of styrene to ester found in the copolymers was 100:30. This is likely the maximum amount of ester that can be integrated in the polymer due to the bulk of the ester chains.

4.2 Future Work

There has been a general push in society to produce biobased materials in all areas of industry. It would be useful to explore any uses for the copolymers that were produced. One likely use for the polymer is a fuel additive for biodiesel to reduce the cloud point, pour point or the cold filter plug point. These polymers long chains that can interrupt the formation of crystals and would be able to incorporate into the biodiesel because they contain the same type of molecules, just like the alpha olefin polymers can incorporate into petroleum disesl. Copolymerizing the materials with other vinyl monomers may also produce useful biobased materials that can be used in industry.

Appendix 1: Theoretical Iodine Value Calculation

The soybean oil in our lab contains the following weight percent of each component (as a FAME)

Weight %	Name	Structure	Molecular weight (g/mol)
4.41	Palmitic	16:0	270.46
3.23	Stearic	18:0	298.56
21.90	Oleic	18:1	296.50
61.59	Linoleic	18:2	294.48
8.87	Linolenic	18:3	292.46

Table 11: Composition of Soybean Oil Used in Experiments

The average molecular weight of a FAME

$$\left(.0441 * 270.46 \frac{g}{mol}\right) + \left(.0323 * 298.56 \frac{g}{mol}\right) + \left(.2190 * 296.56 \frac{g}{mol}\right) + \left(.6159 * 294.48 \frac{g}{mol}\right) + \left(.0887 * 292.46 \frac{g}{mol}\right) = 293.81 \frac{g}{mol}$$

Average C=C per mole

$$.2190 * 1 \frac{C = C}{\text{Mole}} + .6159 * 2 \frac{C = C}{\text{Mole}} + .0887 * 3 \frac{C = C}{\text{Mole}} = 1.72 \frac{C = C}{\text{Mole}}$$

To produce the allyl ester there is an addition of the "allyl" (41.08g/mol) and a "subtraction" of the methyl (15.04g/mol).

$$293.81 \frac{g}{mol} + 41.08 \frac{g}{mol} - 15.04 \frac{g}{mol} = 319.85 \frac{g}{mol}$$

In the allyl "addition" there is an addition of 1 double bond per mole

$$2.72 \frac{C = C}{mol}$$

To produce the methyl ester from the soybean oil the glycerol backbone (41.08 g/mol) is "subtracted" and the methyl (15.04 g/mol) is added, one for each fatty acid in the triglyceride. To work backwards from the FAME there are 3 FAMEs per triglyceride and 3 methyl's need to be removed and one glycerol backbone needs to be added.

$$3 * 293.81 \frac{g}{mol} + (3 * 15.04) \frac{g}{mol} - 41.08 \frac{g}{mol} = 877.39 \frac{g}{mol}$$

Since there are three FAMEs per triglyceride, there are three times the double bonds per mole.

$$\left(3 * 1.72 \frac{C = C}{mol}\right) = 5.16 \frac{C = C}{mol}$$

Iodine values are calculated on a cg of iodine basis and each mol of iodine reacts with a mole of C=C, the following are the theoretical iodine values for each ester and the starting soybean oil reactant.

The Fame

$$1g * \frac{mol}{293.81g} * \frac{1.72C = C}{mol} * \frac{mol\, I_2}{mol\, C = C} * \frac{254g\, I_2}{mol\, I_2} * \frac{100cg}{g} = 148.69$$

The allyl ester

$$1g * \frac{mol}{319.85g} * \frac{2.72C = C}{mol} * \frac{mol\, I_2}{mol\, C = C} * \frac{254g\, I_2}{mol\, I_2} * \frac{100cg}{g} = 216.00$$

The soybean oil

$$1g * \frac{mol}{877.39g} * \frac{5.16C = C}{mol} * \frac{mol\, I_2}{mol\, C = C} * \frac{254g\, I_2}{mol\, I_2} * \frac{100cg}{g} = 149.38$$

Appendix 2: Equilibrium Constant Calculation Method

The equilibrium constant is calculated using the general kinetics equation; the concentration of the products divided by the concentration of the reactants, each concentration is raised to the power of its stoichiometric ratio (equation 1).

$$K = \frac{[Glycerol][Allyl\ Ester]^3}{[Allyl\ Alcohol]^3[Soybean\ Oil]} \quad (1)$$

The initial masses of materials are the variables S (Soybean oil), and A (Allyl Alcohol).

