NEW BIO-ACTIVE AND SURFACE ACTIVE PLANT OIL DERIVATIVES

by

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To my family

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ABSTRACT

NEW BIO-ACTIVE AND SURFACE ACTIVE PLANT OIL DERIVATIVES

The search for biodegradable materials from renewable resources instead of petroleum oil based materials is motivated by the growing concern for sustainability. The vegetable biomass is one of the promising renewable material resources due to their low cost and high availability. In this thesis, synthesis of biodegradable soybean oil based, bio-active and surface active materials were carried out. Starting material for synthesis was soybean oil – maleic anhydrides adduct (SOMA) which has highly reactive anhydride groups attached to the triglyceride. First novelty in this thesis is quantitative determination of the number of anhydride groups per triglyceride by NMR analysis using the mono-benzyl ester derivative of SOMA. Secondly, the number of anhydride groups per triglyceride was maximized by the use of Lewis Acid catalyst. SOMA is an excellent reactant for reaction with molecules having primary hydroxyl and amino groups. When these molecules are water soluble, an amphoteric molecule having an oleophilic end and a hydrophilic end is produced and these would act as excellent bio-based emulsifying agents. In this thesis glucose, riboflavin, polyethylene glycols and their monoesters, and Jeffamines were attached to soybean oil triglyceride. In total three new bioactive derivatives and three new surface active amphoteric derivatives of soybean oil were synthesized. The products were characterized by FT-IR spectroscopy and NMR spectroscopy.

ÖZET

BİTKİSEL YAĞ TEMELLİ YENİ BİYOLOJİK OLARAK AKTİF VE YÜZEY AKTİF MATERYALLER

Sürdürülebilirlik için artan endişe, petrolün hammadde olarak kullanıldığı malzemeler yerine yenilenebilir kaynaklardan bio-bozunur malzemelerin üretimi için büyük bir motivasyon yaratmıştır. Bitkisel biokütle hem düşük maliyeti hem de kolay ulaşılabilirliği sayesinde umut verici yenilenebilir hammadde kaynaklarından biri olmuştur. Bu tezde, soya yağı temelli biyolojik olarak aktif ve yüzey aktif maddelerin üretimi başarılmıştır. Başlangıç maddesi soya yağına işlevselleştirmek için takılan süksinik anhidritten oluşan soya yağı – maleik anhidrit katılma ürünüdür (SOMA). Bu tezdeki yeniliklerin ilki trigliserit üzerine takılmış anhidrit sayısının, SOMA'nın monobenzil ester türevinin NMR analizi incelenerek kantitatif olarak belirlenmesidir. İkincil olarak trigliserit üzerine takılan anhidrit miktarı Levis asit katalizörler yardımı ile artırılmıştır. SOMA primer alkol veya amin grubu bulunan moleküller için harika bir tepkiyendir. Eğer bu moleküller suda çözülebilen moleküller olursa SOMA ile reaksiyonlarından bir ucu lipofil diğer ucu hidrofil olan amfoter moleküller sentezlenip mükemmel bio-temelli emülgatörler meydana gelir. Bu tezde soya yağı trigliseritlerine glükoz, riboflavin, polietilenglikol ve monoester türevleri ile Jeffamin takılmıştır. Toplamda soya yağının üç yeni bio-aktif türevi ve üç yeni yüzey-aktif amfoterik türevi sentezlenmiştir. Ürünler FT-IR spektroskopisi ve NMR spektroskopisi ile karakterize edilmiştir.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ACRONYMS / ABBREVIATIONS

ATR IR	Attenuated Total Reflectance Infrared
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
FT-IR	Fourier Transform Infrared Spectroscopy
HLB	Hydrophilic Lipophilic Balance
MPEG 450	Methoxy Polyethylene Glycol
Mwt	Molecular Weight
NMR	Nuclear Magnetic Resonance
PEG	Polyethylene Glycol
ppm	parts per million
SOMA	Soybean Oil Maleic Anhydride Adduct
Trigonox C	tert-butylperoxybenzoate

1. INTRODUCTION

Humankind has named the periods of his history by the materials that he used for progress: The Stone Age, the Bronze Age, and the Iron Age etc. So, an appropriate name for our own era would be the "Polymer Age" [1]. The presence of polymeric materials is found in almost all areas of life, both for high-value applications in electronics, automotive components, marine and aerospace industries, military equipment as well as for mass-produced products used in the fields of construction, packaging, agriculture, household appliances and personal care products. Up to now, the need of raw material for polymer industry has been supplied by petroleum resources mostly. In recent years, the ever-growing environmental awareness, as well as the depletion in crude oil reserves and the rising cost of petroleum oil derived raw materials have encouraged chemists to begin using renewable resources as raw materials. So, the next era will be the "Renewable Resources Based Polymer Age".

This situation has led to considerable attention being focused on the use of renewable agricultural feedstock to produce a wide range of base chemicals and other industrial products. The most common renewable raw materials are natural oils and fats because of their high availability and versatile applications. Vegetable oils constitute about 80% of the global oil and fat production, with 20% (and declining) being of animal origin [2]. The use of these materials offers an alternative approach that is both sustainable and, with the right application, far more environmentally benign than fossil sources. Other agricultural products, such as starch, cellulose, sugars, and lignin are also being used as raw materials for polymer synthesis.

1.1. Natural Oils

1.1.1. Composition and Chemistry

Natural oils and fats form part of a large family of chemical compounds known as lipids. Natural oils are predominantly made up of triglyceride molecules, which have the

three-armed star structure shown in Figure 1.1. Triglycerides comprise of three fatty acids joined at a glycerol junction. Most of the common oils contain fatty acids that vary from 14 to 22 carbons in length, with 0 to 3 double bonds per fatty acid.

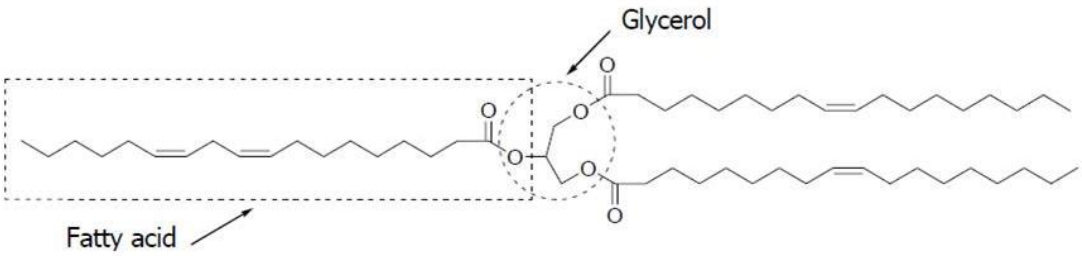


Figure 1.1. General Structure of a Triglyceride.

More than 1000 fatty acids have been identified, but only around 20 are present in appreciable quantities in vegetable oils. Fatty acid compositions vary according to the plant species, the crop, the season and the growing conditions [3]. Table 1.1 [4] lists the most common fatty acids in natural oils and Table 1.2 shows their molecular structure. Due to the fact that triglycerides comprise of mostly aliphatic hydrocarbon chains, they are insoluble in water and soluble in nonpolar solvents like hexane.

The existence of many types of fatty acids indicates that at the molecular level these oils are composed of different types of triglycerides with separate levels of saturation. Newly developed genetic engineering techniques are now generating raw materials available, such as increased content of individual fatty acids or dramatically changed oil quality by the introduction of a new fatty acid. Within this context, “high oleic” soybeans (82.6% oleic acid content) produced using techniques based on genetic engineering have been developed by DuPont (Table 1.1).

Table 1.1. Fatty Acid Percentage Distribution in Various Plant Oils.

Fatty Acid	C:DB[a]	Canola	Corn	Cottonseed	Linseed	Olive	Soybean	Sunflower
Myristic	14:00	0.1	0.1	0.7	0	0	0.1	0
Myristoleic	14:01	0	0	0	0	0	0	0
Palmitic	16:00	4.10	10.9	21.6	5.5	13.7	11	6.1
Margaric	16:01	0.3	0.2	0.6	0	1.2	0.1	0
Margoleic	17:00	0.1	0.1	0.6	0	0	0	0
Stearic	17:01	1.8	0	0.1	0	0	0	0
Oleic	18:00	60.9	2	0.1	3.5	2.5	4	3.9
Linoleic	18:01	21	25.4	2.6	19.1	71.1	23.4	42.6
Linolenic	18:02	8.8	59.6	18.6	15.3	10	53.2	46.4
Arachidic	20:00	0.7	1.2	54.4	56.6	0.6	7.8	1
Gadoleic	20:01	1	0	0	0	0.9	0.3	0
Eicosadienoic	20:02	0	0	0	0	0	0	0
Behenic	22:01	0.3	0.1	0.2	0	0	0,1	0
Erucic	22:01	0.7	0	0	0	0	0	0
Lignoceric	24:00	0.2	0	0	0	0	0	0
DB/triglyceride		3.9	4.5	3.9	6.6	2.8	4.6	3

[a] C, number of carbon atoms; DB, number of C=C double bonds

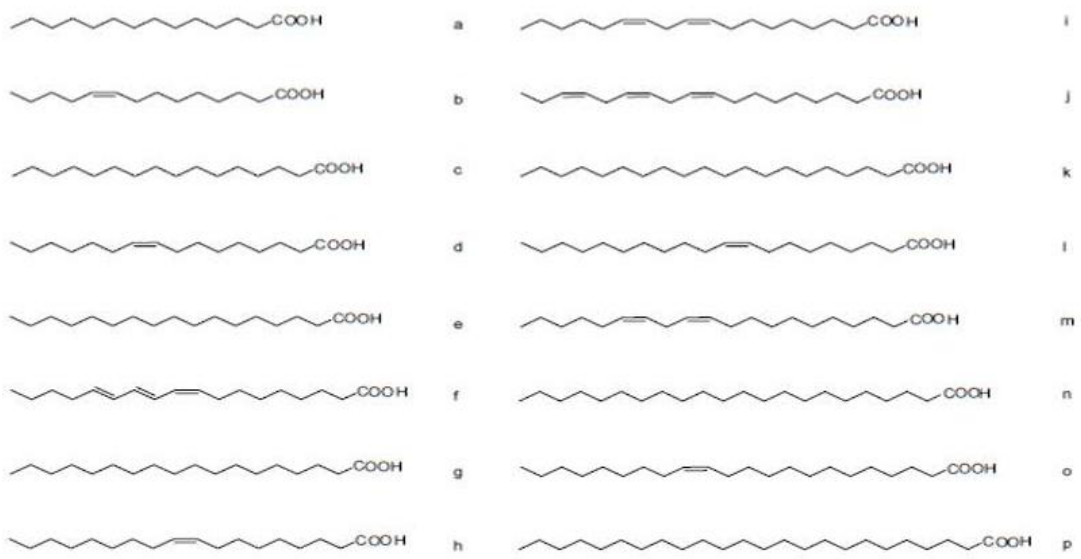


Figure 1.2. Structure of common fatty acids: (a) myristic, (b) myristoleic, (c) palmitic, (d) palmitoleic, (e) margaric, (f) margaroleic, (g) steraic, (h) oleic, (i) linoleic, (j) linolenic, (k) arachidic, (l) gadoleic, (m) eicosadienoic, (n) behenic, (o) erucic, and (p) lignoceric.

1.1.2. Chemical Modifications on Triglycerides

Internal double bonds on fatty acids are not reactive enough to produce different kind of polymers from natural oils directly. To synthesize a polymer from natural oil, it has to be chemically modified and functionalized. Different chemical functionalities allow triglycerides to be converted into several promising monomers. Respectable efforts have been devoted to modifications of triglycerides that could facilitate subsequent reactions to produce new and exotic materials.

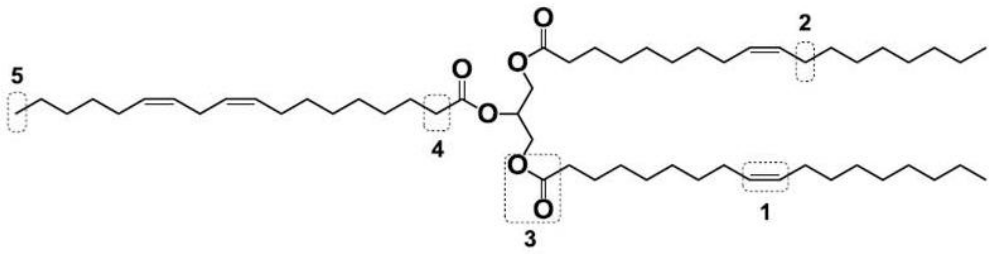


Figure 1.3. Active Sites on a Triglyceride Molecule.

(i) double bond
- oxidation
- epoxidation
- hydroformylation
- dimerization
- ozonolysis
- metathesis
- thiol-ene coupling
- hydrogenation
- pericyclic reaction
- sulfonation
- - carbonylation

(ii) allylic carbon
- maleinization
- halogenation
- hydroperoxidation
- hydroxylation
- electrochemical acetylation

(iv) α-carbon
- α-sulfonation
- α-halogenation
- alkylation
- acylation
- Claisen condensation

(iii) ester group
- hydrolysis
- alcoholysis
- transesterification
- saponification
- halogenation
- reduction
- amidation

(v) ω-carbon
- ω-oxidation

The triglyceride molecules have several active sites such as the double bonds, the allylic carbons, the ester groups, the α-carbonylic carbons and the ω-carbons (Table 1.3), that can be used to introduce polymerizable groups.

In this study, maleinization of natural oils by an "ene" reaction path have been preferred to functionalize natural oil and results in the addition of a succinic anhydride group to the allylic position of the fatty acid. Maleic anhydride has served as an excellent enophile and soybean oil could be efficiently functionalized by maleinization. Maleic anhydride is widely used in chemical industry, is cheap, readily available and reasonably safe to store and handle.

1.2. Soybean Oil

Maleinization is an "ene" type of reaction and results in the addition of a succinic anhydride group to the allylic position of the fatty acid. To be able to attach more succinic group on natural oil, in other words to make the natural oil more reactive for further reactions, it is logical to use the natural oil which has the highest possible amount unsaturation on its fatty acids.

One of the classical but still useful methods to determine the amount of unsaturation in fatty acids is the iodine test. The iodine value is defined as the amount of iodine in grams that react with the double bonds present in 100 gram of a given oil sample under specified conditions. Table 1.4. [5] shows typical iodine values of some common natural oils.

Table 1.2. Iodine Values of Several Natural Oils.

Oil	**Iodine Value (g of I_2 / 100 g of oil)**
Linseed	168 - 204
Sunflower	125 - 140
Soybean	123 - 139
Corn	118 - 128
Rapeseed	100 - 115
Cottonseed	98 - 118
Olive	76 -88
Palm	50 - 55

The table shows that the most appropriate natural oil candidates for this project are linseed oil, sunflower oil and soybean oil. According to the United States Department of Agriculture, soybean oilseeds represent over half of the total production of oilseeds with an annual production of 24 million tons [6]. Besides annual production of linseed and sunflower oil are extremely low with respect to soybean oil, majority of the linseed oil is used as nutritional supplement by herbalists, and sunflower oil is produces for food and feed purposes. Soybean oil was preferred for this project because it is not a popular food source and it is the most economic and abundant plant oil available.

1.2.1. Chemical Modification Of Soybean Oil

1.2.1.1. Thermal Maleinization. Maleinization, the addition of a succinic anhydride group to the allylic position of the fatty acid by an "ene" reaction path, has been applied to plant oils for a long period of time. The "ene" reaction is the indirect addition of a compound with a double bond (enophile) to an olefin possessing an allylic hydrogen (ene). The mechanism involves an allylic shift of one double bond by transferring the allylic hydrogen to the enophile and bonding of the two molecules [7].

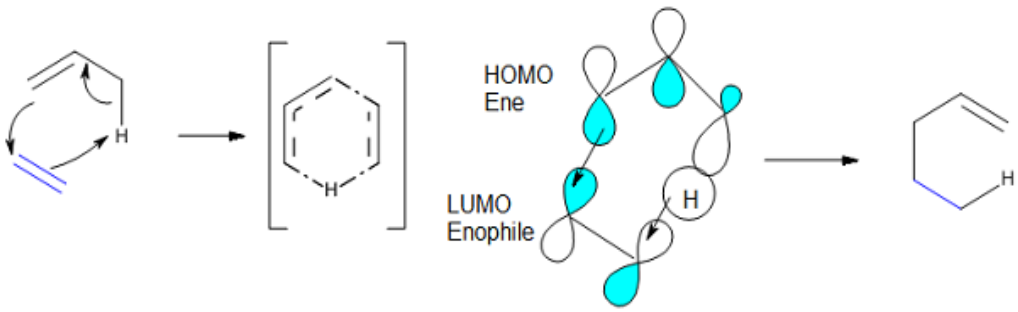


Figure 1.4. Schematic Representation of An Ene Reaction.

Because there is 4n π electrons in that system, this reaction will not take place as easy as Diels- Alder ([4n+2] π systems) reactions and will be thermodynamically unfavorable with respect to Diels-Alder reactions. For that reason, this reaction takes place at elevated temperature of 240^0 C.

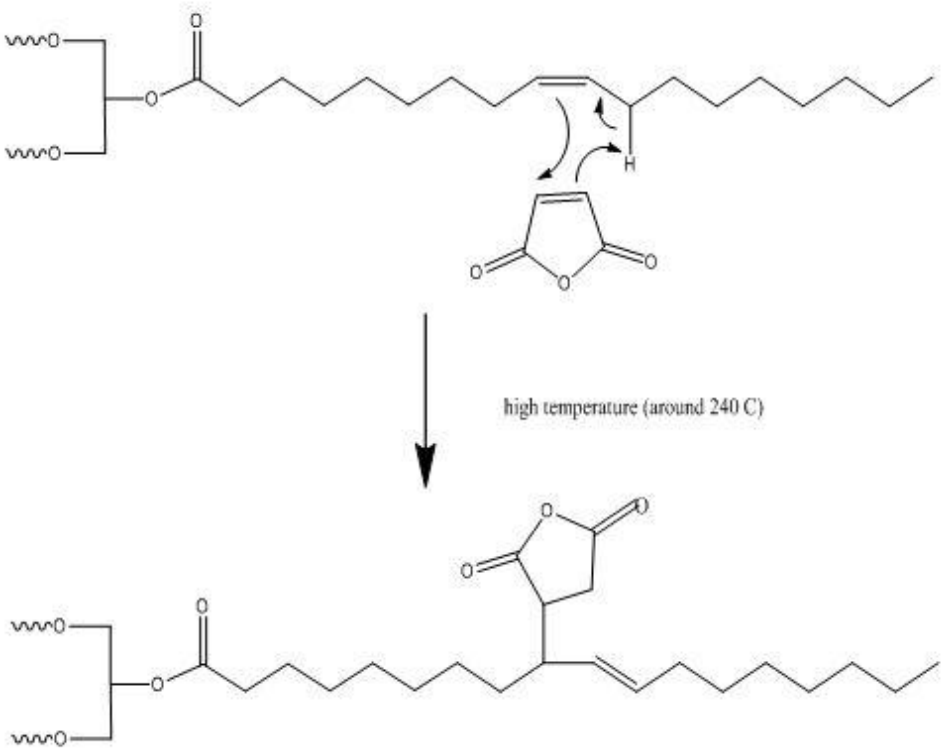


Figure 1.5. Thermal Maleinization of Soybean Oil.

By this technique, Eren and Kusefoğlu [7] were able to attach 0.60 succinic anhydride per triglyceride. This product is described as "soybean oil maleic anhydride adduct" and abbreviated as SOMA. Clearly higher amounts of succinate residues per triglyceride are required for successful functionalization.

1.2.1.2. Free Radical Maleinization. In a subsequent study by Çavuşoğlu and Kusefoğlu [8], succinic anhydride groups were attached to the allylic position of fatty acid by the help of a free radical initiator, Trigonox C. In this mechanism, free radical abstracts one of the doubly allylic hydrogen atoms and forms a triglyceride radical. Then an attack from this position to double bond of the maleic anhydride occurs and succinic anhydride is attached on triglyceride as shown in Figure.1.5. By this method the amount of succinic anhydride per triglyceride has been increased to 0.84.

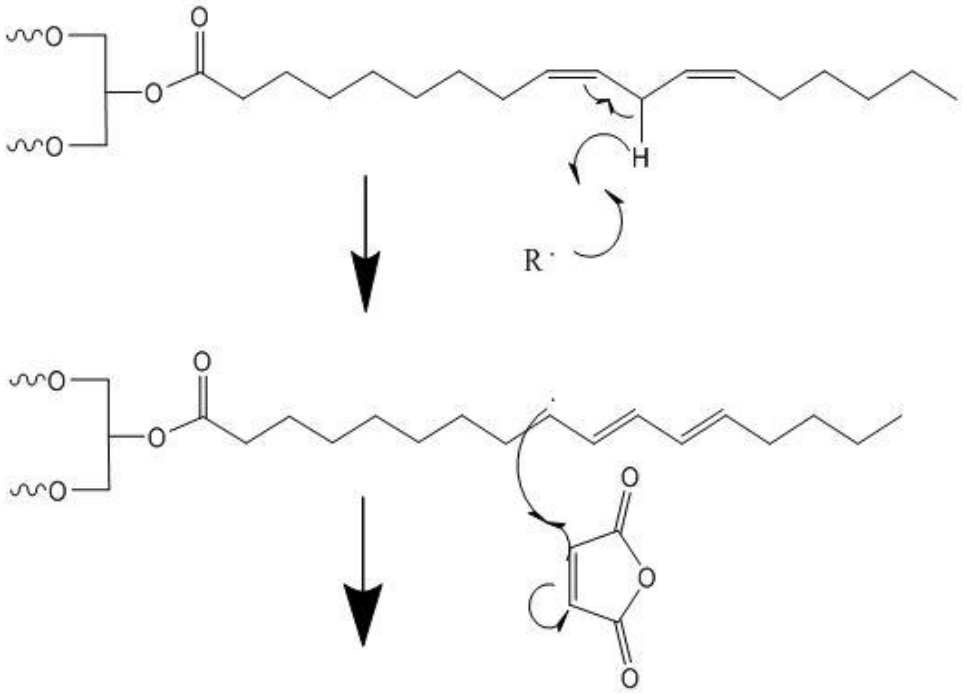


Figure 1.6. Free Radical Maleinization of Soybean Oil.

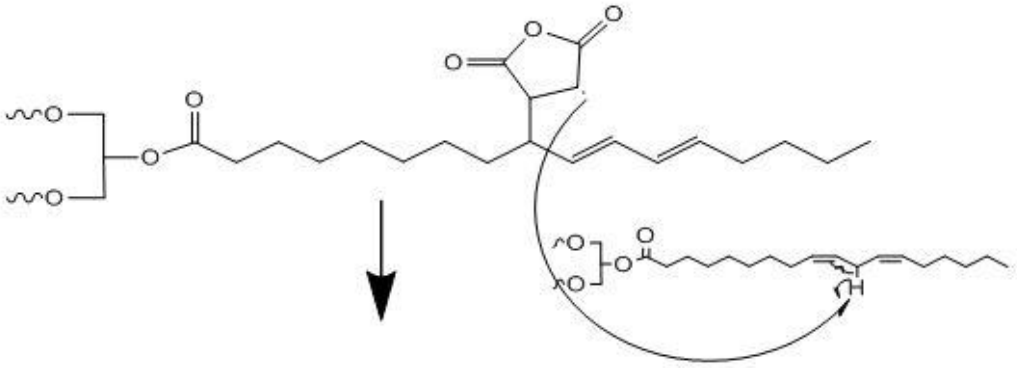


Figure 1.7. New Soybean Oil Radicals Formation.