The moles of initial materials (S_M and A_M, equations 2 and 3) were calculated using the molecular masses for soybean oil (876 g/mole) and allyl alcohol (58 g/mole)

$$S_M = \frac{S}{876} \quad (2) \qquad A_M = \frac{A}{58} \quad (3)$$

The volume of the initial materials (S_V and A_V, equations 4 and 5) were calculated using the density of soybean oil (.92 g/mL) and allyl alcohol (.854 g/mL)

$$S_V = \frac{S}{.92} \quad (4) \qquad A_V = \frac{A}{.854} \quad (5)$$

The total volume of materials was calculated using equation 6

$$T_V = S_V + A_V \quad (6)$$

Next, the concentration of the initial materials in mol/L was calculated using equations 7 and 8

$$S_C = \frac{S}{T_V} * \frac{1}{1000} \quad (7) \qquad A_C = \frac{A}{T_V} * \frac{1}{1000} \quad (8)$$

Using the GC data; where A_{GC} is the percent allyl alcohol in the sample, E_{GC} is the percent allyl ester in the sample, I_{GC} is the percent internal standard in the sample, and I is the grams of internal standard in the GC sample the grams of allyl alcohol (A_G) and allyl ester (E_G) in the GC sample was calculated (equations 9 and 10).

$$A_G = \frac{A_{GC} * I}{I_{GC}} \quad (9) \qquad E_G = \frac{E_{GC} * I}{I_{GC}} \quad (10)$$

T_G (equation 11) represents the amount of allyl alcohol and allyl ester in the original GC sample. The amount of soybean in the original GC sample is calculated using the initial material placed in the GC vial (M) and the amount of ester and alcohol calculated (equation 12).

$$T_G = A_G + E_G \quad (11) \qquad S_G = M - T_G \quad (12)$$

The masses that were placed in the GC vial were then used to calculate the percentages of soybean oil (S_P), allyl alcohol (A_P) and allyl ester (E_P) in the original product (equations 13, 14 and 15).

$$A_P = \frac{A_G}{(T_G + S_G)} * 100 \quad (13) \qquad E_P = \frac{E_G}{(T_G + S_G)} * 100 \quad (15) \qquad S_P = \frac{S_G}{(T_G + S_G)} * 100$$

(16)

However to calculate the equilibrium constant the amount of glycerol in the product also needs to be calculated. This creates a circular argument since the total mass of the end product depends on the amount of glycerol produced but the amount of glycerol produced is dependant on the amount of reactants used (in this case the amount of allyl alcohol used, A_{PG}). Using a computer, the circular argument seen using equations 17 through 21 was solved.

$$A_{PG} = \frac{A_P * T}{100} \quad (17) \qquad S_{PG} = \frac{S_P * T}{100} \quad (18)$$

$$E_{PG} = \frac{E_P * T}{100} \quad (19) \qquad G_{PG} = \frac{A_{PG} * 92}{958} \quad (20) \qquad T = S + A - G_{PG} \quad (21)$$

These equations produce the mass of allyl alcohol (A_{PG}), soybean oil (S_{PG}), allyl ester (E_{PG}) and glycerol (G_{PG}, this is calculated using the mass of allyl alcohol, the molecular weight of glycerol, 92g/mole and the molecular weight of total ester used, 958g/mole) after the reaction as well as the total mass of the material after the reaction less the mass of glycerol (T).

From the masses calculated the volumes of each component in the product was calculated, using the densities of each in g/mL (S_{PV} is soybean oil, A_{PV} is allyl alcohol, E_{PV} is the allyl ester and G_{PV} is the glycerol), along with the total volume, T_{PV} (equations 22-26)

$$S_{PV} = \frac{S_{PG}}{.92} \quad (22) \qquad A_{PV} = \frac{A_{PG}}{.854} \quad (23) \qquad E_{PV} = \frac{E_{PG}}{.875} \quad (24)$$

$$G_{PV} = \frac{G_{PG}}{1.261} \quad (25) \qquad T_{PV} = S_{PV} + A_{PV} + E_{PV} + G_{PV} \quad (26)$$