1.2.1.3. Lewis Acid Catalyzed Maleinization. In this study, a Lewis acid catalyst, anhydrous iron (III) chloride, will be used to increase the amount of succinic anhydride per triglyceride. Anhydrous ferric chloride is deliquescent, forming hydrated ferric chloride mists and naked hydronium ions in moist air. The counter ion of the hydronium is so big that although there is not too much solvent, in the presence of few water molecules, they are separated completely and naked hydronium ions form. For that reason, anhydrous ferric chloride is fairly strong Lewis acid.

Hydronium ions and maleic anhydride form succinic anhydride cations which are attacked by the triglyceride double bonds.

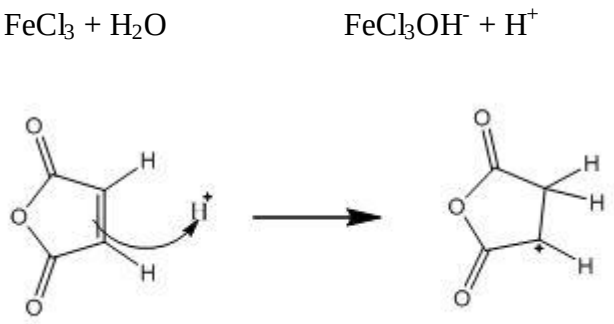


Figure 1.8. Succinic Anhydride Cation Formation.

$FeCl_3$ catalyzed reaction yields the highest succinic anhydride groups per triglyceride and the amount of succinic anhydride per triglyceride has been increased to 2.14.

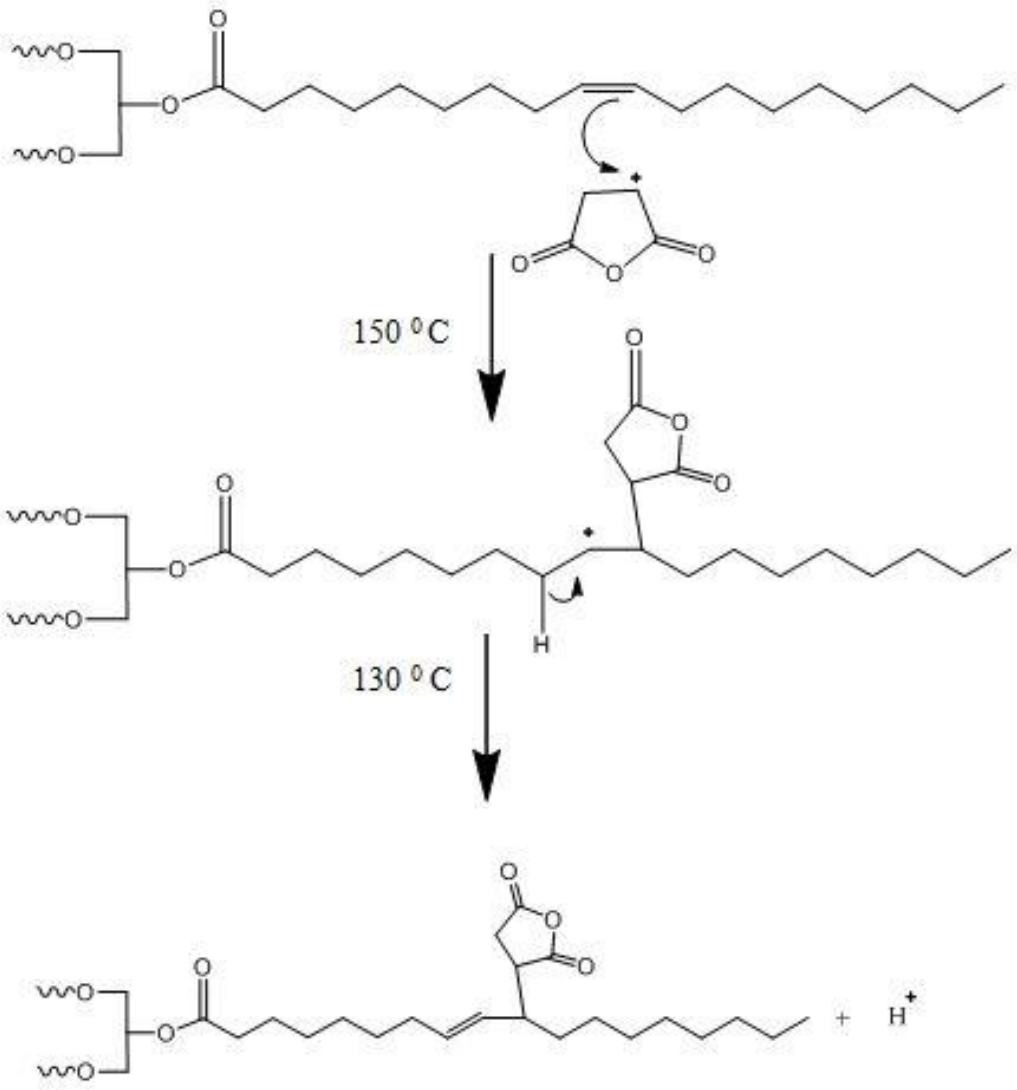


Figure 1.9. SOMA Formation by Lewis Acid Catalysis.

2. STATEMENT OF PURPOSE

The main aim of this thesis is to develop new plant oil based bio-active and surface active materials. Soybean oil is used as the plant oil and is functionalized by reacting with maleic anhydride. Maleinization yield will be increased by using Lewis acid catalyst. The known reactivity of cyclic anhydrides with alcohols and amines will be used to functionalize the triglyceride. The alcohols and amines will be chosen so as to be water soluble or biologically active.

To produce bio-active plant oil derivatives glucose, cholesterol, L-ascorbic acid, and riboflavin have been tried to attach to soy oil triglyceride. To produce surface active plant oil derivatives MPEG 450, MPEG5000, Jeffamine T-403 have been tried to attach to soy oil triglyceride.

3. EXPERIMENTAL

3.1. Materials and Apparatus

3.1.1. Materials

Soybean oil is purchased from BÜKAŞ (İzmir, Turkey) and used after vacuum drying. Maleic anhydride and Trigonox C are supplied by Cam Elyaf A.Ş. (Kocaeli, Turkey) and used as received. Anhydrous $FeCl_3$, anhydrous $ZnCl_2$, anhydrous P_2O_5 and anhydrous $CaCl_2$ are obtained from Çakır Kimya (İstanbul, Türkiye). Benzyl alcohol and aniline are purchased from J.T. Baker (Deventer, Holland) and used without purification. Ascorbic acid is purchased from Acros Organics (New Jersey, US). Glucose is obtained from Merck (Darmstadt, Germany). Cholesterol (99 % pure) is purchased from Sigma Aldrich (Missouri, USA) and used as received. Riboflavin is supplied by Eastman Organic Chemicals (Kingsport, Tennessee, US). Poly(ethylene glycol) methyl ether (average Mn=5000) and Poly(ethylene glycol) methyl ether (average Mn=450) is supplied by Aldrich Chemistry(Missouri, U.S.). Jeffamine T-403 is supplied by Huntsman Corporation (Texas, U.S.). $CDCl_3$, CD_3OD, C_3D_6O which are used for ^{1}H-NMR, supplied by Merck (Darmstadt, Germany). Hexane, ether and acetone are purchased from Merck (Darmstadt, Germany). Acetone is used after being distilled twice.

3.1.2. Apparatus

The IR analysis was performed on a Nicolet 380 FT-IR with Smart Diamond ATR. Each spectrum is an average of 32 scans taken with 4 cm^{-1} resolution in the 600-4000 cm^{-1} range.

All the ^{1}H NMR spectrum are recorded on a Varian 400-MHz NMR instrument operating at a frequency of 399.986 MHz for proton. Chemical shifts (δ) were reported in parts per million (ppm), relative to the internal standard tetramethylsilane (TMS, δ=0.00 ppm).

3.2. Maleinization of Soybean Oil

3.2.1. Thermal Maleinization of Soybean Oil

100 gram (0.115 mole) soybean oil was placed in a flask fitted with a condenser, a magnetic stirrer and a thermometer. 9 grams (0.091 mole) maleic anhydride was added at 180^{0}C. Color of the solution changed from yellow to orange. After one hour, 9 grams more (0.091 mole) maleic anhydride was added at 195 – 200 ^{o}C and sublimation of maleic anhydride was observed. After one hour, the last portion, 9 gram more (0.091 mole) maleic anhydride, was added at 220 – 230 ^{o}C and the mixture was stirred at that temperature for one hour and then cooled to room temperature. The solution became brownish and viscosity increased. NMR spectrum showed that no maleic anhydride was left in the product [8].

FT-IR (cm^{-1}): 3012.14 (C=C, stretching), 2923.57, 2853.63, and 1463.23 (C-H, stretching), 1858.48, 1779.37 and 915.72 (succinic anhydride peaks), 1749.37 (C=O, stretching), 1221.99, 1162.00, and 1096.86 (C-C(=O)-O, stretching), 722.90 (C=C, bending).

^{1}H NMR (C_3D_6O, 400 MHz) ppm: 0.9 (-CH_3 of triglyceride), 1.3 and 1.6 (-CH_2- of triglyceride), 2.0 (-CH_2-CH=), 2.3 (-CH_2-(C=O)-), 2.8 (succinic anhydride H), 4.1 and 4.3 (-O -(C=O)-CH_2-CH-CH_2-(C=O)-O-), 5.3 (-O -(C=O)-CH_2-CH-CH_2-(C=O)-O-).

3.2.2. Free Radical Maleinization of Soybean Oil

A N_2 purged flask which was equipped with magnetic stirrer was sealed with rubber septum. 26.14 g (29.64 mmol) soybean oil and 3.21 g (32.77 mmol) maleic anhydride were mixed at 70 ^oC. Due to the sublimation of maleic anhydride, slight excess maleic anhydride was used (1 mole SO: 1.1 mole maleic anhydride). After the temperature was raised to 150 ^oC and 0.52 g (2 per cent by weight based on soybean oil) tert-butyl peroxy benzoate (Trigonox C) was added. After one hour another portion of 0.2649 g (1 per cent by weight based on soybean oil) Trigonox C was added. The temperature was reduced to 130 ^oC after 30 minutes. The reaction was completed after two hours and finally vacuum was applied to remove excess anhydride. Complete removal was observed when there was no bubble formation in the reaction medium. Final product was a yellow, viscous oil [9]. The characterization of the final product was done with FT-IR. Due to low succinic anhydride functionality per mole of soybean oil, NMR characterization was difficult. However, NMR showed no unreacted maleic anhydride was left in the product.

FT-IR (cm^{-1}): 3008.25 (C=C, stretching), 2923.34, 2853.58, and 1463.21 (C-H, stretching), 1858.52 and 1780.02 (C=O of succinic anhydride), 918.09 (C-O-C of succinic anhydride), 1742.35(C=O, stretching), 1160.40, and 1097.13 (C-C(=O)-O, stretching), 721.81 (C=C, bending).

^1H NMR (C_3D_6O, 400 MHz) ppm: 0.9 (-CH_3 of triglyceride), 1.3 and 1.6 (-CH_2- of triglyceride),2.0 (-CH_2-CH=), 2.3 (-CH_2-(C=O)-), 2.8 (succinic anhydride H), 4.1 and 4.3 (-O -(C=O)-CH_2-CH-CH_2-(C=O)-O-), 5.3 (-O -(C=O)-CH_2-CH-CH_2-(C=O)-O-).

3.2.3. Lewis Acid Catalyzed Maleinization of Soybean Oil

All the materials used in that experiment was kept at 100^oC for two hours in

vacuum oven to be sure that all of the moisture have been removed. 26.4 gram (30 mmol) soybean oil and 0.05 gram (0.3 mmol, 1 per cent by mole based on soybean oil) anhydrous $FeCl_3$ is placed in a N_2 purged, three necked flask which was equipped with magnetic stirrer, and sealed with rubber septum. When temperature reaches 190^oC, 1.5 gram (15 mmol, 50 per cent by mole based on soybean oil) maleic anhydride was added. After one hour, another portion of 1.5 gram (15 mmol) maleic anhydride was added. This process is repeated four more times. After final maleic anhydride addition, the reaction was stirred under the same conditions (under N_2, at 190^oC) for four more hours. Overall, 30 mmol soybean oil and 90 mmol maleic anhydride was added into flask. Some of the excess maleic anhydride was collected on the upper walls of three necked flask. The product was transferred into another flask to remove excess maleic anhydride and kept under vacuum to remove unreacted maleic anhydride in the product.

FT-IR (cm^{-1}): 3007.78 (C=C, stretching), 2923.01, 2853.20, and 1463.21 (C-H, stretching), 1849.80, 1778.69 and 888.07 (succinic anhydride peaks), 1739.94 (C=O, stretching), 1235.69, 1162.16, and 1096.86 (C-C(=O)-O, stretching), 722. 53 (C=C, bending).

^{1}H NMR (CDCl3, 400 MHz) ppm: 0.9 (-CH_3 of triglyceride), 1.2 and 1.6 (-CH_2- of triglyceride),2.0 (-CH_2-CH=), 2.3 (-CH_2-(C=O)-), 2.7 (succinic anhydride H), 4.1 and 4.3 (-O -(C=O)-CH_2-CH-CH_2-(C=O)-O-), 5.3 (-O -(C=O)-CH_2-CH-CH_2-(C=O)-O-).

3.3. Characterization of SOMA

SOMA adduct is dissolved in excess benzyl alcohol and this mixture is stirred at 80^oC for 3 hours under nitrogen and after reaction is completed, mixture is poured into a watch glass to increase vaporization area, then it is kept at vacuum oven at 120^oC for 1 hour to remove excess benzyl alcohol.

FT-IR (cm^{-1}): 2922.63 and 2853.01 (C-H stretching of triglyceride), 1739.51 (C=O stretching of triglyceride), 1708.10 (C=O stretching of newly formed ester linkage), 1162.73(C-C(=O)-O, stretching). 1849.80 and 1778.69 (C=O of succinic anhydride), peaks disappear. It heralds that all of the anhydrides are opened.

^{1}H NMR (C_3D_6O, 400 MHz) ppm: 0.9 (-CH_3 of triglyceride), 1.2 and 1.6 (-CH_2- of triglyceride), 2.0 (-CH_2-CH=), 2.3 (-CH_2-(C=O)-), 2.7 (succinic anhydride H), 4.1 and 4.3 (-O -(C=O)-CH_2-CH-CH_2-(C=O)-O-), 5.3 (-O -(C=O)-CH_2-CH-CH_2-(C=O)-O-), 7.3 (Ar-H).

Based on 2.14 succinates per triglyceride, the calculated molecular weight of $FeCl_3$ catalyzed SOMA is 1190g/mole.

3.4. Plant Oil Based Bio-active Molecules

All of the subsequent reactions of this work was performed on SOMA which is synthesized by $FeCl_3$ catalyst, containing 2.14 succinate groups per triglyceride.

3.4.1. SOMA – Glucose Adduct

Glucose is powdered to increase specific surface area and kept in a desiccator filled with P_2O_5 for one week. In a vial, 1.190 g (1 mmol) of SOMA, 0.385 g (2.14 mmol) glucose, catalytic amount of dry $ZnCl_2$ and a teflon coated stirrer are added. Then the mixture was mechanically stirred at 75^0C for 8 hours under an atmosphere of nitrogen. The reaction was followed by FT-IR spectroscopy. Once the reaction is completed, the crude product was washed with cold water to remove residual glucose, then with hexane to remove unreacted SOMA, then ether. A black solid material was obtained.

FT-IR (cm^{-1}): broad band between 3000 and 3600 (O-H stretching of secondary alcohol groups of glucose), 2923.72 and 2853.66 (C-H stretching of triglyceride), 1736.90 (C=O stretching of triglyceride), 1707.65 (C=O stretching of newly formed acid linkage), and 1163.27(C-C(=O)-O, stretching).

The product is not soluble in common solvents and NMR data could not be taken.

3.4.2. SOMA – Cholesterol Adduct

In a vial, 1.190 g (1 mmol) of SOMA, 0.828 g (2.14 mmol) cholesterol was stirred at 180^0C for 3 days under an atmosphere of nitrogen. The reaction was followed by FT-IR spectroscopy.

FT-IR (cm^{-1}): 2924.62 and 2853.38 (C-H stretching of triglyceride), 1737.75 (C=O stretching of triglyceride), 1708.98 (C=O stretching of newly formed acid linkage), and 1163.20 (C-C(=O)-O, stretching). The only indication of that reaction takes place is the disappearance of succinic anhydride peaks at 1858.48, 1779.37, 915.72 cm^{-1} and newly formed carbonyl stretching of acid linkage at 1708.98 cm^{-1}.

As the cholesterol adduct did not meet the original goal of this study it was not further examined.

3.4.3. SOMA – Riboflavin Adduct

Riboflavin is powdered to increase specific surface area and kept in a desiccators filled with P_2O_5 for one week. To a 100-mL round-bottom flask, 1.190 g (1 mmol) of SOMA, 0.805 g (2.14 mmol) riboflavin, 50 ml of acetone and catalytic amount of dry $ZnCl_2$ were added, and a drying column was placed on the top of the round bottom flask.

Then the mixture was refluxed and mechanically stirred for 10 hours under an atmosphere of nitrogen at reflux temperature. Riboflavin is slightly soluble in acetone. The reaction was followed by FT-IR spectroscopy. Once the reaction was completed, the mixture is filtered when still hot. The newly formed adduct is soluble in hot acetone but not soluble in cold acetone. Solid part, riboflavin, is discarded and acetone is evaporated to obtain the product. The crude product is washed subsequently with hexane to remove unreacted SOMA and excess water to remove residual riboflavin and dried. A shiny orange solid product was obtained.

FT-IR (cm^{-1}): broad band between 3000 and 3600 (O-H stretching of riboflavin), 2923.90 and 2853.55 (C-H stretching of triglyceride), 1780.84 (C=O of succinic anhydride), 1741.11 (C=O stretching of triglyceride), 1716.39 (C=O stretching of riboflavin), 1701.32 (C=O stretching of newly formed acid linkage), 1576.17 (in plane deformation vibration), 1541.19 (C-N stretching of diazine ring in flavin part), and 1156.07 (C-C(=O)-O, stretching).

Because the product is not soluble in common NMR solvents, ^{1}H NMR data is not taken.

3.5. Plant Oil Based Surface Active Molecules

3.5.1. SOMA – MPEG 450 Adduct

MPEG 450 was kept at vacuum oven at 70 ^{0} C for 3 hours before use to remove moisture. In a 25-mL round-bottom flask, 1.190 g (1 mmol) of SOMA, 0.965 g (2.14 mmol) MPEG 450 is placed and stirred vigorously at room temperature under nitrogen atmosphere for 2 days. The reaction is followed by FT-IR spectroscopy.

The product was soluble in both polar and non-polar solvents. MPEG 450 is water soluble and organic solvents insoluble. So, an organic solvent is used to remove excess MPEG 450. 15 ml hexane was added to the mixture and unreacted MPEG 450 is separated as a lower layer. The remaining hexane solution is kept in evapotary rotavap and solvent is removed to obtain the product. The product is a yellow viscous material.

FT-IR (cm^{-1}): 2923.30, 2855.45 (C-H, stretching of triglyceride), 1849.80, 1737.33 (C=O, stretching), 1097.46 (H_2C-O, stretching of monomethyl propylene glycol).

^1H NMR ($CDCl_3$, 400 MHz) ppm: 0.8 (-CH_3 of triglyceride), 1.1 and 1.4 (-CH_2- of triglyceride), 1.9 (-CH_2-CH=), 2.1 (-CH_2-(C=O)-), 2.6 (succinic anhydride H), 3.2 (solvent residual peak), 3.5 (-CH_2-0-CH_2-, of polyethylene glycol group), 4.0 and 4.2 (-O -(C=O)-CH_2-CH-CH_2-(C=O)-O-), 5.2 (-O -(C=O)-CH_2-CH-CH_2-(C=O)-O-).

3.5.2. SOMA – MPEG 5000 Adduct

MPEG 5000 was kept at vacuum oven at 70 ^{0} C for 3 hours before use to remove moisture. In a 50-mL round-bottom flask, 1.190 g (1 mmol) of SOMA, 10.7 g (2.14 mmol) MPEG 5000 was placed and stirred magnetically at 80 ^{0} C under nitrogen atmosphere for 1 day. The reaction was followed by FT-IR spectroscopy.

The product was soluble in both polar and non-polar solvents. MPEG 5000 is water soluble and organic solvents insoluble. So, an organic solvent is used to remove excess MPEG 5000. 25 ml hexane was added to the mixture and unreacted MPEG 5000 is separated as a lower layer. The remaining hexane solution is kept in evapotary rotavap and solvent is removed to obtain yellow crystalline product.

FT-IR (cm^{-1}): 2922.53, 2853.33 (C-H, stretching of triglyceride), 1740.08 (C=O, stretching), 1097.91 (H_2C-O, stretching of monomethyl propylene glycol).

^{1}H NMR ($CDCl_3$, 400 MHz) ppm: 0.8 (-CH_3 of triglyceride), 1.2 and 1.5 (-CH_2- of triglyceride), 1.9 (-CH_2-CH=), 2.2 (-CH_2-(C=O)-), 2.6 (succinic anhydride H), 3.3 (solvent residual peak), 3.5 (-CH_2-0-CH_2-, of polyethylene glycol group), 4.0 and 4.2 (-O -(C=O)-CH_2-CH-CH_2-(C=O)-O-), 5.2 (-O -(C=O)-CH_2-CH-CH_2-(C=O)-O-).

3.5.3. SOMA – Aniline Adduct

1.190 gr (1mmol) of SOMA was placed in a vial and 0.199 gr (2.14 mmol) aniline was added dropwise at room temperature. Immediate color change was observed. Color of material turned from transparent dark brown into opaque light brown immediately

FT-IR (cm^{-1}): broad band between 3000 and 3600 (O-H stretching of carboxylic acid), 2923. 90 and 2853.55 (C-H stretching of triglyceride), 1741.11 (C=O stretching of triglyceride), 1716.39 (C=O stretching of newly formed amide linkage), 1599.48 (in plane deformation vibration), 1272.33 (C-N stretching). Disappearance of peak at 1618.45 cm^{-1} proves that there is no primary N-H bending, it means all of the aniline has reacted with succinic anhydrides.

Because aniline is a toxic organic compound, this product was not a desired product. This experiment is done just to show that primary amines could attack anhydride rings. Reaction is followed by FT-IR Spectrum and further examination is not found necessary.

3.5.4. SOMA – Jeffamine Adduct

1.190 g (1 mmol) of SOMA, and 0.862 gr (2.14 mmol) Jeffamine T-403 were dissolved in 10 ml acetone separately. Both solutions were kept at 4 ^{0}C. Then the solutions were mixed in a beaker and stirred vigorously until the mixture became homogeneous.

After five minutes the reaction was over and acetone is removed under vacuum. The reaction is followed by FT-IR spectrum.

FT-IR (cm^{-1}): broad band between 3000 and 3600 (O-H stretching), 2924.55 and 2854.39 (C-H stretching of triglyceride), 1736.15 (C=O stretching of triglyceride), 1711.66 (C=O stretching of newly formed urethane linkage), 1101.29 (H_2C-O, stretching in Jeffamine molecule). Disappearance of peak at 1618.45 cm^{-1} proves that there is no primary N-H bending, it means all of the aniline has reacted with succinic anhydrides.

^{1}H NMR (CD_3OD, 400 MHz) ppm: 0.9 (-CH_3 of triglyceride), 1.2 and 1.6 (-CH_2- of triglyceride), 3.4 (-O-CH_2-C=N of Jeffamine) 2.0 (-CH_2-CH=), 2.3 (-CH_2-(C=O)-), 3.4 (-O-CH_2-C- of Jeffamine), 4.1 and 4.3 (-O -(C=O)-CH_2-CH-CH_2-(C=O)-O-).

Solvent uptake test is applied to measure water absorption capacity of SOMA-Jeffamine T-403 adduct. 2 small samples of SOMA-Jeffamine adduct were taken and kept in a desiccators filled with anhydrous $CaCl_2$. Both of the samples are immersed in a water bath for 24 hours at room temperature. Further weight gain was observed. The percentage of water uptake was calculated as follows:

$$\text{Degree of swelling} = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \times 100 \qquad (3.1)$$

Table 3.1 Solvent uptake capacity of SOMA – Jeffamine T-403 Adduct in water.

	dry sample weight (g)	wet sample weight (g)	degree of solvent uptake (%)
sample 1	0.0225	0.0258	12.8
sample 2	0.0301	0.0339	11.2

Solvent uptake capacity of the SOMA - Jeffamine T-403 is around 12%.

4. RESULTS AND DISCUSSION

4.1 Synthesis of SOMA

In this project, Maleinization of triglycerides by an "ene" type of reaction was optimized. The succinate group that is now attached to the triglyceride is used to attach primary –OH an $–NH_2$ containing molecules to the triglyceride. Maleinization of soybean oil has been studied in our research group earlier and results have been published [7]. The ene reaction has a higher activation energy than the Diels-Alder ([4n+2] π systems) and usually requires highly activated substrates and/or high temperatures. However, increasing temperature above 190 ^{0}C, there are some handicaps:

(i) Although reaction is run in a closed system, maleic anhydride sublimes at 202^{o}C and may deposit at colder region.
(ii) Increasing temperature is not enough to increase functionality; thermodynamic barrier should be brought down by activating substrates.

Because of these reasons, necessity of a catalyst arises and a fairly strong Lewis acid catalyst, anhydrous ferric chloride, is preferred. Although a catalyst is used, the ene reaction still is a thermal reaction and high temperature favors this reaction. Reaction is carried out at maximum possible reaction, 190^{o}C. Reaction mechanism has been explained in Section 1.2.3.

4.2. Characterization of SOMA

NMR and FT-IR analysis are performed for qualitative characterization.

In FT-IR spectrum, in Figure 4.2, there are new peaks at 1778.69 cm^{-1} (s) and 1849.80 cm^{-1}, and they belong to five membered ring anhydrides' carbonyl stretching. A new medium peak at 888.07 cm^{-1} which is characteristic for C-O-C group of the anhydrides is observed. The fatty acid unsaturation remains at 1162.16 cm^{-1}. These observations prove the structure.

A strong broad band between 2500 cm^{-1} and 3000 cm^{-1} is frequently diagnostic of OH group of carboxylic acid, a strong peak between 1700 cm^{-1} and 1710 cm^{-1} is associated with carboxylic acids' carbonyl stretching frequencies. In FT-IR spectrum of SOMA, none of these peaks were observed. So, it is concluded that, ring opening of cyclic anhydrides does not take place and SOMA adduct is synthesized successfully.

In NMR spectrum, in Figure 4.3, there is no peak around 7.0 ppm which is a characteristic signal for maleic anhydride protons. Thus there is no unreacted maleic anhydride left in the medium; Maleic anhydride is either reacted with triglyceride or removed, and the reaction product can be used for the next step without further purification.

To determine the stoichiometry of the next step, it is necessary to determine the number of available succinic anhydride groups per soybean oil triglyceride. This was done by the help of NMR. Cyclic anhydride is reacted with excess benzyl alcohol to give the benzyl esters, and this compound is analyzed by NMR. Reaction of the succinate with benzylic –OH groups is very fast and complete at 80 ^{0}C.

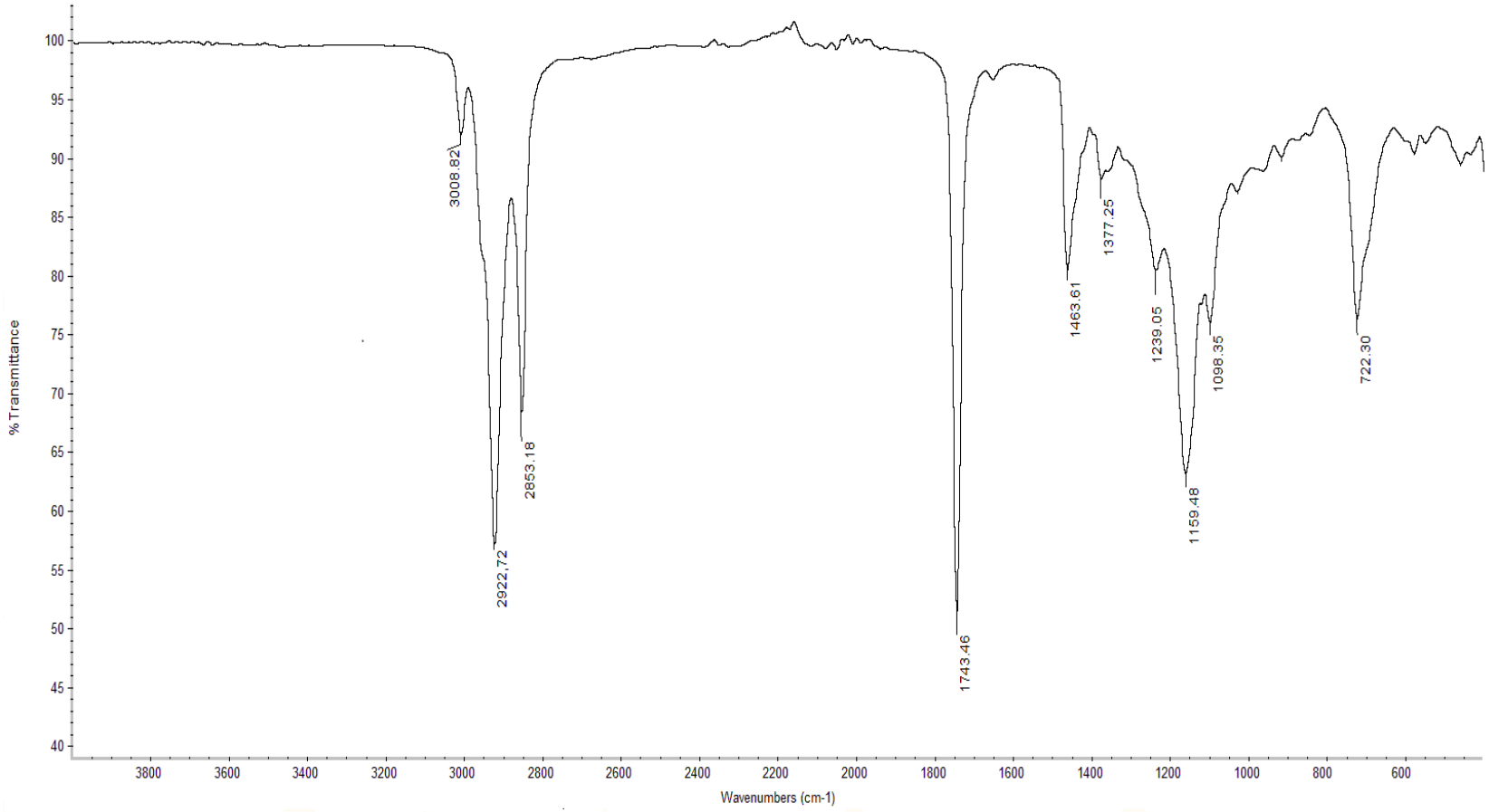


Figure 4.1. FT-IR Spectrum of Soybean Oil.

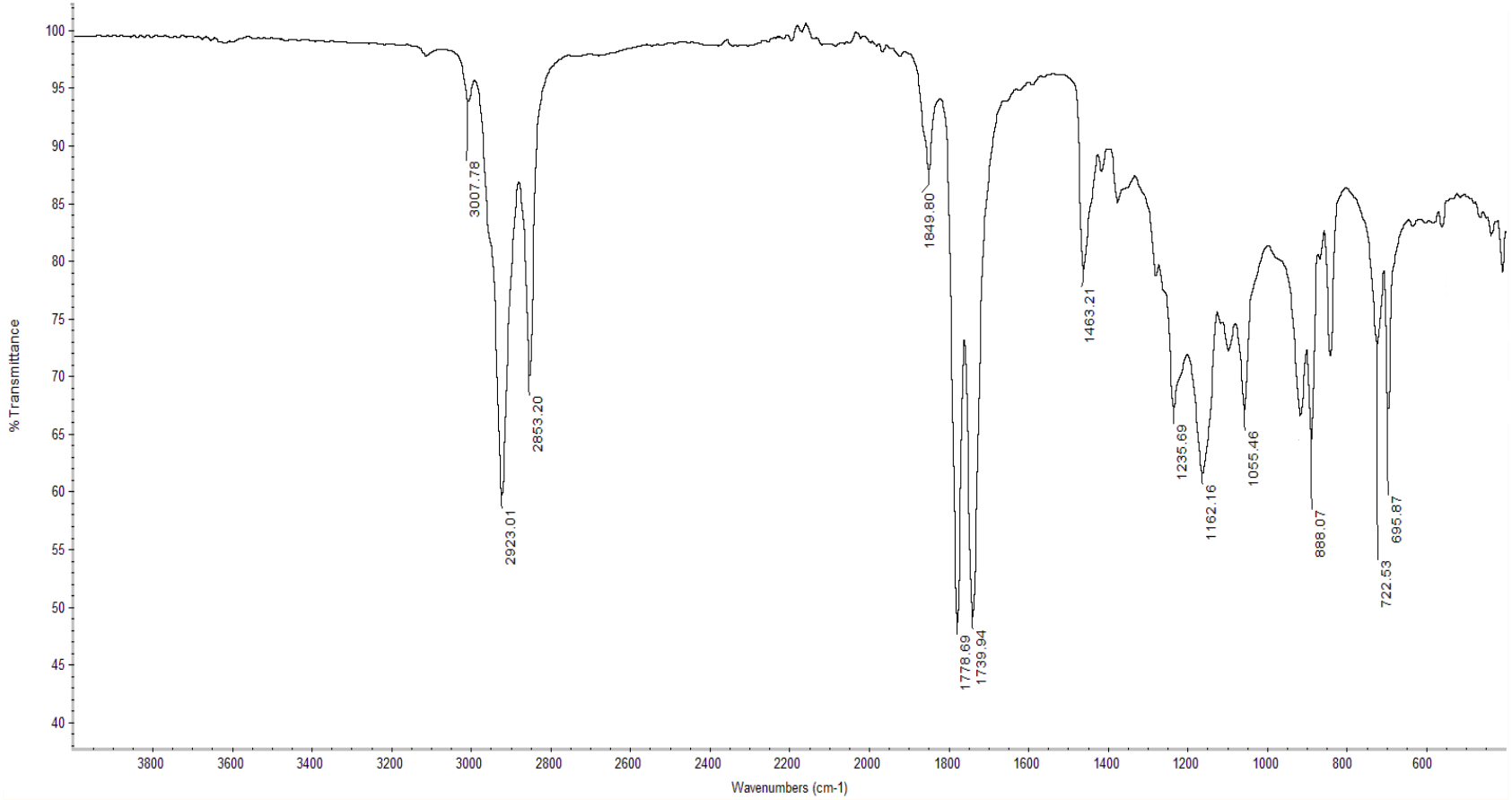


Figure 4.2. FT-IR Spectrum of SOMA.

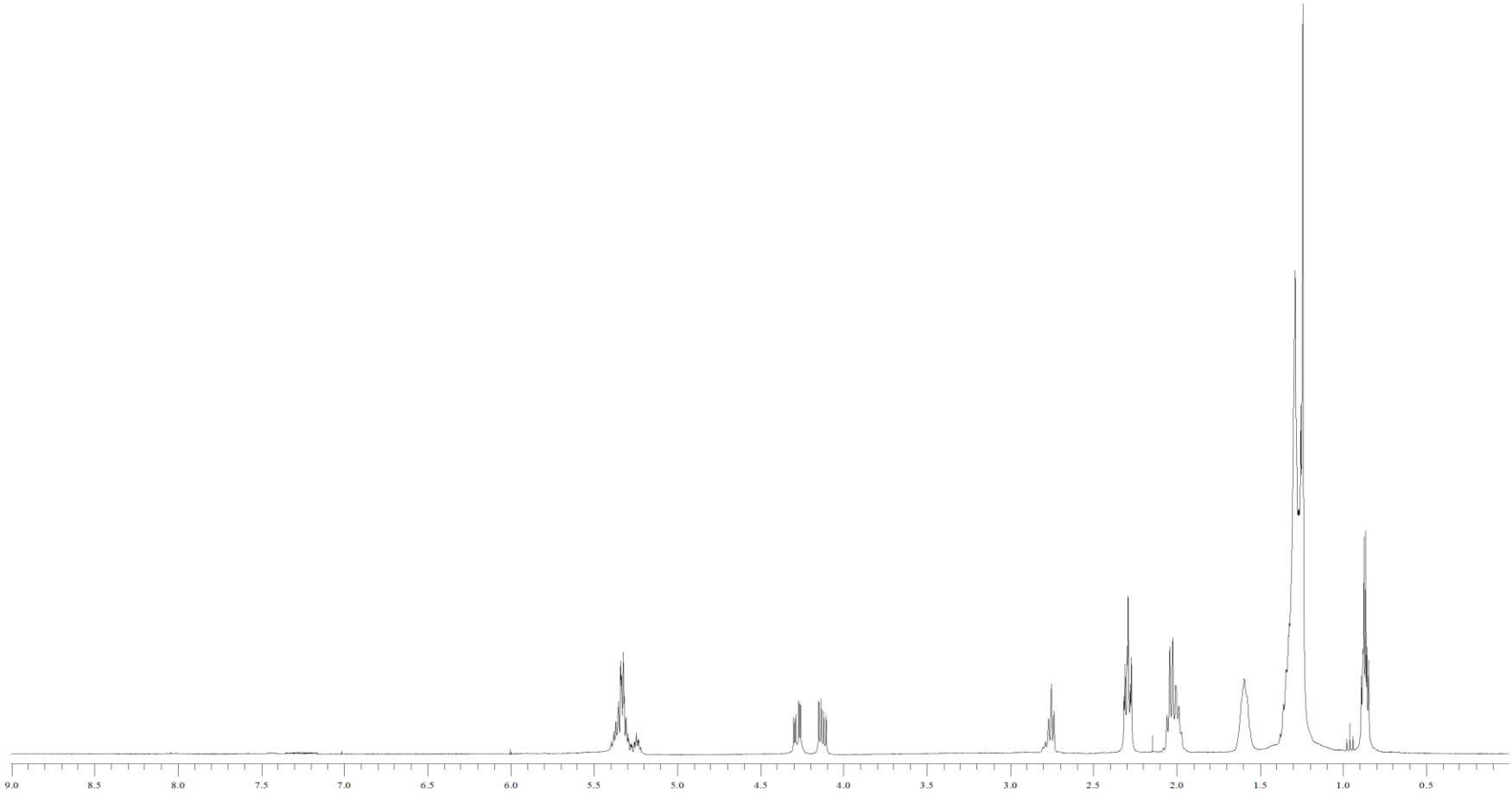


Figure 4.3. 1H NMR Spectrum of SOMA.

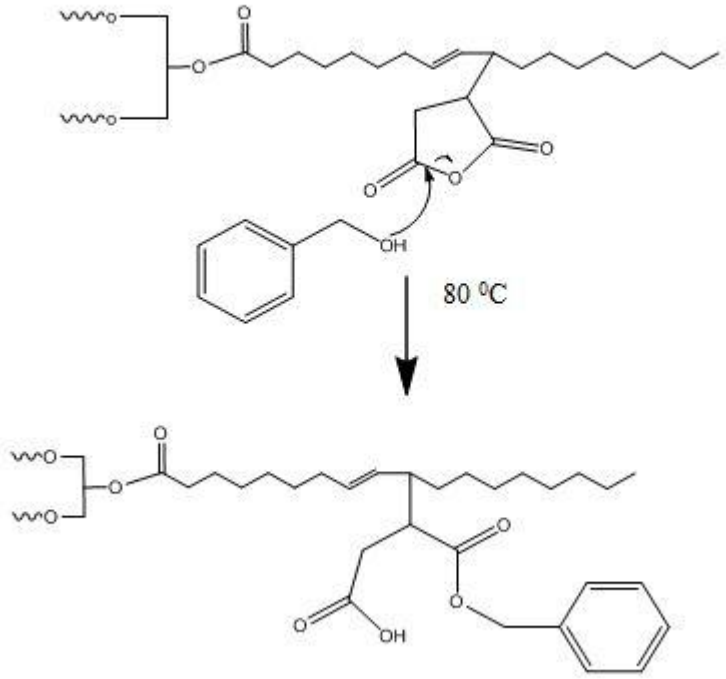


Figure 4.4. Succinic Anhydride Ring Opening With Benzyl Alcohol.

Two carbonyl of anhydride peaks at 1789.97 cm^{-1} and 1849.80 cm-1, and C-O-C stretching of anhydride peak at 888.07 cm^{-1} disappear completely as can be seen in Figure 4.5. It is certain that all of the anhydride peaks are opened. A new and strong peak at 1708.10 cm^{-1} is observed and this peak heralds the formation of a new acid group. Also, a broad band between 2500 cm^{-1} and 3500 cm^{-1} is observed, and it signifies hydroxyl group of carboxylic acid.

In ^{1}H NMR, terminal hydrogen atoms of triglyceride appear around 0.9 ppm and there are nine terminal hydrogen atoms in one triglyceride molecule. Hydrogen atoms on benzyl group should around 7.3 ppm and there are five aromatic hydrogen atoms on one benzyl ether group. By comparing their integration ratios, we could calculate the amount of succinic anhydride per triglyceride. Integration shows that every nine protons at 0.9 ppm, there are 10.7 aromatic protons at 7.4 ppm. As there are five protons on a benzene ring the number of benzyl alcohol per triglyceride can be found by dividing 10.7 by 5. Because one benzyl alcohol molecule

opens one succinic anhydride ring, we could find out how many succinic anhydride molecules are attached on triglyceride molecule. By the thermal maleinization method, 0.6 succinic anhydride is found on one triglyceride molecule. By free radical maleinization this number increases to 0.84. Now, with the help of Lewis acid catalyst 2.14 succinic anhydride functionality per triglyceride is reached. This number is the highest degree of functionalization ever achieved either by our group or by other groups. The number of succinates per triglyceride was thus maximized and this SOMA sample was used in subsequent synthesis.

Table 4.1. Number of Anhydride Groups per Triglyceride by Different Maleinization Techniques.

Technique	**Number of Anhydride Groups Per Triglyceride**
Thermal Maleinization	0.60
Free Radical Maleinization	0.84
Lewis Acid Catalyzed Maleinization	2.14

4.3. Suitable Solvent Determination

After functionalizing soybean oil and determine its functionality exactly, its reactions with different alcohols was attempted. Unfortunately, SOMA is a very viscous material and may cause some stirring problems. To overcome that problem, a suitable solvent was searched. Solvents can be broadly classified into three categories: nonpolar, polar protic and polar aprotic solvents.

Since polar protic solvents, such as water, ethyl alcohol etc., could open succinic anhydride ring and yield esters, they interfere with the desired reactions and reduce the yield. For that reason, polar protic solvents are not suitable.

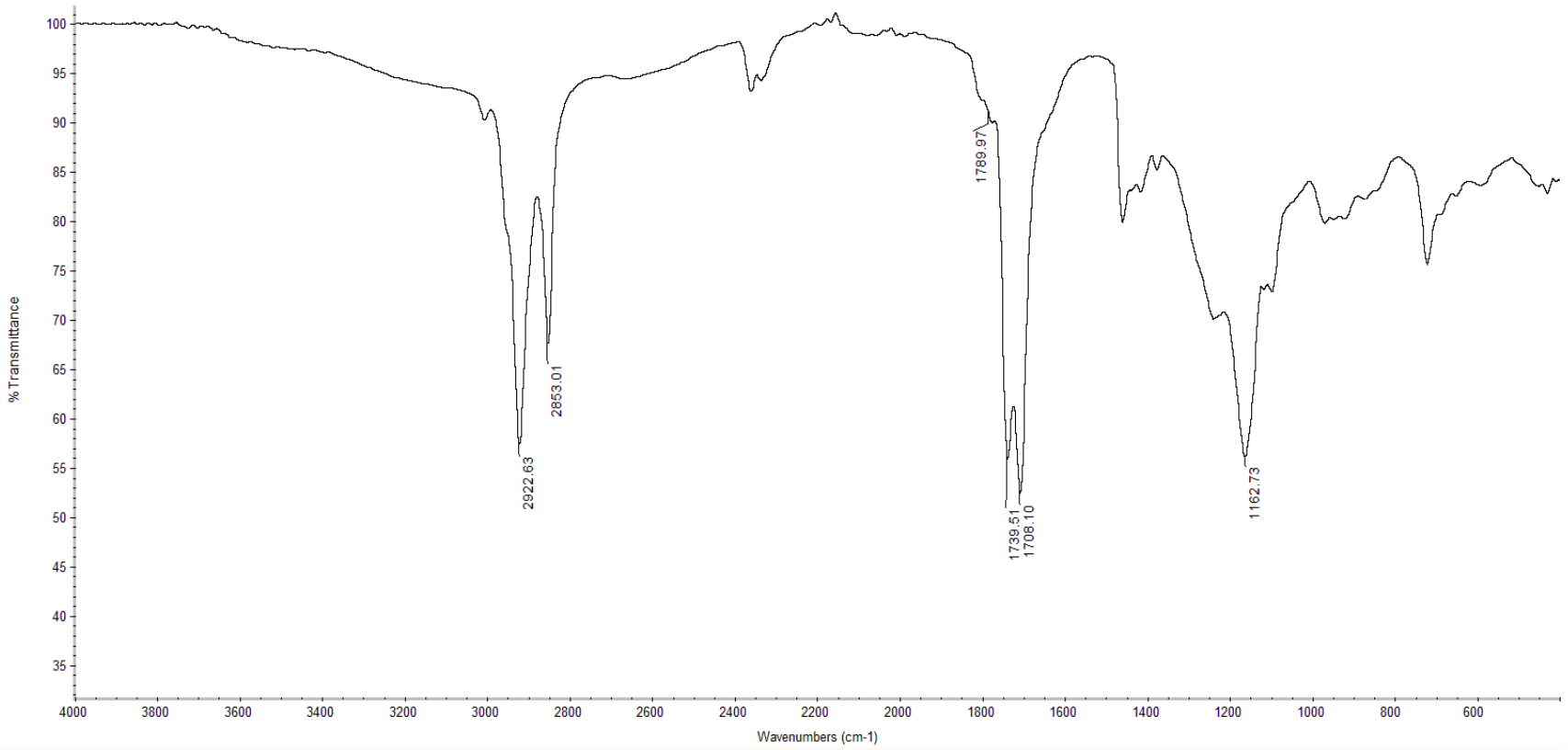


Figure 4.5. FT-IR Spectrum of SOMA and Benzyl Alcohol Adduct.