The moles of Product were calculated next, equations 27-30, using the molecular weight of each component in g/mole (S_{PM} is soybean oil, A_{PM} is allyl alcohol, E_{PM} is the allyl ester and G_{PM} is the glycerol)

$$S_{PM} = \frac{S_{PG}}{876} \quad (27) \qquad A_{PM} = \frac{A_{PG}}{58} \quad (28)$$

$$E_{PM} = \frac{E_{PG}}{319.33} \quad (19) \qquad G_{PM} = \frac{G_{PG}}{92} \quad (30)$$

Next the concentrations of each component in the product were calculated in mol/L (equations 31-34) using the moles and volumes calculated previously.

$$S_{PC} = \frac{S_{PM}}{T_{PV}} * \frac{1}{1000} \quad (31) \qquad A_{PC} = \frac{A_{PM}}{T_{PV}} * \frac{1}{1000} \quad (32)$$

$$E_{PC} = \frac{E_{PM}}{T_{PV}} * \frac{1}{1000} \quad (33) \qquad G_{PC} = \frac{G_{PC}}{T_{PV}} * \frac{1}{1000} \quad (34)$$

Finally the equilibrium constant was calculated using the general kinetics equation was calculated (equation 35) as well as the percent conversion (equation 36).

$$K = \frac{[Glycerol][Allyl\ Ester]^3}{[Allyl\ Alcohol]^3[Soybean\ Oil]} \qquad K = \frac{G_{PC} * E_{PC}^3}{A_{PC}^3 * S_{PC}} \qquad (35)$$

$$C = \frac{S_M - S_{PM}}{S_M} * 100 \qquad (36)$$

Appendix 3: TGA Traces of the Copolymer Samples

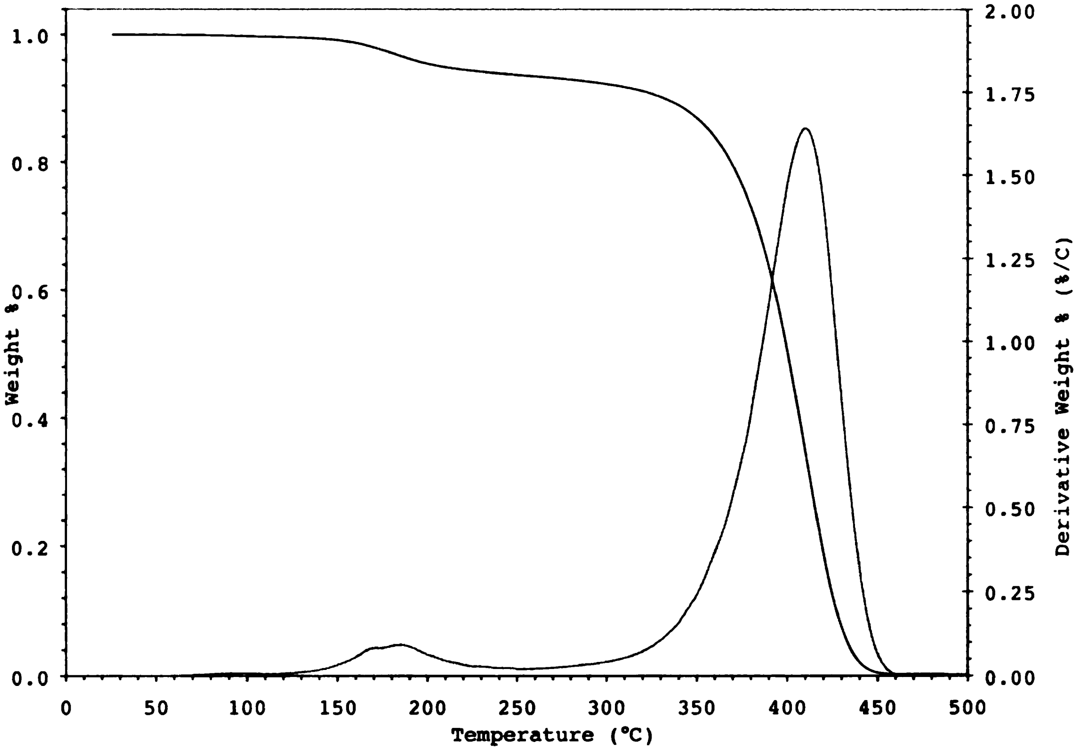