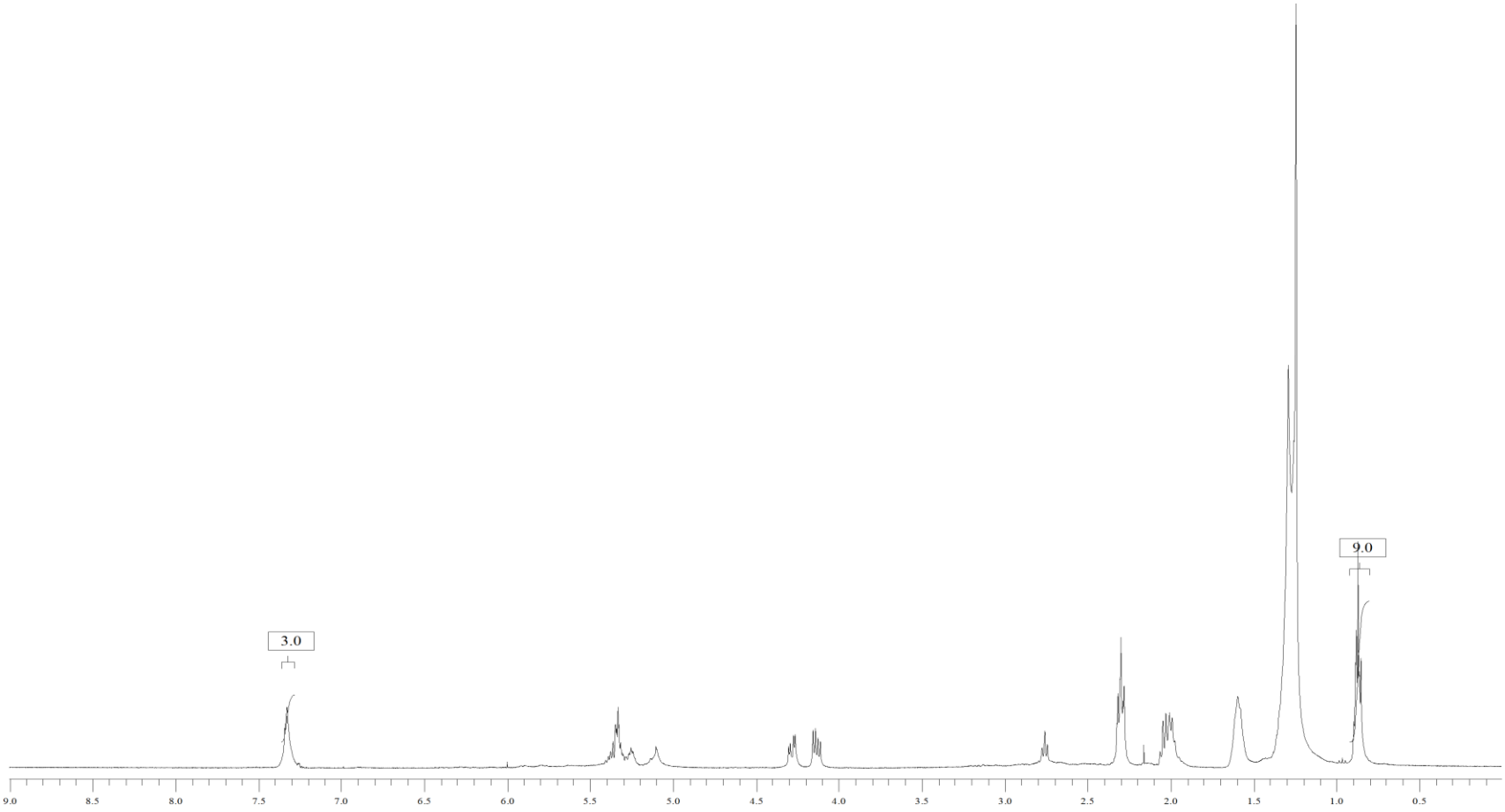


Figure 4.6. ^{1}H NMR Spectrum of Thermally Maleinized SOMA and Benzyl Alcohol Adduct.

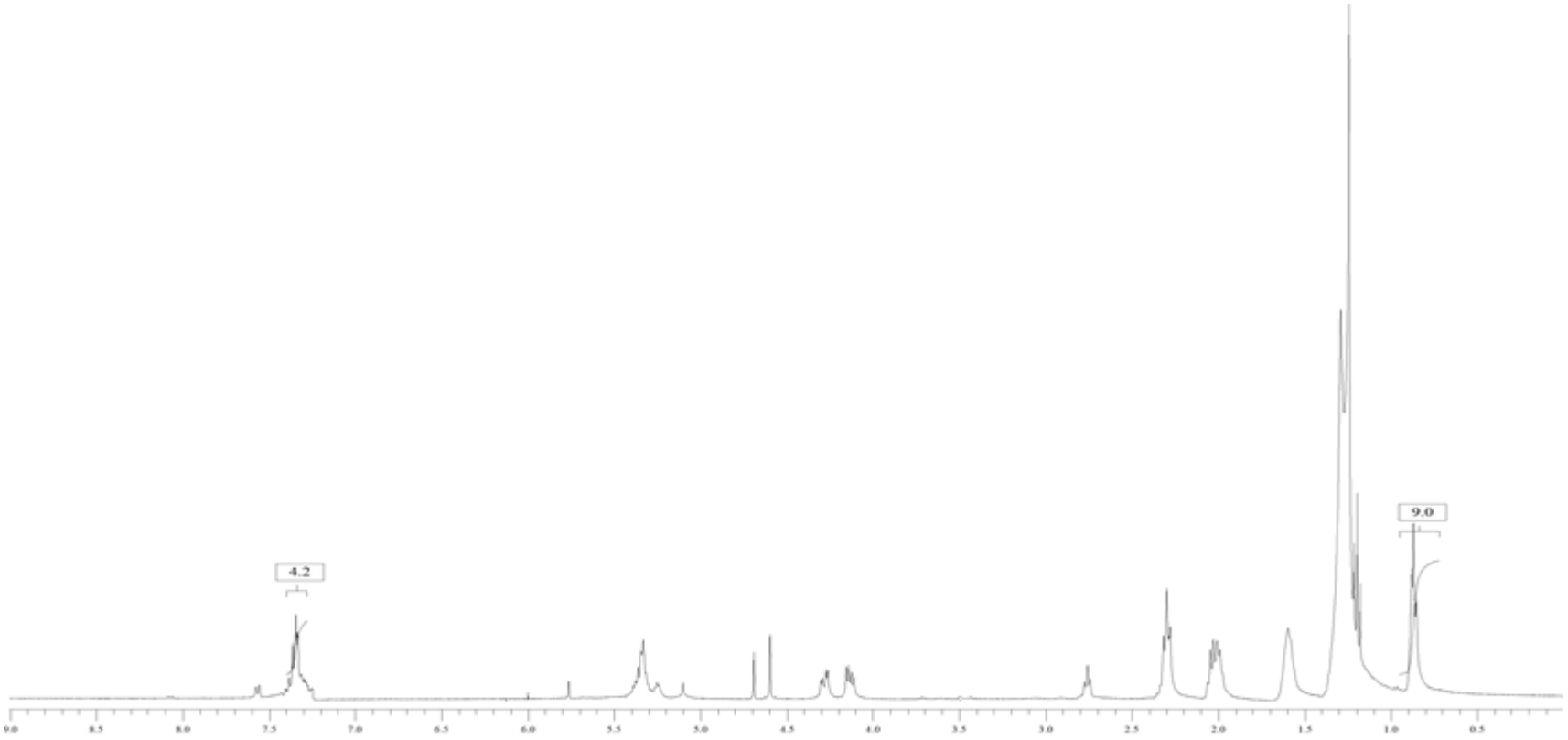


Figure 4.7. ^{1}H NMR Spectrum of Free Radical Catalyzed SOMA and Benzyl Alcohol Adduct.

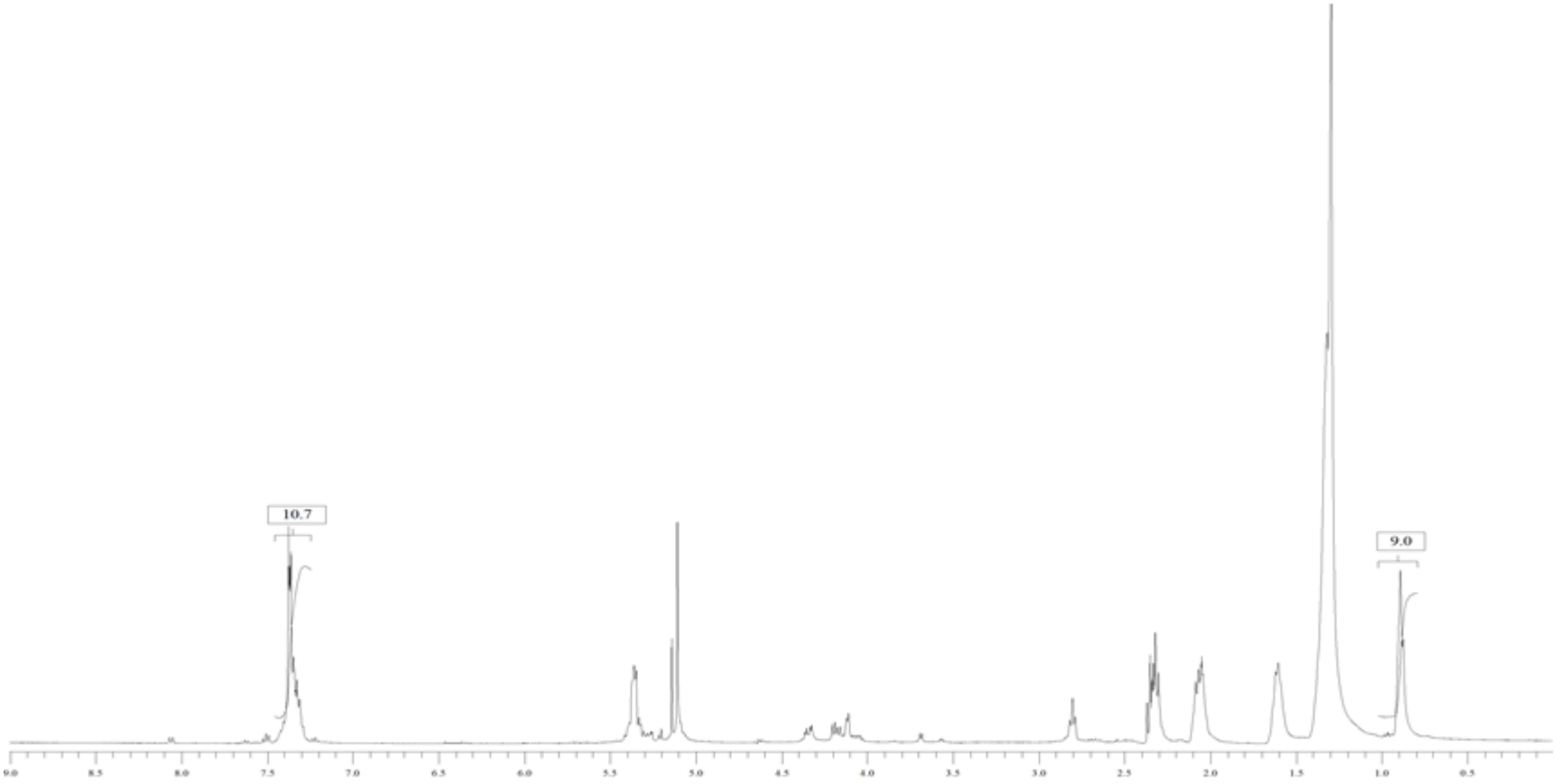


Figure 4.8. ^{1}H NMR Spectrum of Lewis Acid Catalyzed SOMA and Benzyl Alcohol Adduct.

To produce new bio-active or surface active molecules from soybean oil, polar molecules need to be attached on SOMA adduct. It is not possible to dissolve these polar reagents in non-polar solvents. If both substances are not dissolved in the same solvent, the reactions are either impossible or very slow. So, non-polar solvents, such as hexane, toluene, chloroform etc., are not suitable.

At first glance, polar aprotic solvents seem appropriate because they do not have interference or solvation problem. Unfortunately, succinic anhydride ring opening reactions take place at high temperatures. It is not possible to run this reaction even at reflux temperatures if polar aprotic solvents with low boiling points, are used. Therefore solvents such as dichloromethane, acetone, tetrahydrofurane etc. are not suitable.

After all these eliminations, only two candidates remain: dimethylformamide (DMF) and dimethylsulfoxide (DMSO). When SOMA adduct is kept in anhydrous DMF for two hours at 100^{o}C, carbonyl of anhydride peaks at 1778.69 cm^{-1} and 1849.80 cm^{-1} become smaller and C-O-C stretching of anhydride peak at 888.07 cm^{-1} disappears. Also, there is a new carbonyl formation at 1708.10 cm^{-1} in FT-IR spectrum, in Figure 4.10,. From NMR data, it is seen that there are two new peaks at 2.84 and 2.94 ppm and they belong to methyl groups. Also, a new peak at 8.00 ppm is observed and it stems from aldehyde group's hydrogen. In short, succinic anhydride rings are opened in presence of DMF and all of the hydrogens are still there. An undesired reaction which is probably an amide-amide exchange reaction is clearly taking place. The structure of the product was not further examined.

When SOMA adduct is kept in anhydrous DMSO for two hours at 100^{o}C, carbonyl of anhydride peaks at 1778.28 cm^{-1} and 1860.26 cm^{-1} are reduced and C-O-C stretching of anhydride peak at 888.07 cm^{-1} disappears. Also the broad band between 3050 cm^{-1} and 3700 cm^{-1} heralds us a hydroxyl group formation in Figure 4.11. From NMR datum, in Figure 4.12, it is observed that there is a new peak at 2.54 ppm and it corresponds to methyl groups' hydrogen atoms. The structure of this product was not further examined. In brief, DMSO opens succinic anhydride rings and all of the hydrogens are still there. So, DMSO also is not a suitable solvent for this project.

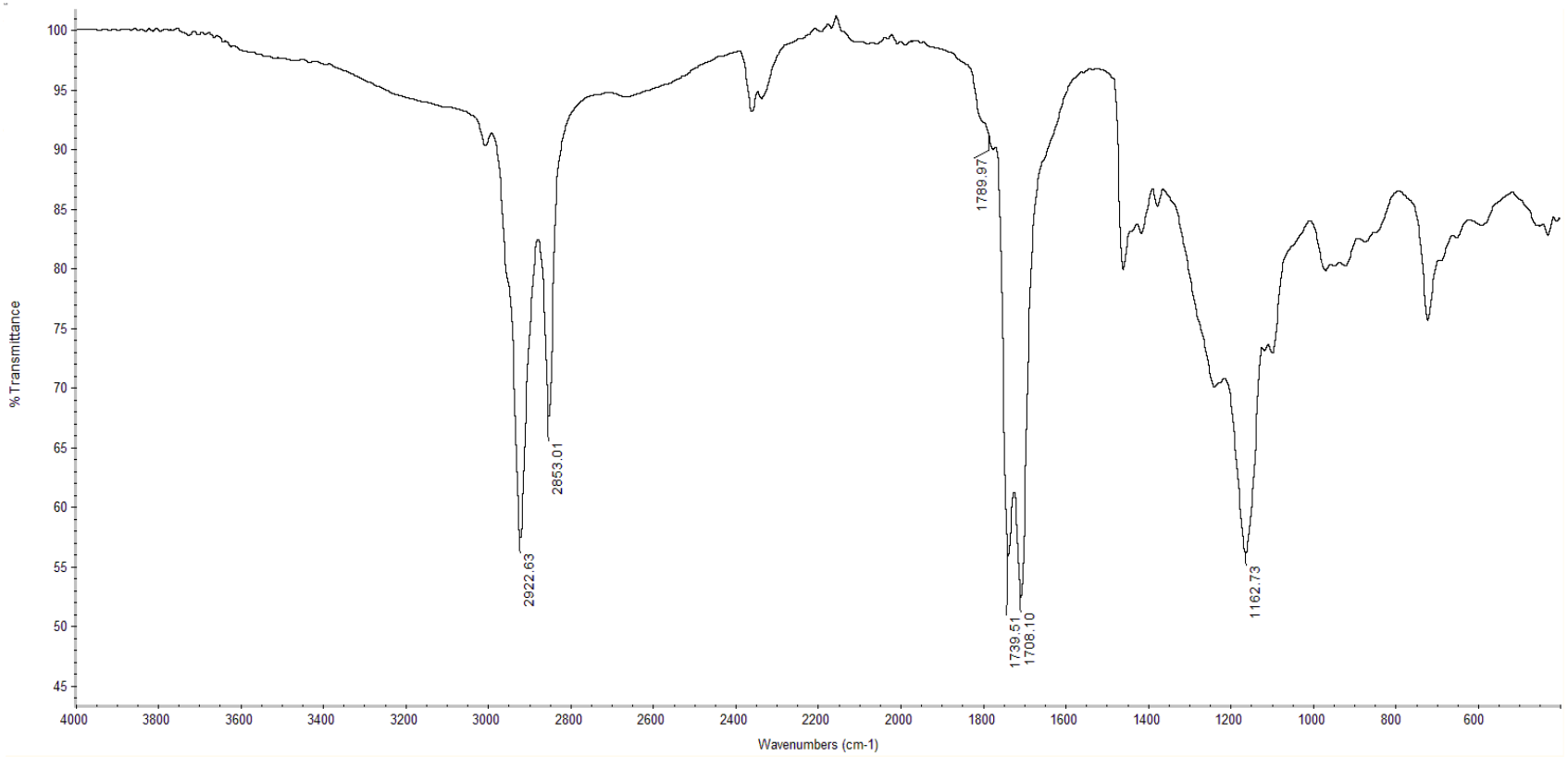


Figure 4.9. FT-IR Spectrum of SOMA and DMF Adduct.

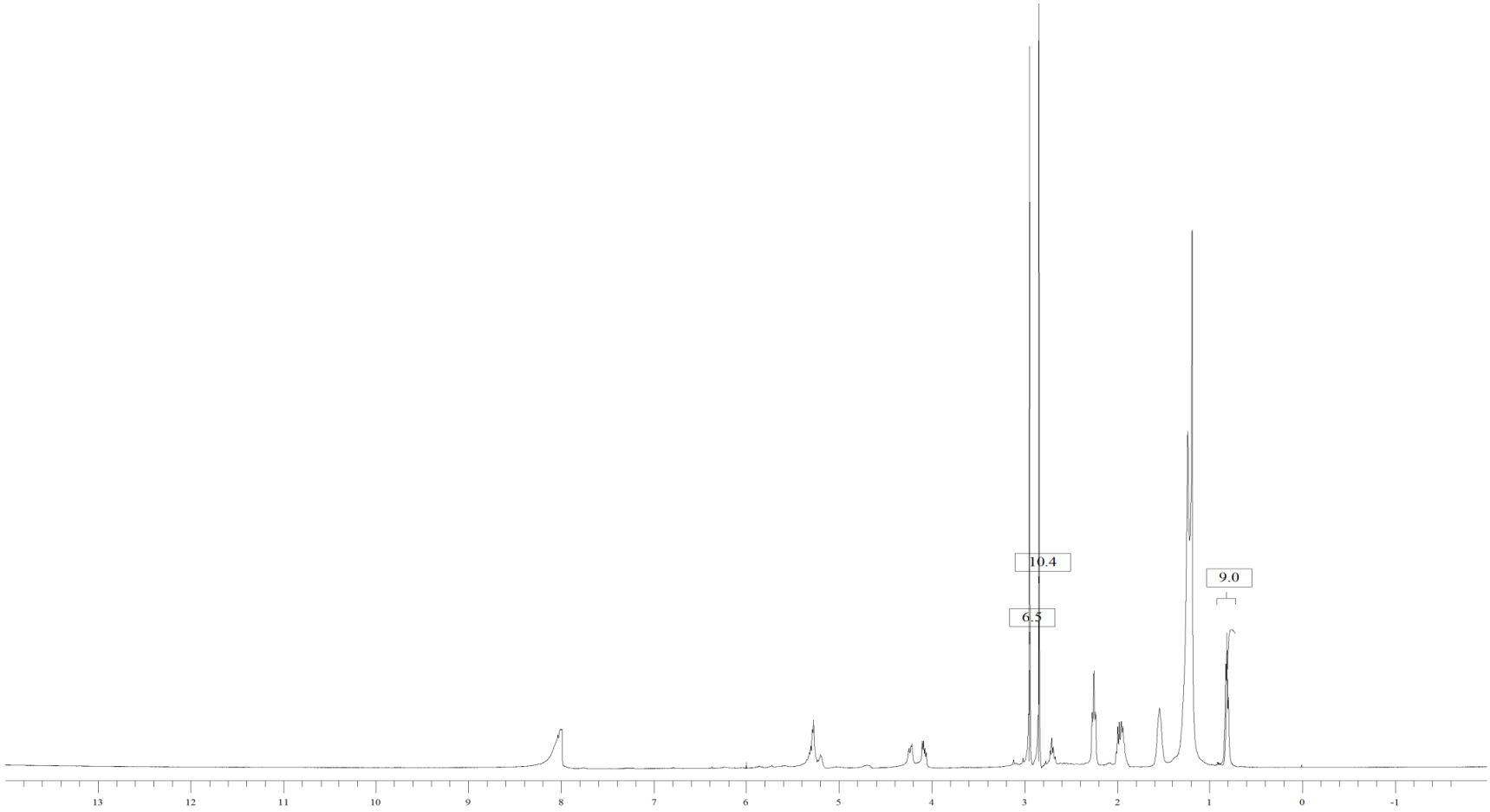


Figure 4.10. ^{1}H NMR Spectrum of SOMA and DMF Adduct.