Figure 31: TGA Trace for Copolymer Sample 2

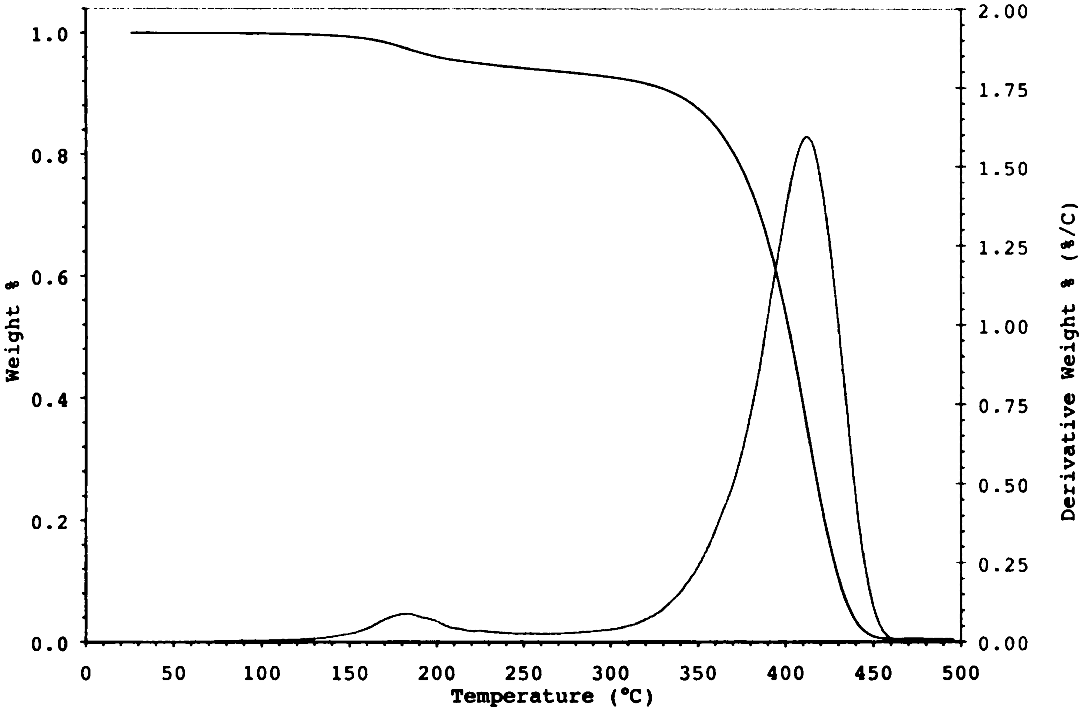


Figure 32: TGA Trace for Copolymer Sample 3

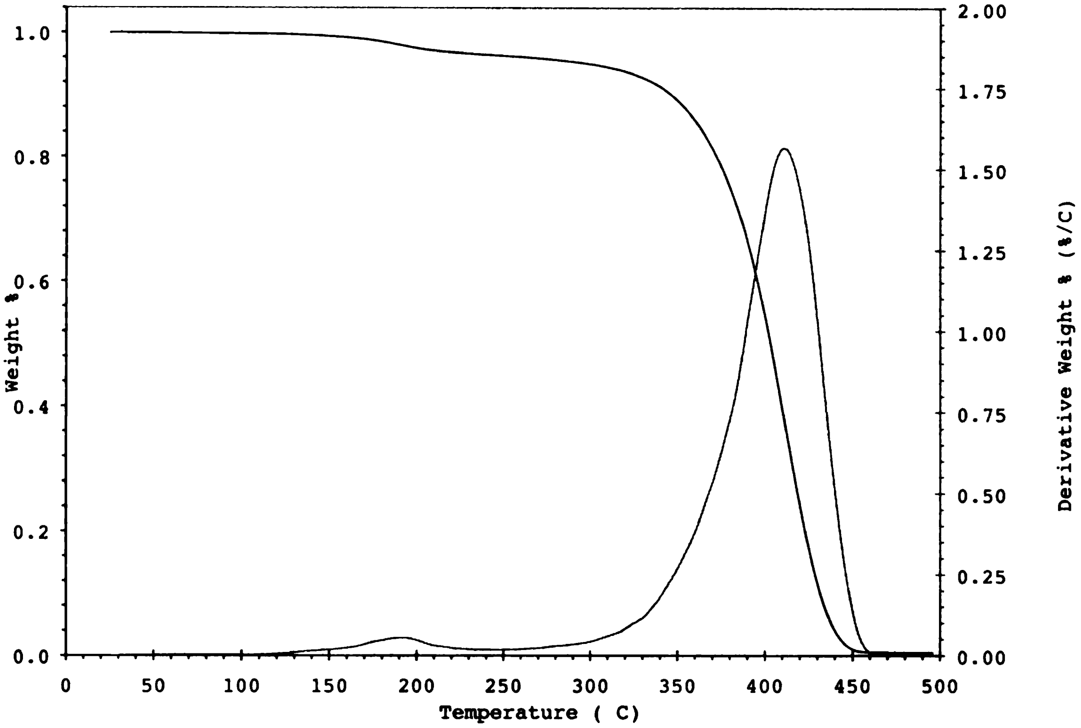


Figure 33: TGA Trace for Copolymer Sample 4

Appendix 4: H-NMR Spectra of the Copolymer Samples

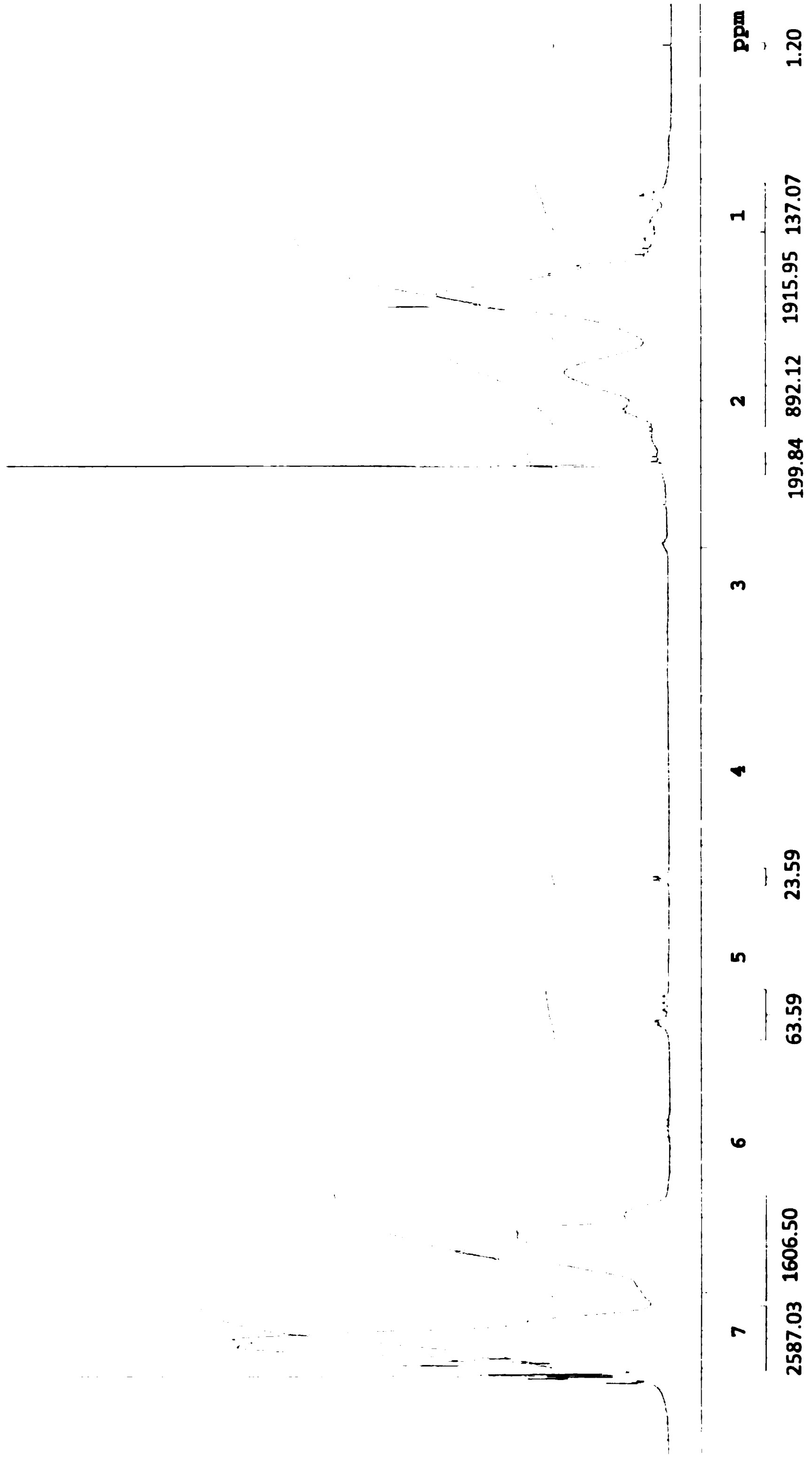


Figure 34:H-NMR Spectrum for Copolymer Sample 1