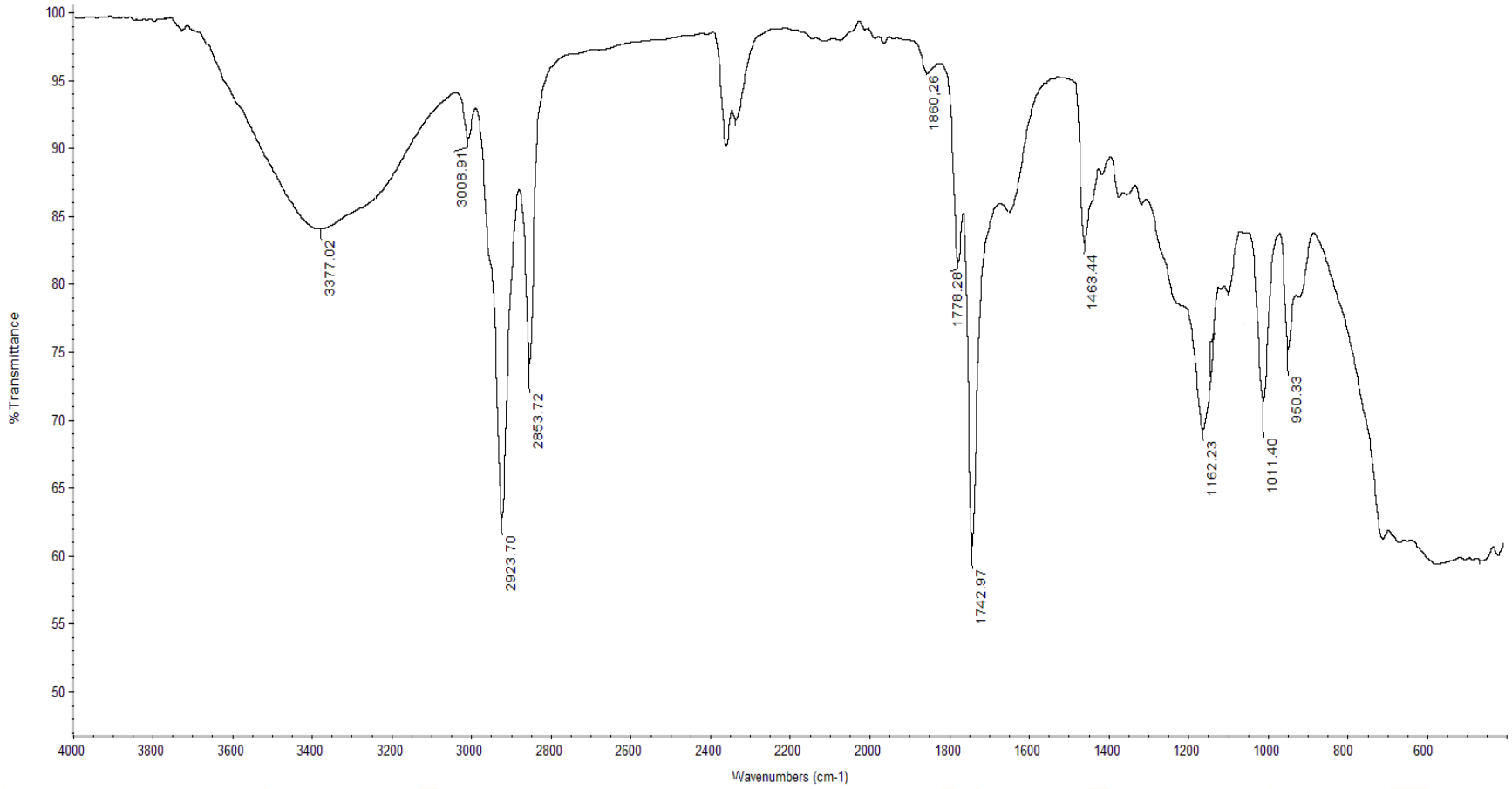


Figure 4.11. FT-IR Spectrum of SOMA and DMSO Adduct.

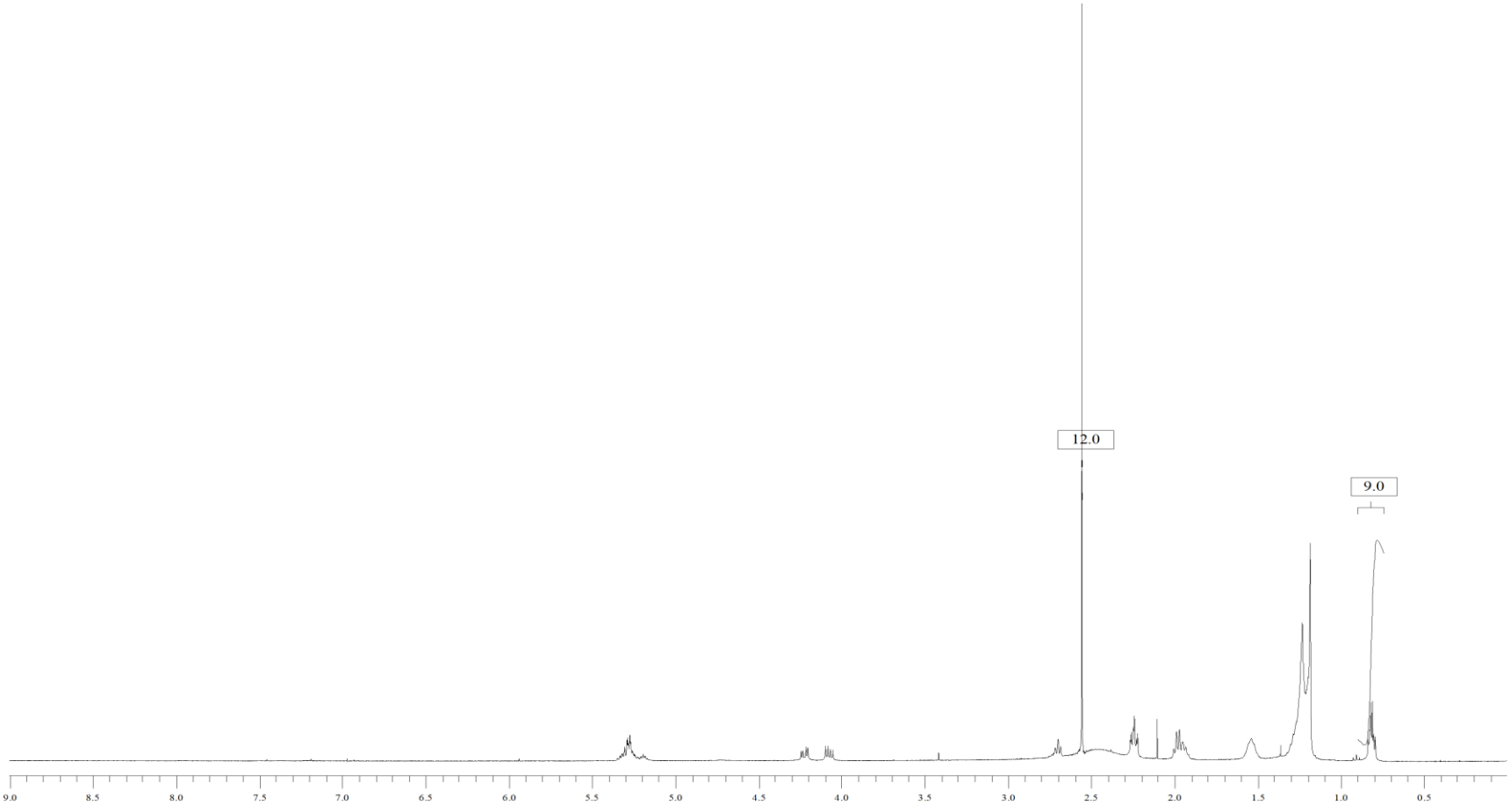


Figure 4.12. ^{1}H NMR Spectrum of SOMA and DMSO Adduct.

In conclusion, a convenient solvent could not be found. The reactions had to be run at high temperature, at high stirring rates, in a heterogeneous mixture. For this method to succeed, only primary alcohols that are liquids at the reaction temperature were suitable.

4.4. Plant Oil Based Bio-Active Molecules

4.4.1. SOMA – Glucose Adduct

It is easy to run a succinic anhydride opening reaction with a liquid primary alcohol by thermal energy as it could be observed from SOMA benzyl alcohol reaction from Section 4.2.

First candidate tried is an aldosic monosaccharide and a solid primary alcohol, D-glucose. The product is expected to have a number of polar and water soluble groups attached to a very non polar and water insoluble triglyceride Anhydride – Alcohol reaction in a solvent free, heterogeneous medium is quite slow. Therefore the use of a catalyst would be beneficial. Anhydride – Alcohol reactions are acid catalyzed. Different kinds of anhydrous acids, such as anhydrous ferric chloride, Amberlite* CG-120 were tried as catalyst and $ZnCl_2$ turned out to be the best. Although a catalyst is used, high temperature is still needed but at high temperatures glucose caramelizes. Because there is not an extensive research about caramelization mechanism, it is not properly understood what happens during reaction. It is estimated that caramelization is a complex series of chemical reactions and it starts at different temperatures depending on the type of carbohydrate.

The second parameter that determines reaction temperature is chemical environment. Caramelization reaches the slowest rate at neutral media and it accelerates under both acidic (especially pH below 3) and basic (especially pH above 9) conditions [11]. When all of these obstacles are taken into consideration, the most suitable

temperature seems around 75 ^{0}C. 8 hour reaction with fast stirring at 75 ^{0}C gave a dark colored solid. This was washed with water and hexane to remove glucose.and unreacted SOMA respectively.

Table 4.2. Initial Caramelization Temperatures of Common Carbohydrates [10].

Sugar	**Temperature (^{0}C)**
Fructose	110
Galactose	160
Glucose	160
Maltose	180

FT-IR spectrum of the product could be observed at Figure 4.15. Carbonyl of anhydride peaks at 1776.38 cm^{-1} and 1846.97 cm^{-1}, C-O-C stretching of anhydride peak at 888.07 cm^{-1} disappears. A new broad band, which stems from hydroxyl groups of glucose, is observed between 3000 and 3600 cm^{-1}. A new and strong peak at 1707.65 cm^{-1} is observed and this peak herald us an ester group. In glucose FT-IR spectrum, there is a strong peak at 1008.84 cm^{-1} which arises from ring structure form of glucose. In the product's FT-IR spectrum, this peak is not observed. So, it could be concluded that glucose is in its open chain form after reaction with SOMA.

The product was insoluble in all of the common solvents. Most probably, insolubility stems from the fact that the final product is a network rather than a SOMA-glucose adduct. Secondary hydroxyl groups of glucose may attack the anhydrides and give a copolymeric network.

When a lipophilic molecule with a secondary alcohol, cholesterol, was reacted with SOMA and it is observed that maleic anhydride opening reactions of SOMA are extremely slow even for miscible molecules as shown Section 4.4.2. The other presumption is, double

bonds in triglyceride may go under cationic polymerization reaction in the presence of Lewis Acid catalyst ($ZnCl_2$).

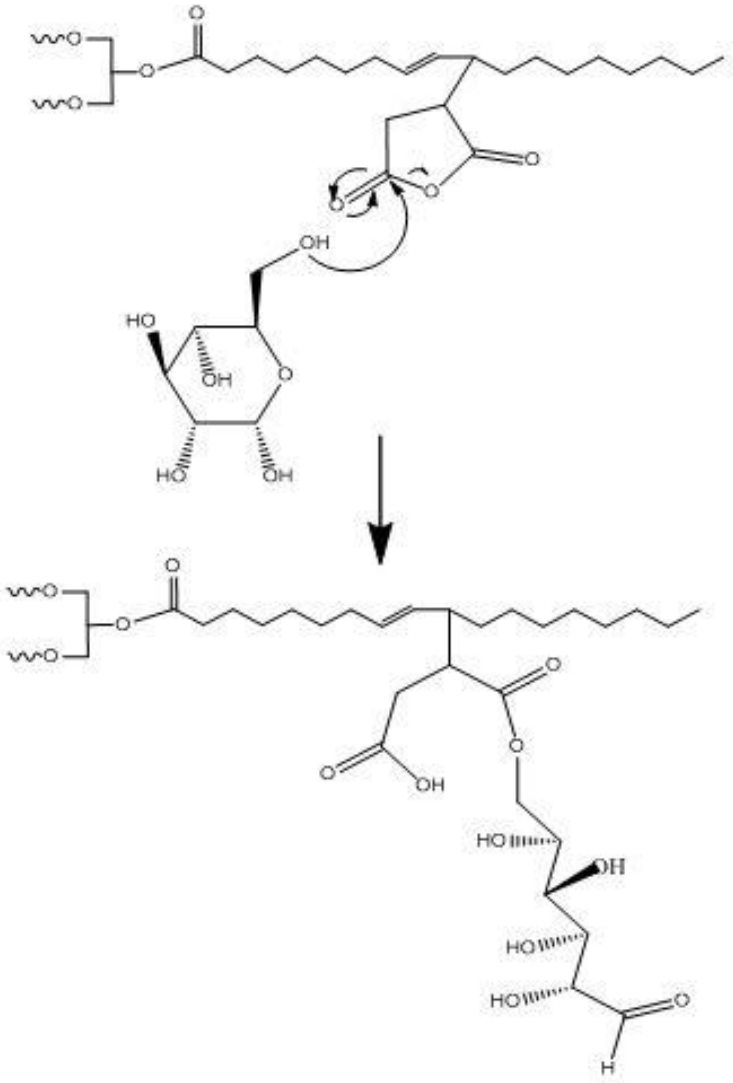


Figure 4.13. Succinic Anhydride Ring Opening With Glucose.

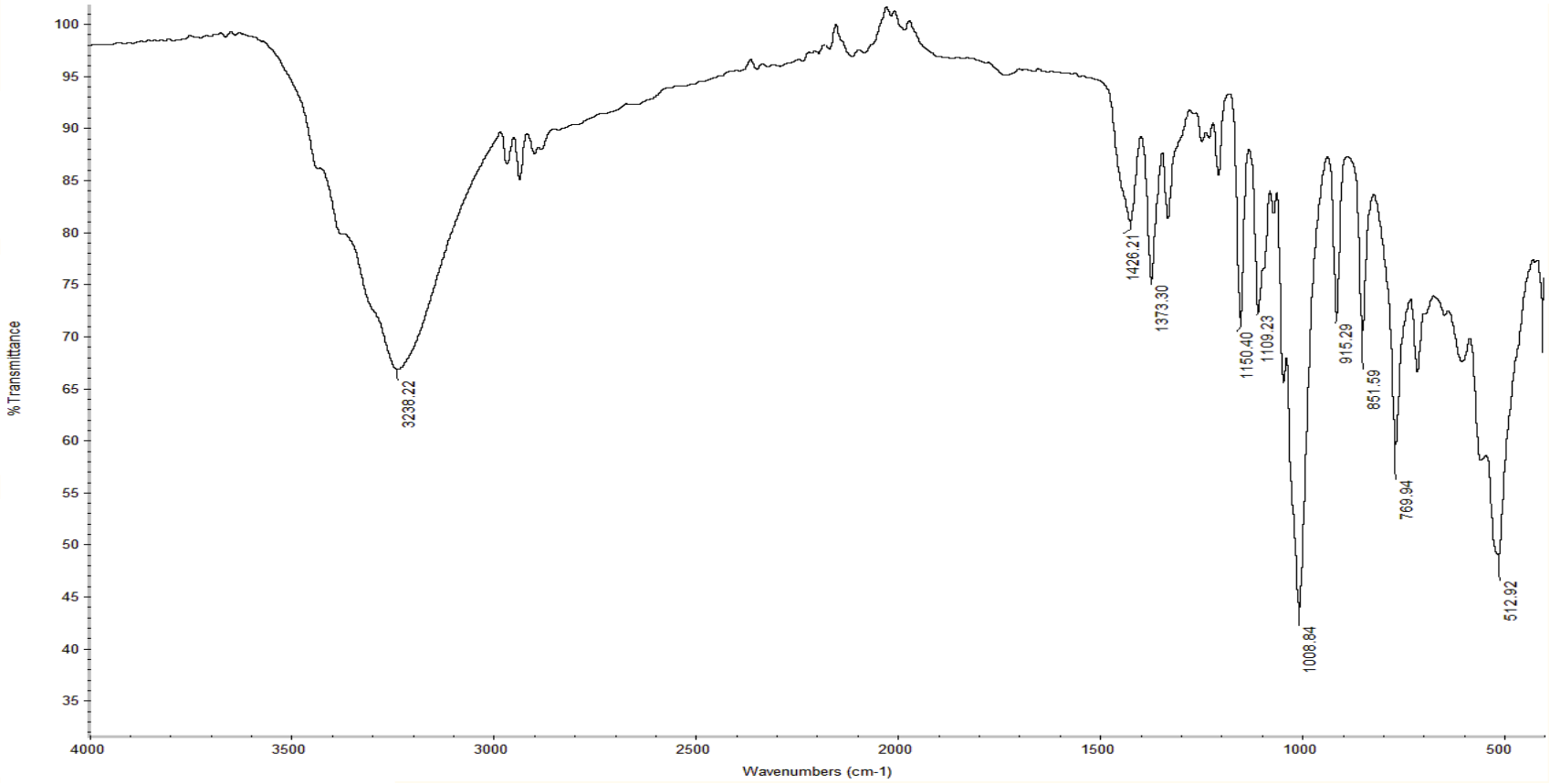


Figure 4.14. FT-IR Spectrum of Glucose.

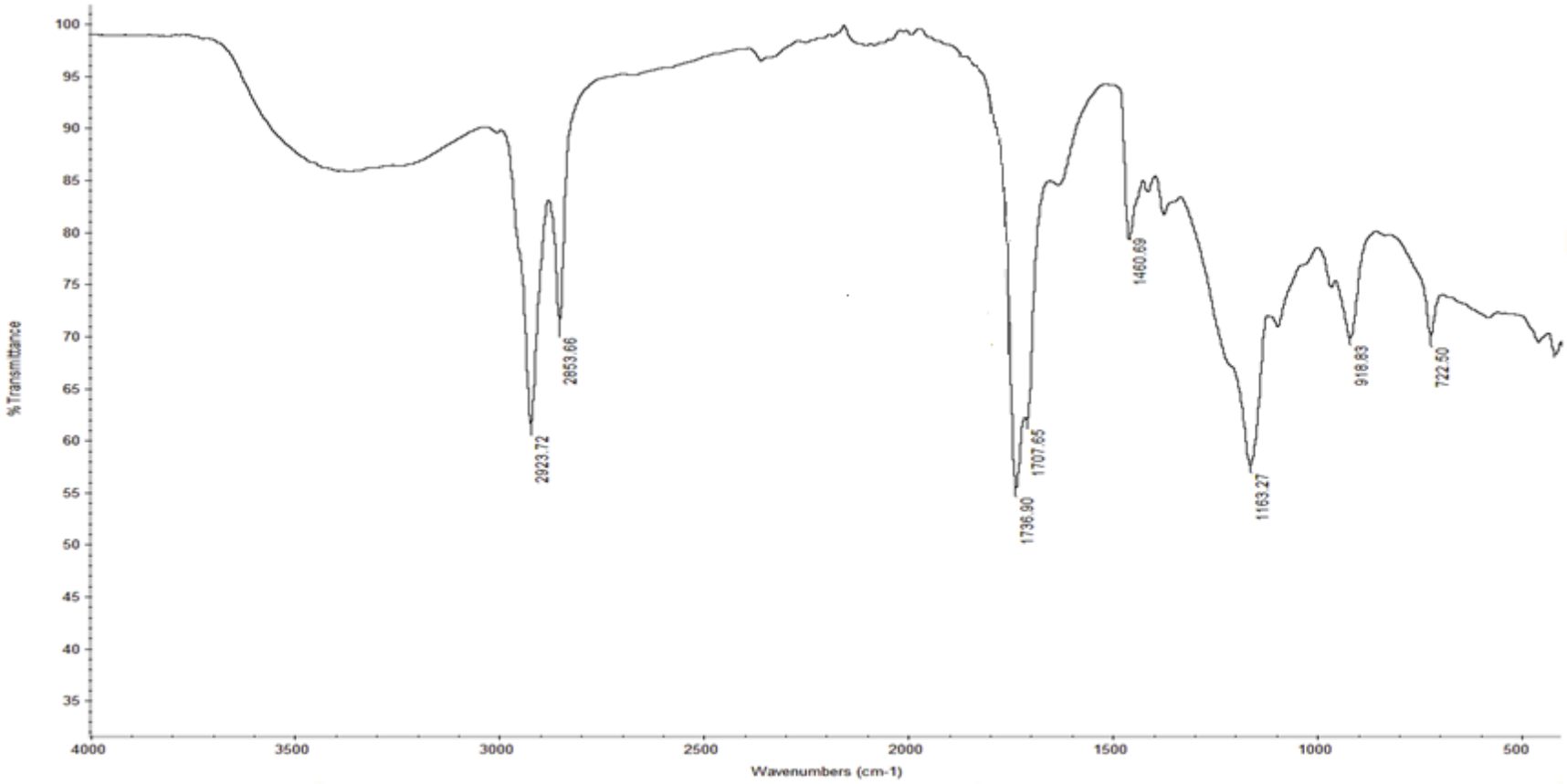


Figure 4.15. FT-IR Spectrum of SOMA and Glucose Adduct.

4.4.2. SOMA – Cholesterol Adduct

The second candidate is the only lipophilic molecule which was attached on SOMA adduct in this project. Cholesterol is a lipid molecule which is biosynthesized by all animal cells and is miscible with SOMA. This fact allows a homogeneous reaction medium without a solvent. It is a white solid at room temperature and liquefies at 147 - 149 ^{0}C. Both to overcome mixing problems by melting cholesterol and increasing thermal energy given to the system, this reaction was run at 180 ^{0}C for two days. In FT-IR spectrum of the product, in Figure 4.16, carbonyl of anhydride peaks at 1781.09 cm^{-1} and 1849.80 cm^{-1} disappears and C-O-C stretching of anhydride peak at 888.07 cm^{-1} disappears. Also, a new peak at 1708.98 cm^{-1} is observed and it signifies an ester group formation. This means that reaction is managed successfully and cholesterol molecules are attached on SOMA via an ester linkage.

This compound is the first example of a secondary alcohol reacting with SOMA in our or in other groups' work. This example takes place in this thesis to show that if both of the reactants are lipophilic, even a secondary alcohol could open a succinic anhydride on soybean oil without the help of a catalyst. However as both segments of the adduct are lipophilic this molecule was not examined for its surfactant properties.

As cholesterol adduct did not meet the original goal of this study, it was not further examined and NMR data was not taken.

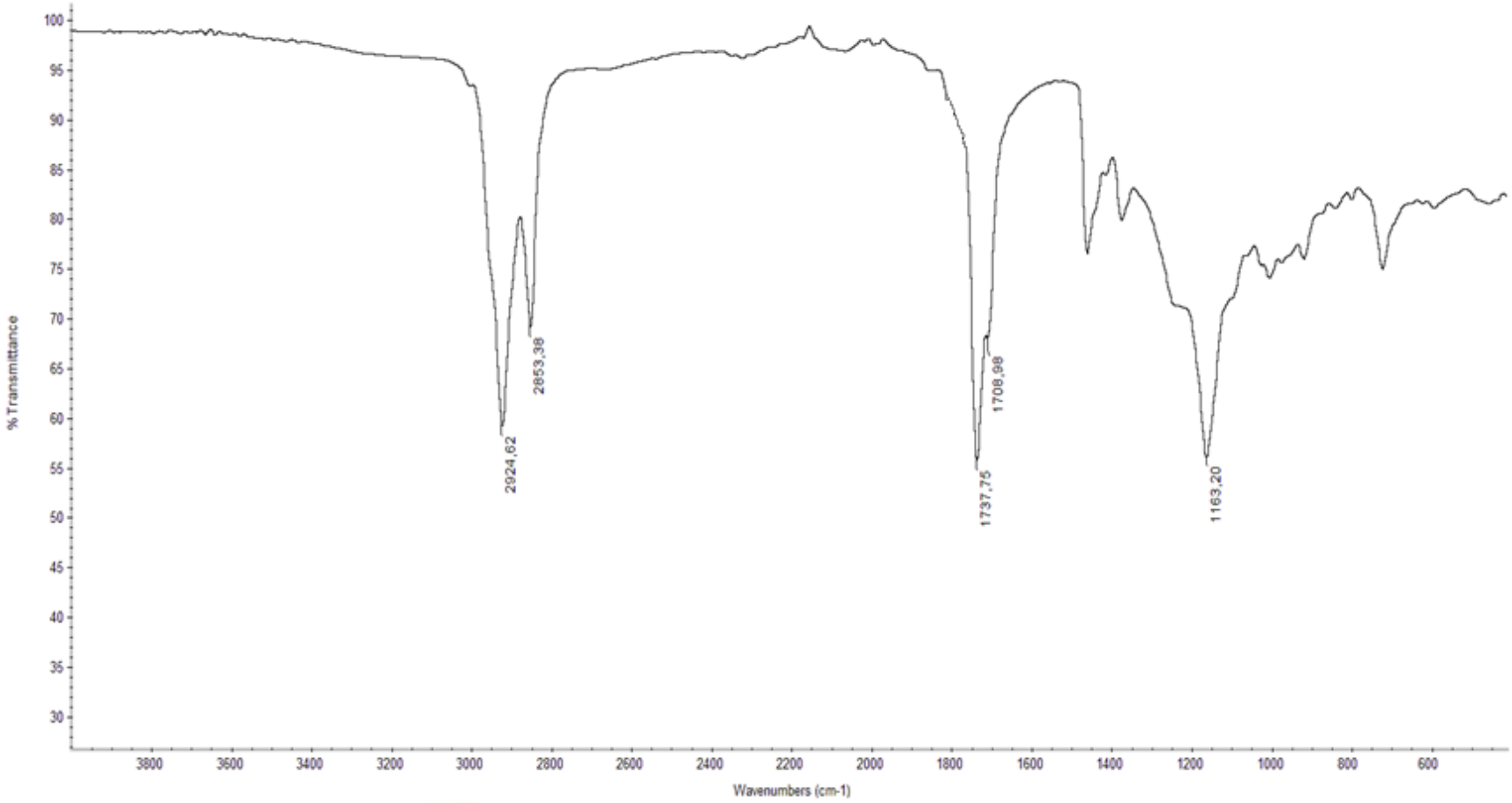


Figure 4.16. FT-IR Spectrum of SOMA and Cholesterol Adduct.

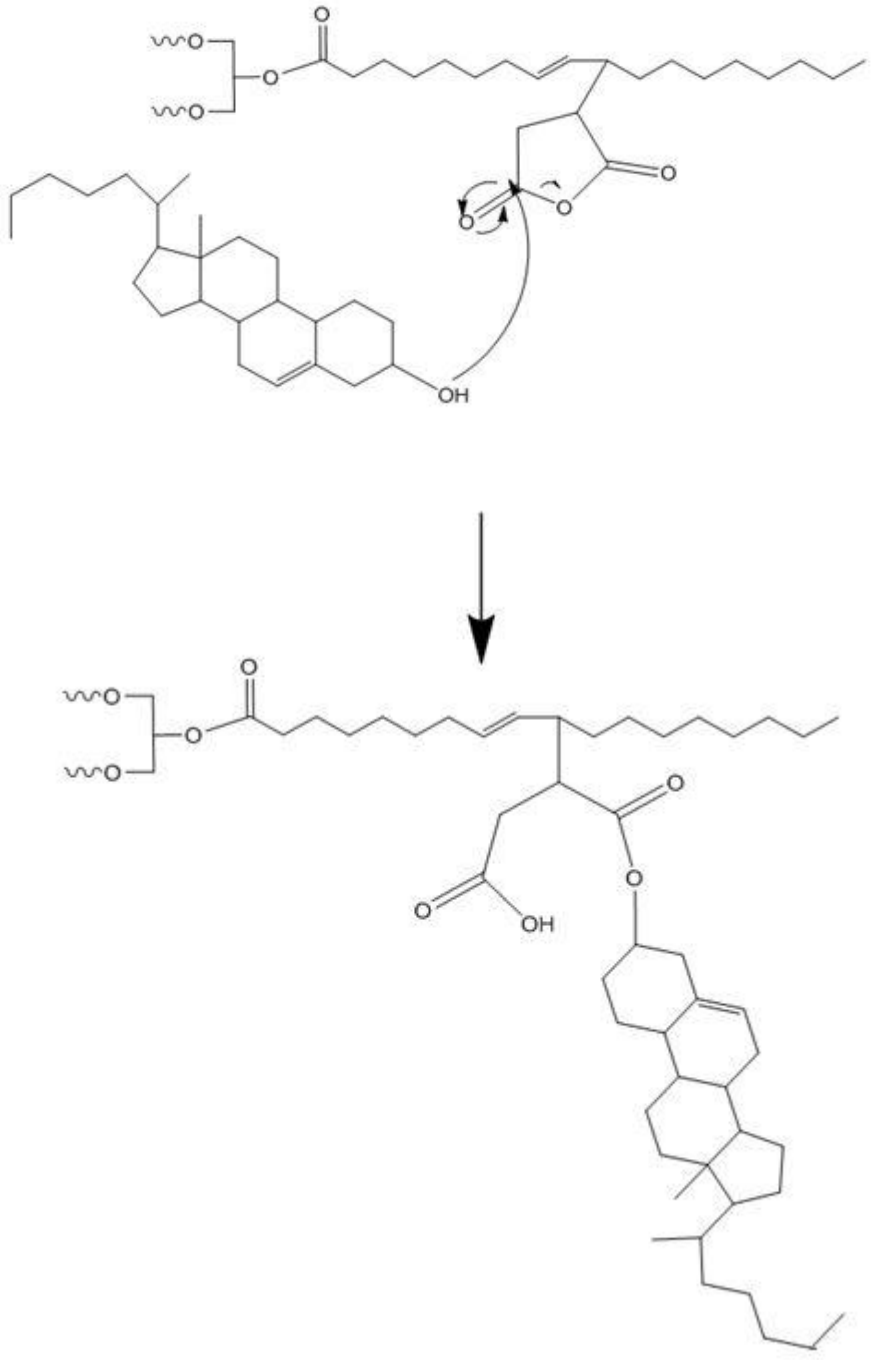
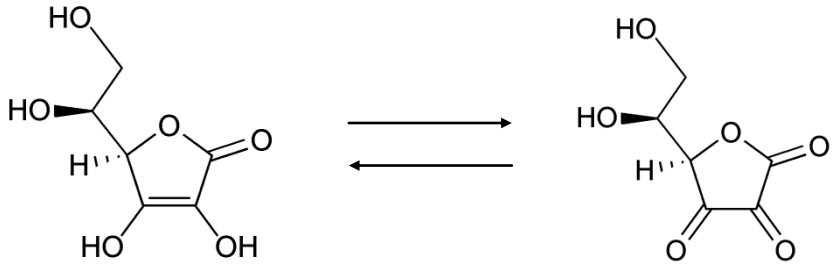


Figure 4.17. Succinic Anhydride Ring Opening With Cholesterol.

4.4.3. SOMA – L-Ascorbic Acid Adduct

The most desirable candidate in bio-active molecules group is ascorbic acid. It was first isolated by a Hungarian biochemist Albert Szent-Györgyi and answer of "what is the function of ascorbic acid?" question brought him Nobel Prize in medicine in 1937. In the presence of enzymes, ascorbic acid plays role of co-factor in various biochemical processes like synthesis of amino acids, wound healing, tissue growth, preventing bleeding from capillaries etc. Besides, in non-enzymatic media it is a powerful reducing agent which is capable of scavenging reactive oxygen species rapidly. Ascorbic acid is the enolic form of α-ketolactone. In the presence of reactive oxygen species, it plays role as a reducing agent and easily oxidized to dehydro ascorbic acid, diketo form of molecule. Ascorbic acid is water soluble and fat insoluble.



Ascorbic acid (reduced form)

Dehydroascorbic acid (oxidized form)

Figure 4.18. Reduced and Oxidized Form of Ascorbic Acid Structure.

As it can be seen from Figure 4.18, there is one primary alcohol, one secondary alcohol, and two enol groups on ascorbic acid molecule. As mentioned in Section 4.4.2 succinic anhydride ring opening reactions with alcohols occurs so fast with respect to competitors like secondary alcohols, enols etc. that it seems possible to attach ascorbic acid on SOMA from primary end, and synthesize a plant oil based reducing molecule which is fat soluble.

Ascorbic acid is a water soluble molecule and solubility problems for previous reagents come up again for this case. In literature, there are some examples which say that an esterification reaction between ascorbic acid and a non-polar molecule like decanoic acid, tetradecanoic acid is possible by dissolving both of the reactants in acetone at 50^0C in the presence of a lipase enzyme [12]. In this work, SOMA and ascorbic acid reaction was tried in the same conditions and no reaction was observed.

Although the decomposition of ascorbic acid by heat could not be explained clearly, it could be said that ascorbic acid is a carbohydrate structurally. So, it is estimated that decomposition of ascorbic acid is more or less like Caramelization or Maillard reaction, a well-known reaction between reducing sugars and amino acids in chemistry. In Maillard reaction carbonyl group of sugars reacts with amino group of an amine. However, unlike the Maillard reaction, this process does not require amino acids [13]. Like caramelization reactions, in this process degradation takes place at lower temperatures in the presence of strong acid catalysts. For that reason, this reaction could not be done by the help of an acidic catalyst.

In this work, this reaction was tried at room temperature without catalyst and solvent for eleven days. But no reaction is observed and desired product could not be synthesized.

4.4.4. SOMA – Riboflavin Adduct

Riboflavin, vitamin B_2, is a nutrient which plays a key role in maintaining health in humans and other animals' body. It is water soluble and fat insoluble. The name "riboflavin" comes from "ribose" sugar and "flavin" (from Latin *flavus*, "yellow"). Due to the ring-moiety in flavin part, riboflavin is fluorescent under UV light. By virtue of being fluorescent, it is often used to detect leaks and to find cracks and other defects on the surface of a part in industry. In that project, we aim to attach riboflavin on SOMA and

produce new plant oil based fluorescent monomers and a fat soluble molecule with a riboflavin moiety.

Riboflavin can be quickly broken down by heat and upon exposure to light and converted to lumiflavin. For that reason, this reaction has to be run at lower temperatures. At lower temperatures, viscosity of SOMA is so high that stirring problems come up again and it is impossible to mix the reagents without dissolving them in a solvent. In Section 4.3, it was claimed that there is not a suitable solvent to dissolve both of the reactants. But the solvents which are eliminated due to their low boiling point could be used if it could dissolve both of the reagents. Acetone, boiling point is 57 ^{0}C, dissolves SOMA completely and riboflavin partially, was chosen. To lower reaction temperature, anhydrous $ZnCl_2$ catalyst is used. The product of the reaction after suitable extraction steps ia a bright orange crystalline substance.

The product is a cross-linked insoluble polymeric material that is insoluble in all common solvents. It is believed that the secondary hydroxyl groups of riboflavin also react and this leads to a crosslinked network.

In FT-IR spectrum of the product, in Figure 4.21, carbonyl of anhydride peaks at 1780.84 cm^{-1} and 1852.85 cm^{-1} lessen and C-O-C stretching of anhydride peak at 888.07 cm^{-1} disappears. A new broad band, which stems from O-H stretching of riboflavin, is observed between 3000 and 3600 cm^{-1}. A new and strong peak at 1701.32 cm^{-1} is observed and this peak herald us an acid group formation. The peak at 1716.39 cm^{-1} occurs due to carbonyls of riboflavin. The peak at 1576.17 cm^{-1} is associated with in plane deformation vibration and 1541.19 cm^{-1} is linked with C-N stretching of diazine ring in flavin part. This FT-IR spectrum confirms that riboflavin is adducted on SOMA successfully by opening succinic anhydride on soybean oil with primary alcohol on ribose part of it. The expected reaction mechanism is:

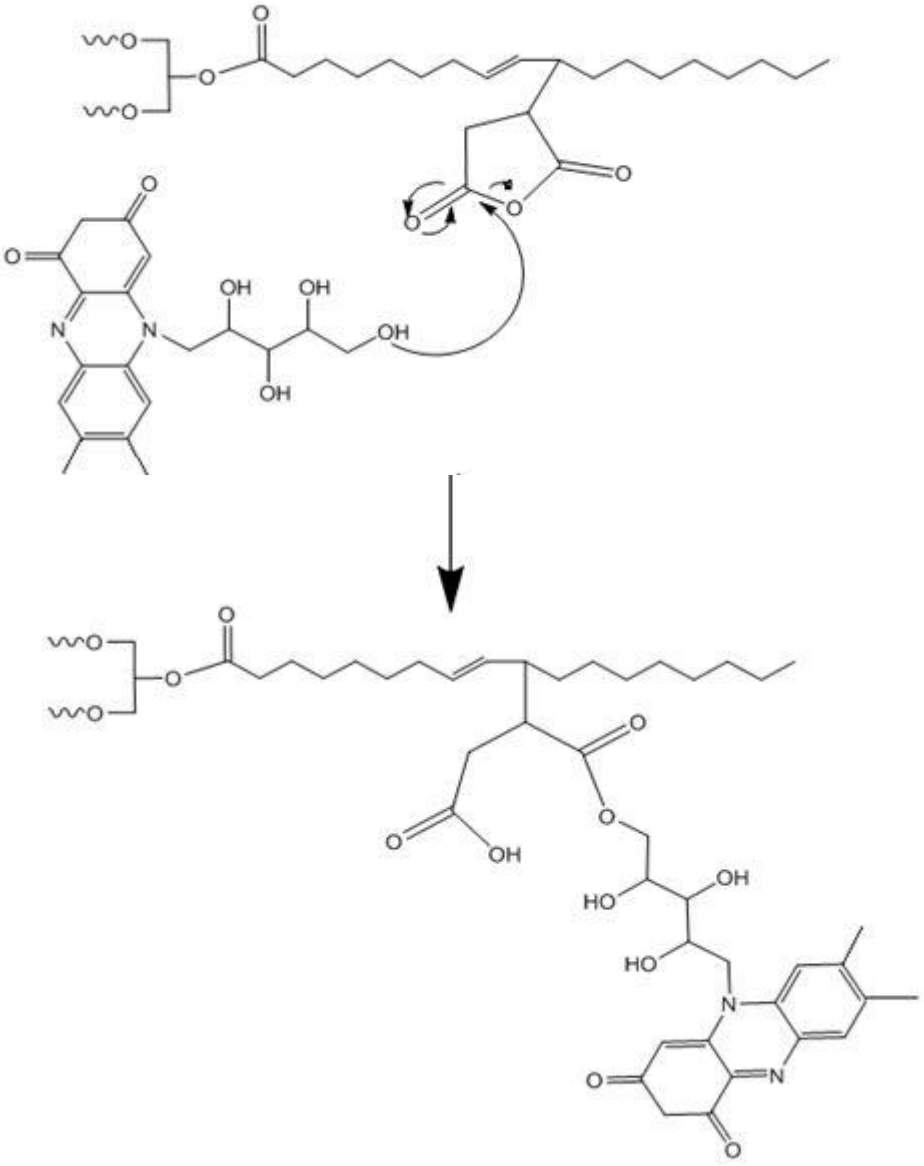


Figure 4.19. Succinic Anhydride Ring Opening With Riboflavin.

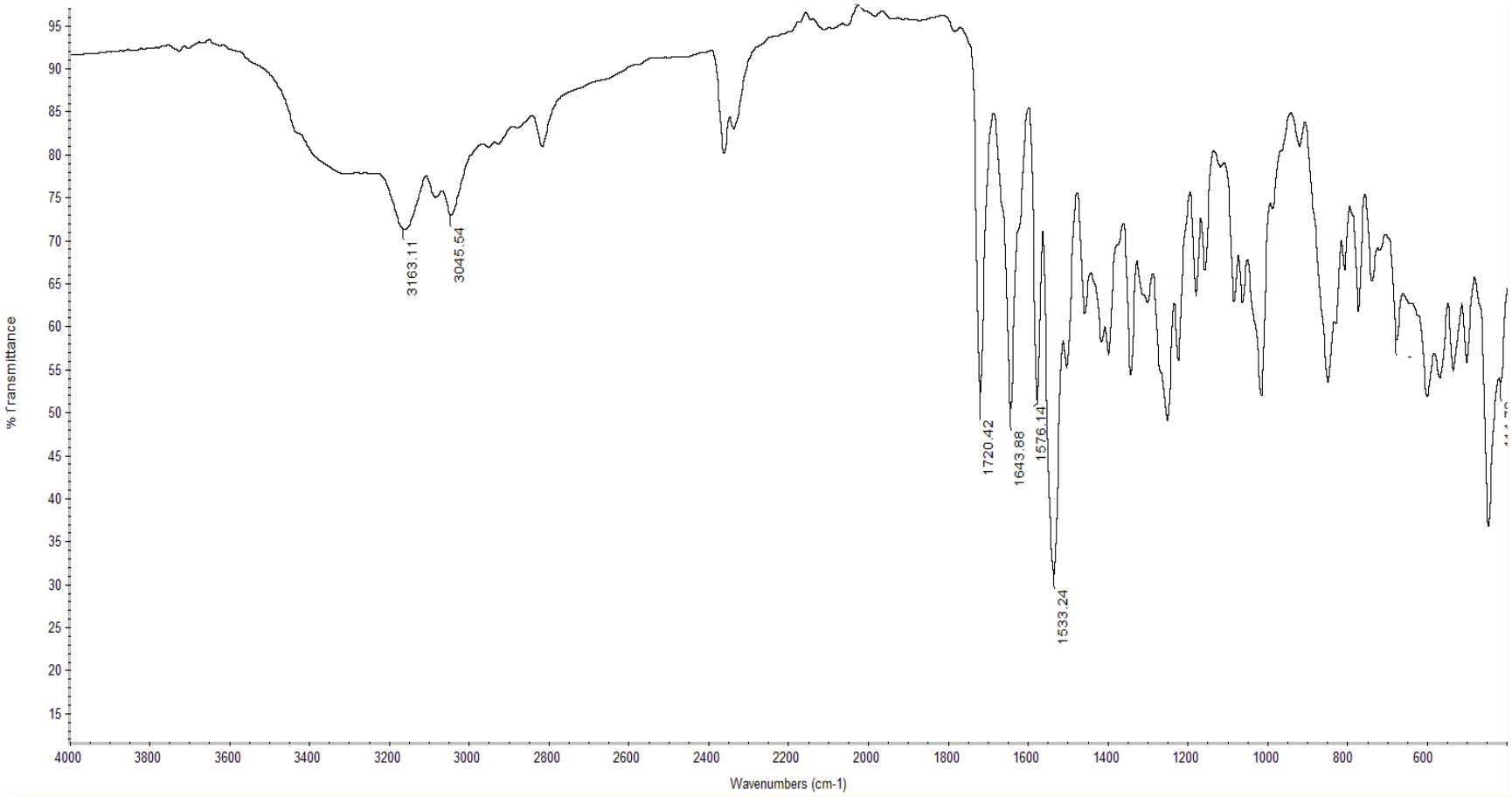


Figure 4.20. FT-IR Spectrum of Riboflavin .

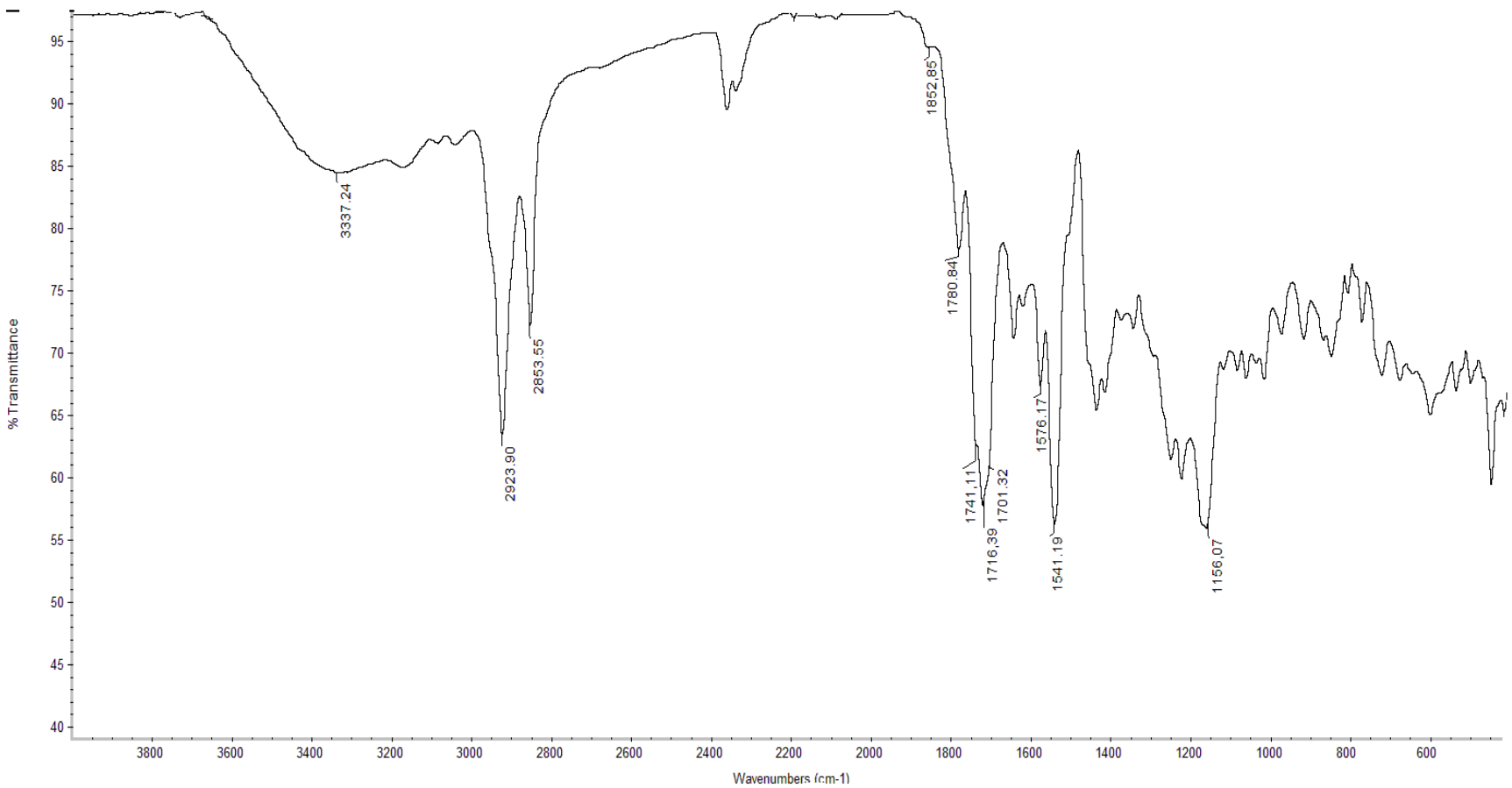


Figure 4.21. FT-IR Spectrum of SOMA and Riboflavin Adduct.

4.5. Plant Oil Based Surface Active Molecules

Surface active agents (surfactants) are the molecules composed of a hydrophilic and a lipophilic groups that are covalently bonded each other and clearly separated in the molecular structure. While hydrophilic group engages with electrostatic interactions (i.e. hydrogen bonding, dipolar interactions etc.), lipophilic group associates with non-polar structure via Van Der Waals interactions.

If the molecular structure of two liquids is very different, they are immiscible. Surfactants are used to increase solubility of non-polar structures in aqueous solutions or solubility of polar structures in organic solutions by reducing surface tension differences. They are used to stabilize emulsions, foams and dispersions.

Unfortunately, surfactants are eventually discarded and find their way into ground water and land, and some of them are known to be toxic to the ecosystem. When natural product based surfactants are degraded into their components (i.e. hydrophobic and hydrophilic parts) it is known that they enter into the ecological cycles without any remarkable toxicological impact. In this part of the project, we aim to synthesize new surfactants which are based on natural or biodegradable products instead of petrochemicals to produce renewable and non-toxic surfactants to reduce environmental damage.