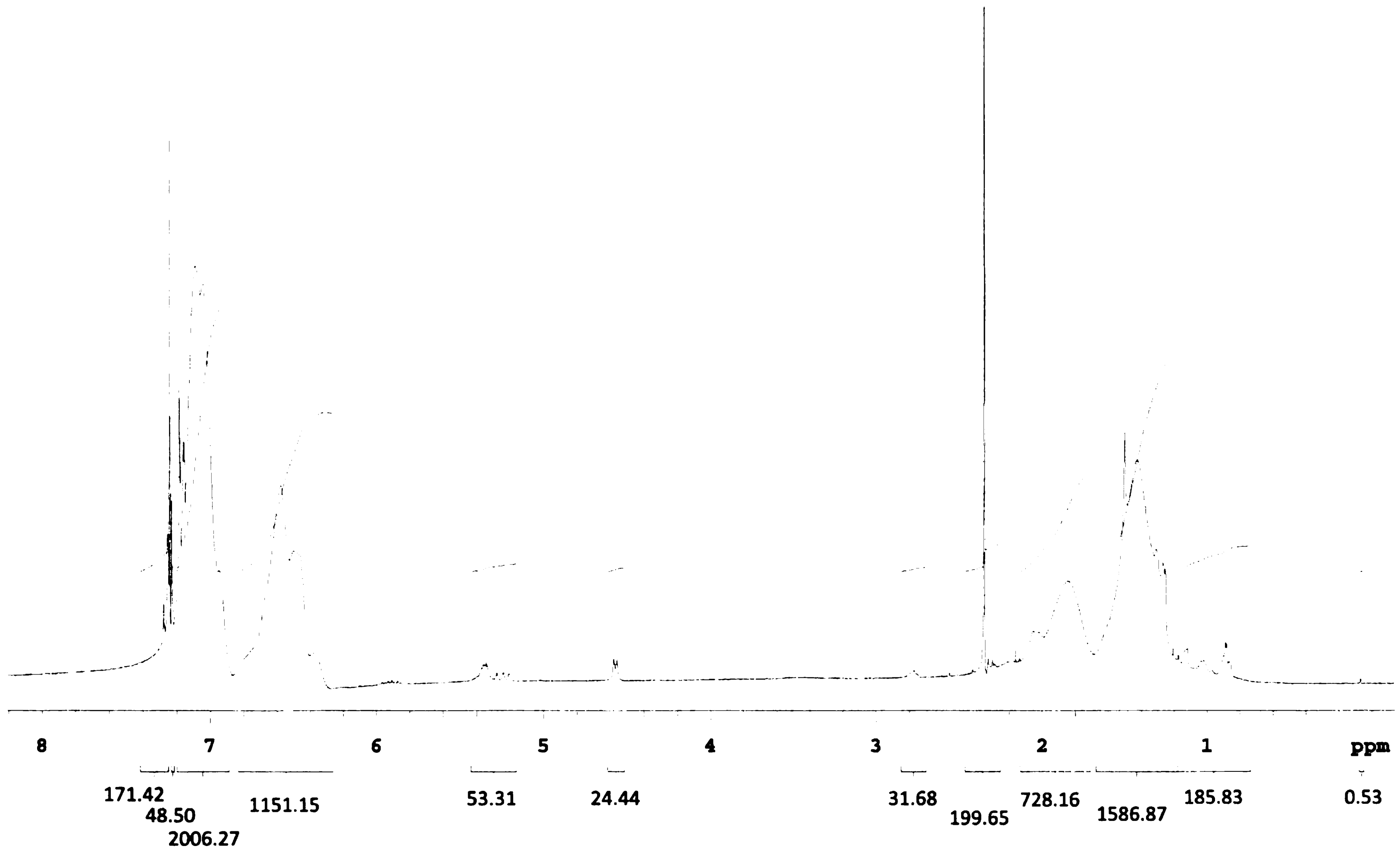


Figure 35: H-NMR Spectrum Copolymer Sample 2

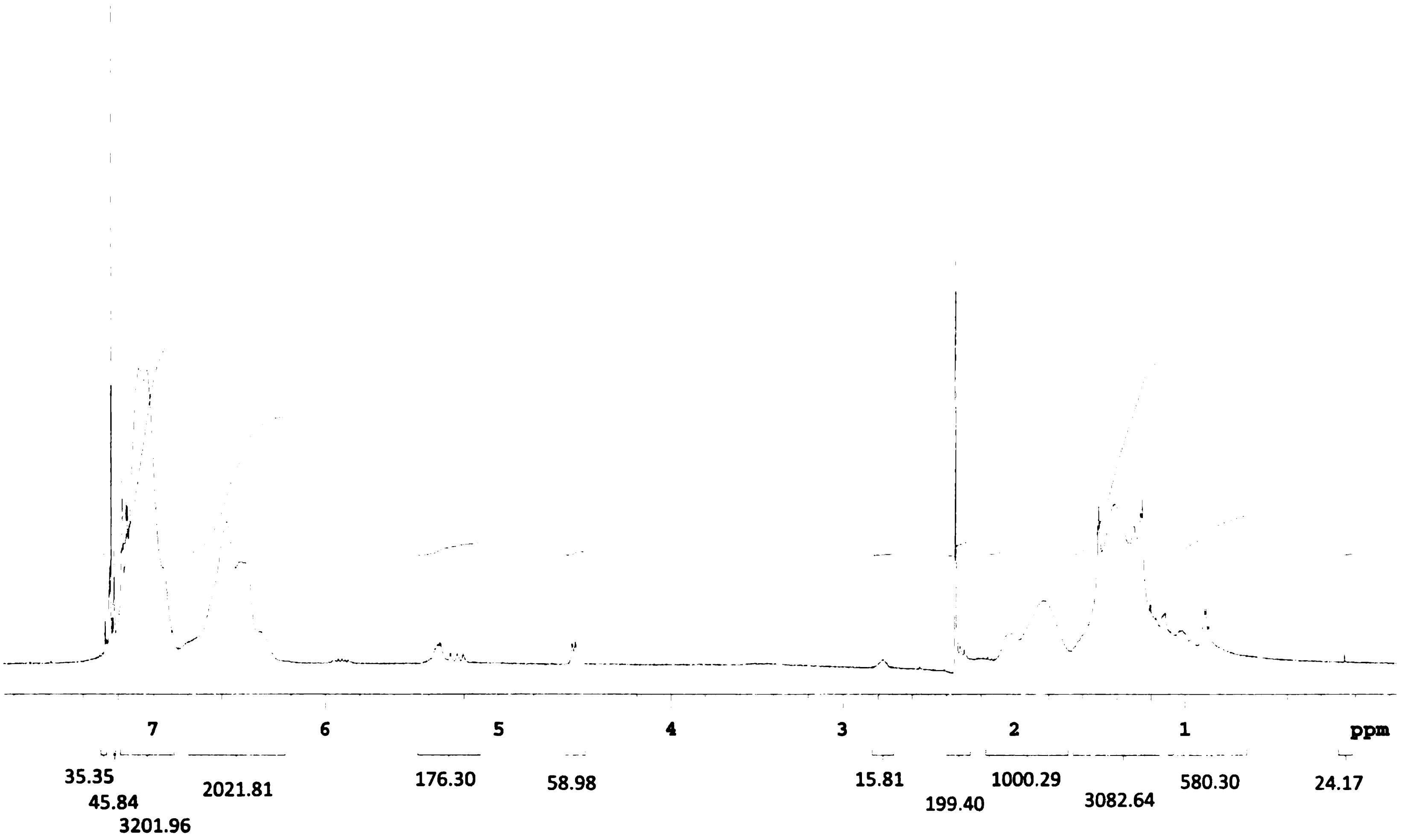