4.5.1. SOMA – Methoxy Polyethylene Glycol 450 Adduct

To produce a surfactant from a triglyceride molecule, we need a hydrophilic group with high molecular weight. As mentioned in Section 4.4.1, it is easy to open a succinic anhydride ring with a primary alcohol. Therefore, the first hydrophilic reagent that we chose is Polyethylene glycol (PEG). Polyethylene glycol and its derivatives are well known surfactants used in medicine, pharmaceutics, and cosmetic industry due to their low

toxicity. A polyethylene glycol molecule with only one primary alcoholic end is chosen. Because functionality of the SOMA is above two and the product would be a thermoset polymer if the alcohol has more than one functional group. For that reason, a PEG molecule with only one primary alcoholic end, monomethyl polyethylene Glycol 450, is preferred. This compound is a liquid at room temperature, so there is no stirring problem to overcome. The number 450 refers to the average molecular weight of the polymer and it corresponds to a degree of polymerization of 10. Although the reactants do not actually dissolve each other, maximum anhydride and alcohol contact achieved by vigorous stirring. Succinic anhydride opening by primary alcohol reaction is run at room temperature for three days. A brownish, honey like product is obtained.

FT-IR spectrum of the product in Figure 4.24 shows the disappearance of carbonyl of anhydride peaks at 1782.63 cm^{-1} and 1862.63 cm^{-1} and C-O-C stretching of anhydride peak at 888.07 cm^{-1}. A new strong peak comes about 1097.46cm^{-1} which stems from C-O stretching of -(CH_2-CH_2-O)-. The ^{1}H NMR spectrum in Figure 4.25 gives additional evidence of the success of the MPEGylation reactions with the emergence of a new peak at around δ 3.53 ppm arising from the hydrogen atoms on the carbon atom which is adjacent to oxygen in polyethylene glycol group and at δ 3.40 ppm arising from hydrogen atoms of methoxy group at the end of MPEG 450. The ^{1}H NMR spectrum also gives information about the quantitative results of that experiment. The integration of nine terminal hydrogen atoms of triglyceride, which appears around δ 0.7 ppm, is 9. So, integration of one hydrogen atom should be 1. The peak integration which results from hydrogen atoms in MPEG 450's repeating group is 42.5. It means that there are 42.5 hydrogen atoms on average in repeating groups MPEG 450 molecule that is attached on SOMA.

To calculate the number of repeating group, we subtract the weight of alcohol and methyl groups from total molecular weight of methoxy polyethylene glycol molecule. Then, divide the result into molecular weight of repeating group.

$$\text{number of repeating group} = \frac{\text{mwt of MPEG 450} - \{[\text{mwt of O} + \text{mwt of H}] + [\text{mwt of C} + (3\text{x mwt of H})]\}}{[(2\times \text{mwt of C}) + (4\times \text{mwt of H}) + (\text{mwt of O})]} \quad (4.1)$$

$$\text{number of repeating group} = \frac{450-32}{44} = 9.5 \quad (4.2)$$

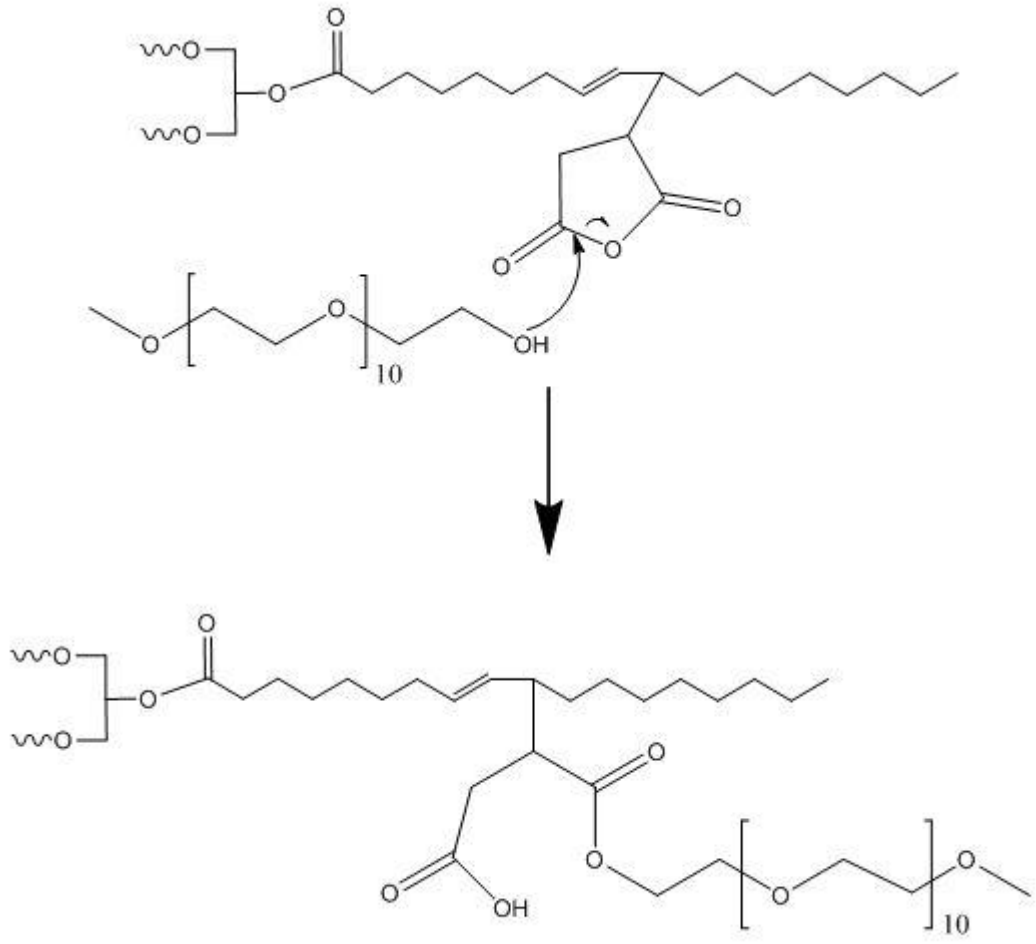


Figure 4.22. Succinic Anhydride Ring Opening With Monomethyl Polyethylene Glycol450.

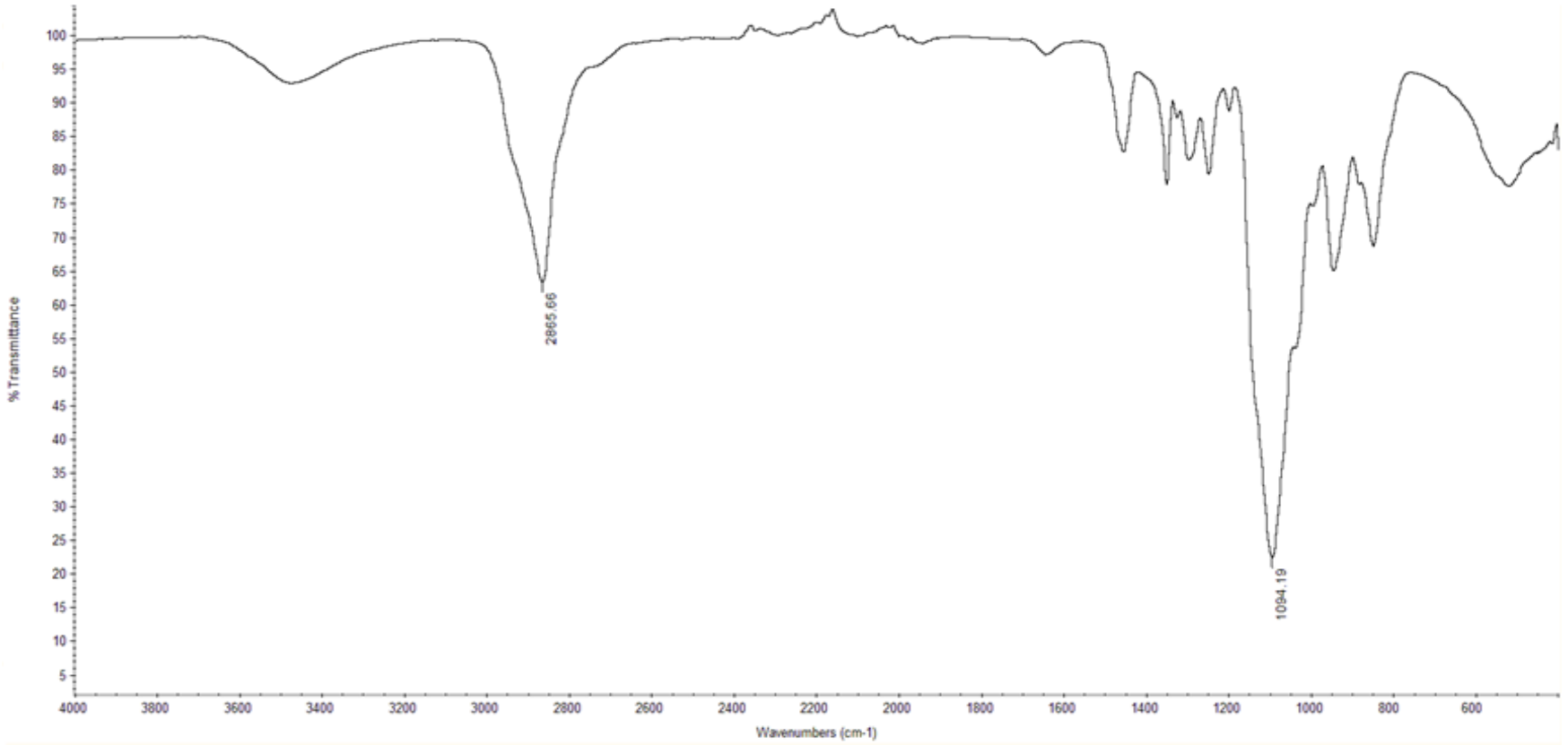


Figure 4.23. FT-IR Spectrum of Monomethyl Polyethylene Glycol 450.

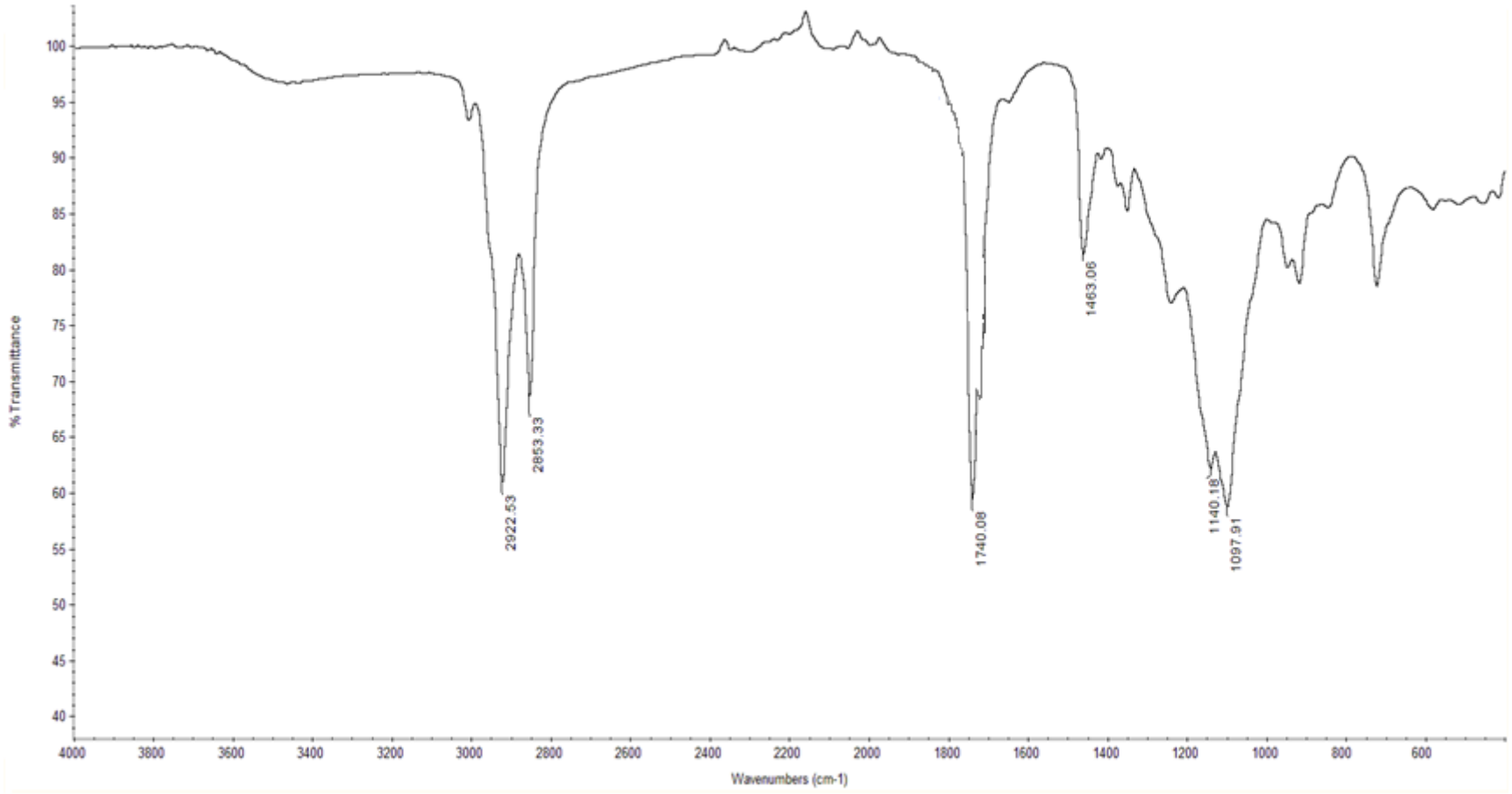


Figure 4.24. FT-IR Spectrum of SOMA - Monomethyl Polyethylene Glycol 450 Adduct.

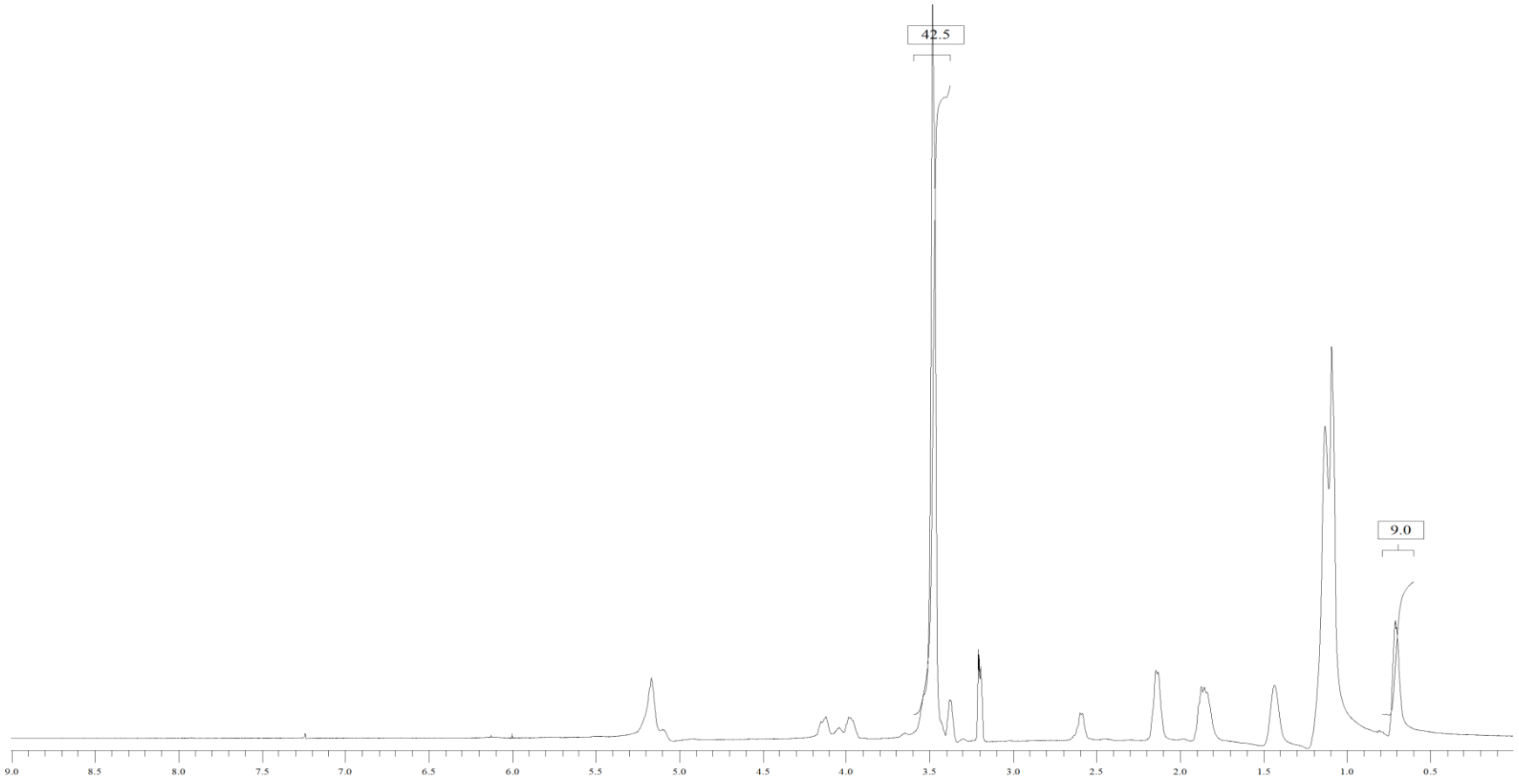


Figure 4.25.[1]H NMR Spectrum of SOMA - Monomethyl Polyethylene Glycol 450 Adduct.

There are four hydrogen atoms in each repeating group and 9.5 repeating group in one MPEG 450 molecule. Also, there are 2.14 succinic anhydride functional groups on one SOMA molecule which can react with an alcohol. To sum up, 2.14 x 4 x 9.5 = 81.32 hydrogen atoms are expected around δ 3.5 ppm in NMR spectrum. But with respect to our calculations there are only 42.5 hydrogen atoms. This means that we could attach 42.5/(4 x 9.5) ≅ 1.12 MPEG 450 on each SOMA molecule instead of 2.14. This ratio is lower than the expected ratio. Although the amount of unreacted succinic anhydride rings on SOMA could not be calculated from FT-IR spectrum, it could be definitely said that there is some unopened anhydride ring by observing the peak at 1782.63 cm^{-1}. The reason may be the hygroscopic nature of MPEG. It is impossible to obtain it dry. The water molecules, which make hydrogen bonding with MPEG 450 molecules, could easily open succinic anhydride rings. So, the yield is lower than expected.

Surfactants are classified according to their HLB (hydrophilic-lipophilic balance) value. It is a numerical value which is defined as the weight percent of hydrophilic region in the molecule divided by five.

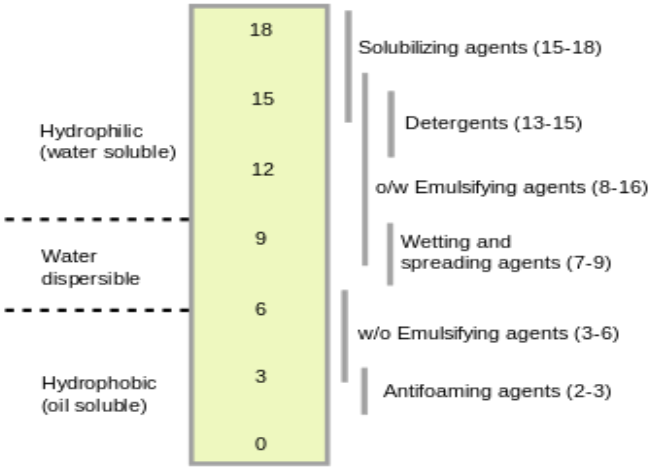
$$\text{HLB} = \frac{1}{5} \times \left(\frac{\text{molecular mass of hydrophobic portion}}{\text{molecular mass of whole molecule}} \times 100 \right) \tag{4.3}$$

Molecules with lower HLB value are expected to be more oil soluble while the ones with higher HLB value are expected to be more water soluble.

$$\text{HLB Value of SOMA–MPEG450 Adduct} = \frac{1}{5} \times \left(\frac{(450 \text{ x } 1.12)}{1064 + (450 \text{ x } 1.12)} \times 100 \right) \tag{4.4}$$

$$HLB = \frac{1}{5} \times \left(\frac{504}{1568} \times 100 \right) = 6.43 \tag{4.5}$$

Table 4.3 HLB scale showing classification of surfactant function [14].



A molecule which has a HLB value between 6 and 7 is suitable to be used as a wetting agent. It could emulsify silicone oil, petrolatum, jojoba oil etc. in water [15].

4.5.2. SOMA – Methoxy Polyethylene Glycol 5000 Adduct

To increase the HLB value of the surfactant synthesized, the hydrophilic part of the surfactant must be made bigger. This would produce a new surfactant for different purposes. Methoxy polyethylene glycol 5000 was used instead of methoxy polyethylene glycol 450. MPEG 5000 is a solid material and its melting point is around 60 – 64 ^{0}C. the PEG chain on this molecules was an average degree of polymerization of 113 Because we do not want to deal with stirring problems besides mixing a polar and an apolar molecule each other, we give thermal energy to system and reaction is run at 80 ^{o}C. The product is a pale yellow solid at room temperature.

$$number\ of\ repeating\ \ group = \frac{\text{mwt of MPEG 5000} - \{[\text{mwt of O} + \text{mwt of H}] + [\text{mwt of C} + (3 \times \text{mwt of H})]\}}{[(2 \times \text{mwt of C}) + (4 \times \text{mwt of H}) + (\text{mwt of O})]} \qquad (4.6)$$

$$number\ of\ repeating\ group = \frac{5000 - 32}{44} = 113 \quad (4.7)$$

The FT-IR analysis of that product in Figure 4.30 is a straightforward way to confirm the opening of succinic anhydride rings opening by the primary alcoholic end of MPEG5000 molecule. The diminution of the peaks at 1782.63 cm^{-1} and 1862.63 cm^{-1} is attributed to opening of anhydride ring and new peak at 1097.91 cm^{-1} is allocated to C-O stretching of -$(CH_2$-CH_2-O)- .

The ^1H NMR in Figure 4.29 analysis confirms the addition of MPEG5000 molecules to SOMA molecules by appearance of new signals around δ 3.5 ppm assigned to hydrogen atoms of MPEG 5000. To determine the quantitative result of this experiment, we compare the integration of nine terminal hydrogen atoms of triglyceride which appears around δ 0.9 ppm and four repeating group hydrogen atoms which appear around δ 3.53 ppm. The integration of terminal hydrogen is 9. This means that integration of one proton is 1. The integration of ethylene groups is 821.5. This means that there should be 821.5 hydrogen atoms on average in the repeating groups of MPEG5000 which is attached covalently SOMA via an ester linkage.

There are four hydrogen atoms in each repeating group and 113 repeating group in one MPEG 5000 molecule. So, every 4 x 113 = 452 hydrogen atoms integration around δ 3.5 ppm in NMR spectrum represents one MPEG 5000 molecule is attached on SOMA. NMR integration indicates we could attach 821/452 ≅ 1.82 MPEG5000 molecule on each SOMA molecule. Again the yield is lower than the expected value due to facts that are mentioned in Section 4.5.1.