Figure 36: H-NMR Spectrum Copolymer Sample 3

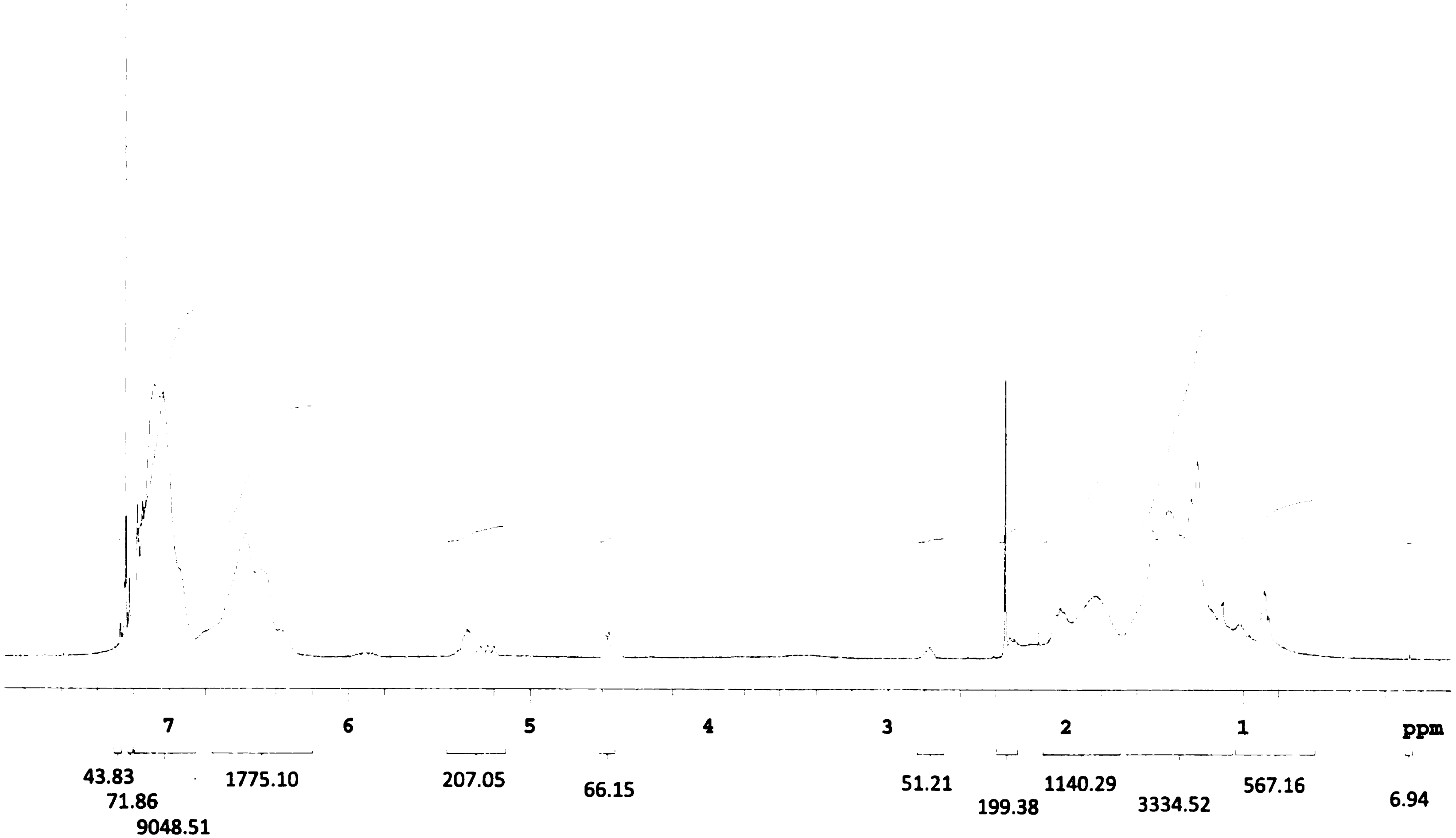


Figure 37:H-NMR Spectrum Copolymer Sample 4

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