The calculated HLB value of the new surfactant is:

$$\text{HLB Value of SOMA–MPEG5000 Adduct} = \frac{1}{5} \times \left(\frac{(5000 \text{ x } 1.82)}{1064 + (5000 \text{ x } 1.82)} \times 100 \right) \quad (4.8)$$

$$HLB = \frac{1}{5} \times \left(\frac{9100}{10164} \times 100 \right) = 17.9 \quad (4.9)$$

A surfactant whose HLB value is between 15 and 18 is defined as solubilizer or hydrotope with respect to Griffin's Method. It could emulsify oleic acid, stearyl alcohol, pine oil etc. in water [13].

When two or more emulsifiers are combined or blended, the HLB values are additive in behavior [16]. Thus if one part of an emulsifier "A" having an HLB value 6 and two part of an emulsifier "B" having an HLB value 15 is blended, the resulting HLB value is the sum of one third of 6 and two third of 15, i.e. 2+10=12. Thus, we could blend SOMA – Methoxy Propylene Glycol 450 and SOMA – Methoxy Propylene Glycol 5000 adducts in different ratios and get surfactant with desired HLB value.

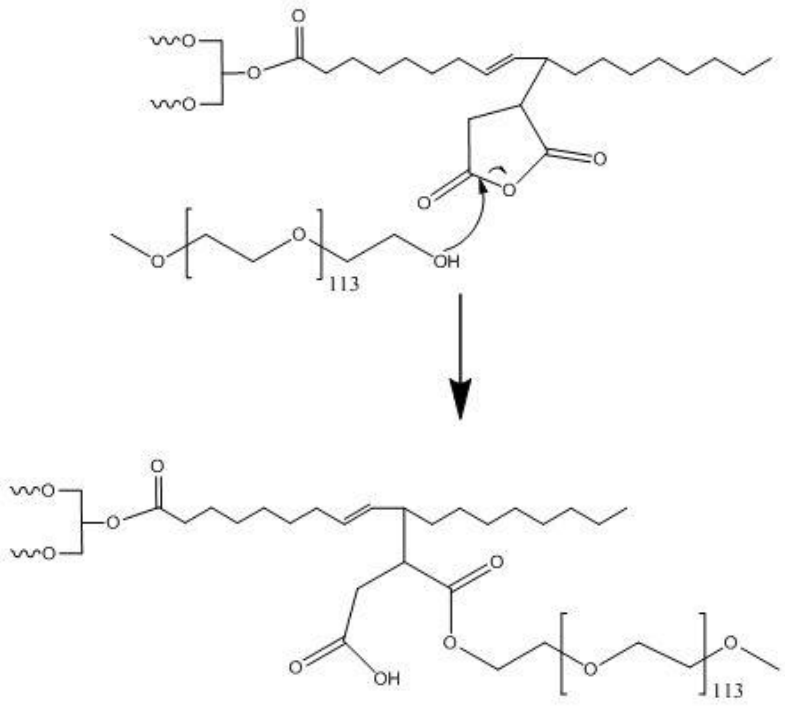


Figure 4.26. Succinic anhydride ring opening with Monomethyl Polyethylene Glycol 5000.

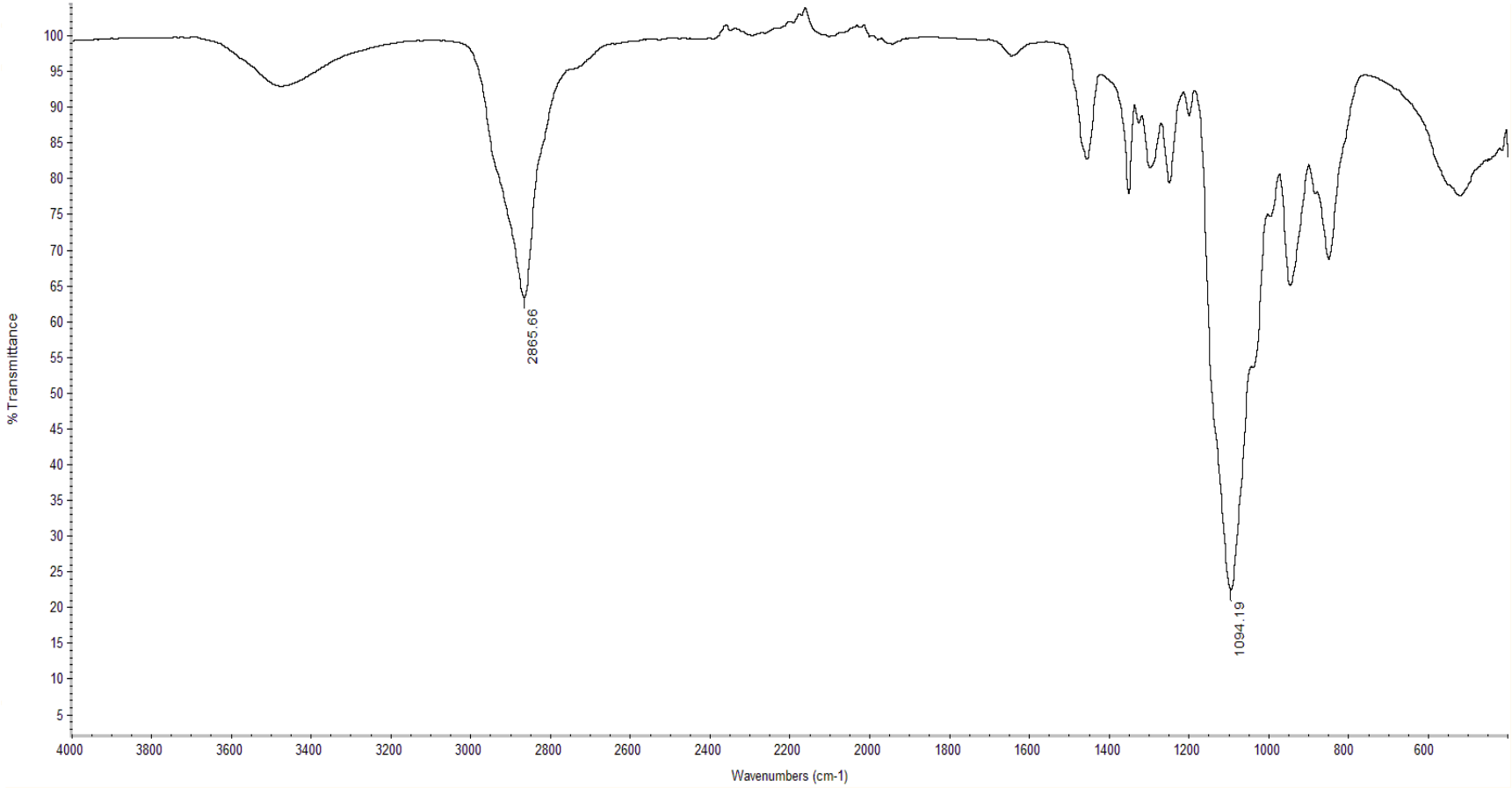


Figure 4.27. FT-IR Spectrum of Monomethyl Polyethylene Glycol 5000.

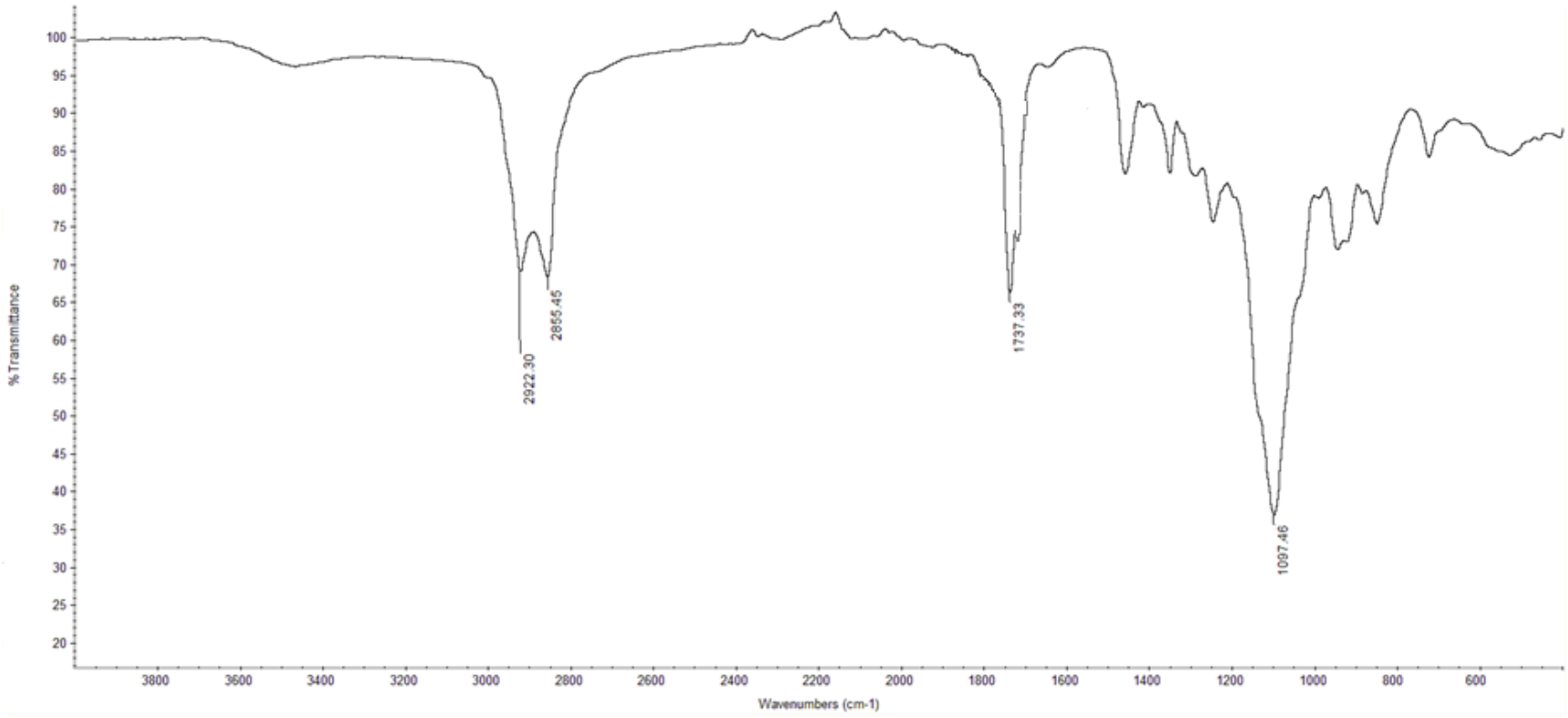


Figure 4.28. FT-IR spectrum of SOMA - monomethyl Polyethylene Glycol 5000 Adduct.

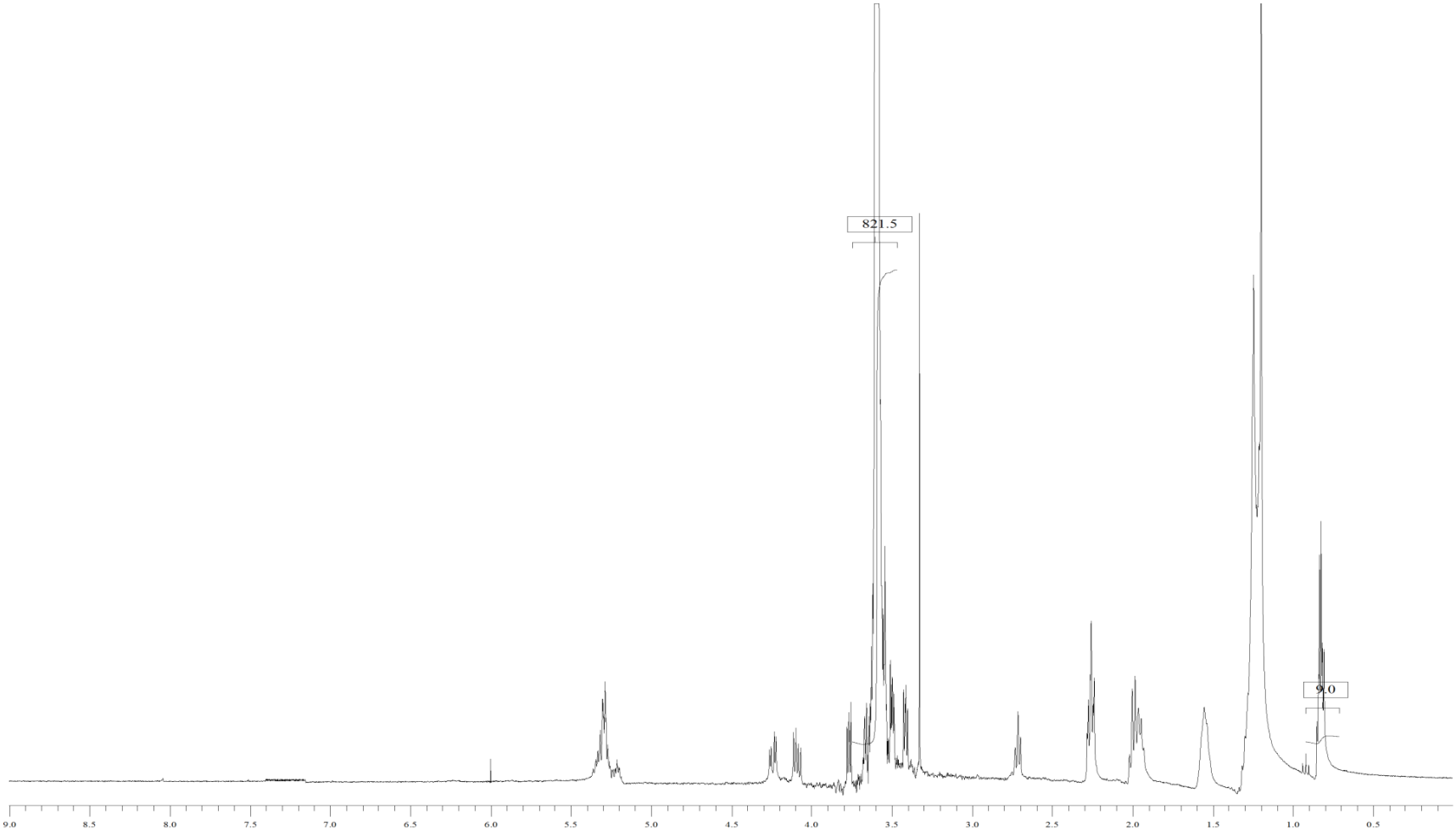


Figure.4.29. ^{1}H NMR Spectrum of SOMA - Monomethyl Polyethylene Glycol 5000 Adduct.

4.5.3. SOMA – Aniline Adduct

After obtaining favorable results by opening succinic anhydride rings with the alcohols, it is desirable to obtain more alternatives and try similar reactions with molecules having primary amine functional groups. The first reactant with amine functional group that was used is aniline. Although none of its properties fits our criteria (non- toxic, edible etc.), we ran a sample reaction with a cheaply available primary amine to observe whether succinic anhydride opening reaction will easily go amines. The FT-IR spectrum in Figure 4.31 clearly confirmed the success of this reaction by nonexistence of the peaks at 1780.84 cm^{-1} and 1852.85 cm^{-1} indicating opening of anhydride ring and presence of the new peaks at 1716.39 cm^{-1} is attributed to carbonyl of amide ,and 1541.19 cm^{-1} is attributed to C – N stretching of amide. The peak at 1618.45 cm^{-1} in Figure 4.30 is attributed to N-H bend in primary amines and non-existence of this peak in Figure 4.31 heralds that all of the primary amines in the media give reaction.

This reaction takes place at room temperature in just fifteen minutes. So, it could be said that molecules with amine functional groups are better nucleophiles than molecules with alcoholic functional groups and interesting molecules with amino end groups can be attached to attach on SOMA and produce new plant oil based polymers. At the mild conditions used there is no evidence of ester-amide exchange reactions which usually occurs when esters are placed in presence of primary amines. There was also no salt formation between the amine and carboxylic acid produce as produce as the succinic anhydride group is opened.

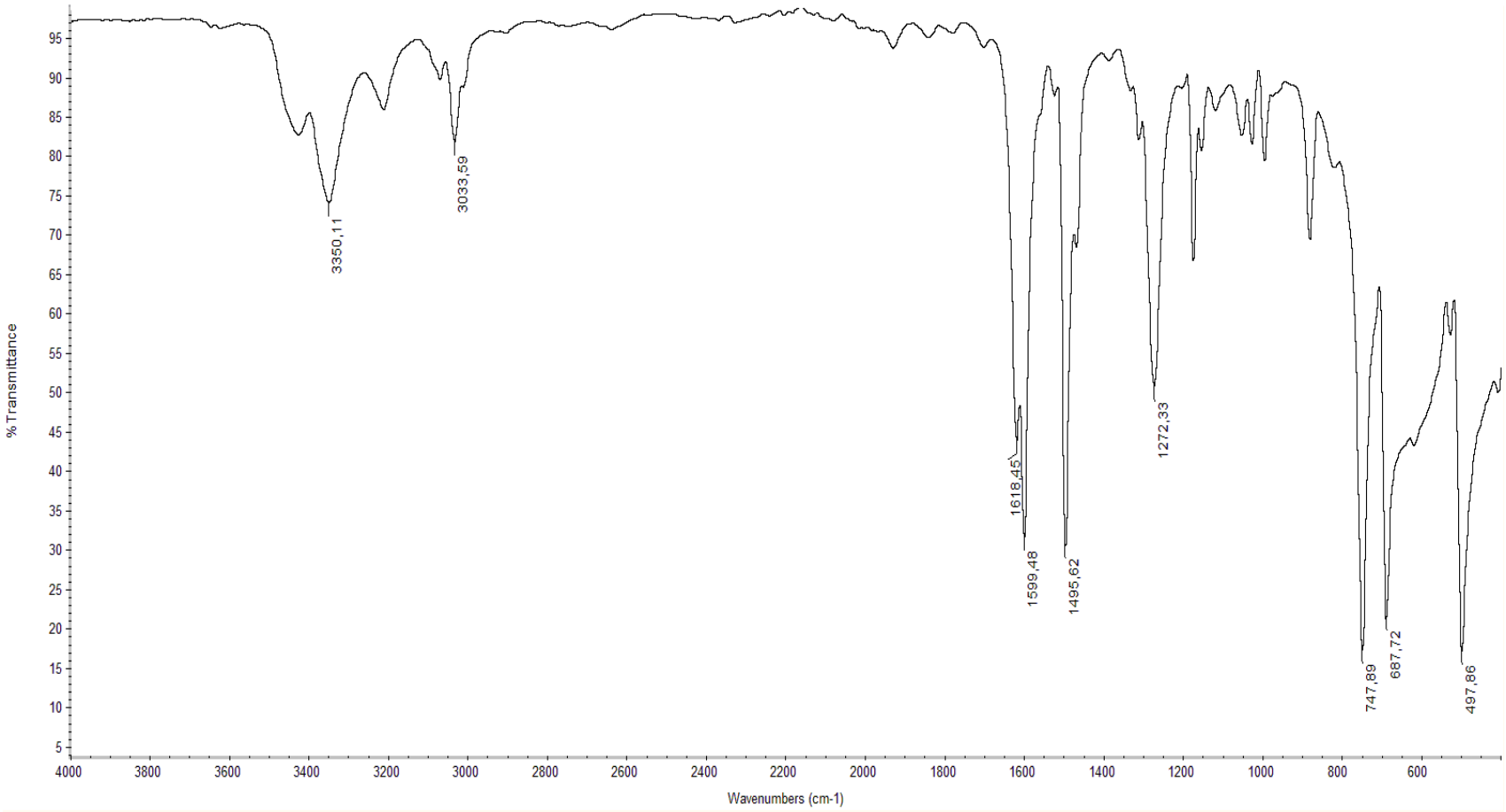


Figure 4.30. FT-IR spectrum of Aniline.

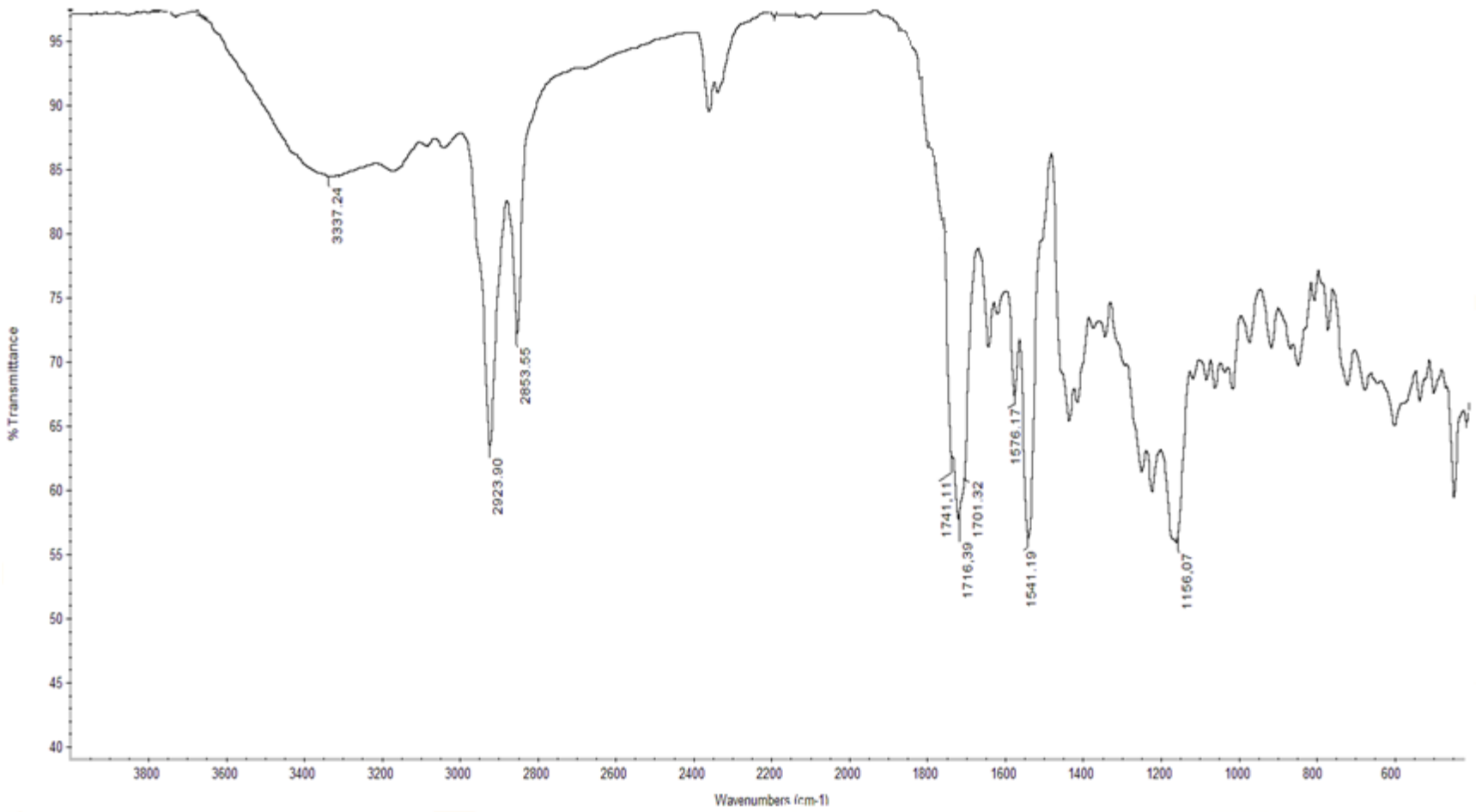


Figure 4.31. FT-IR Spectrum of SOMA - Aniline Adduct.

The proposed reaction mechanism is:

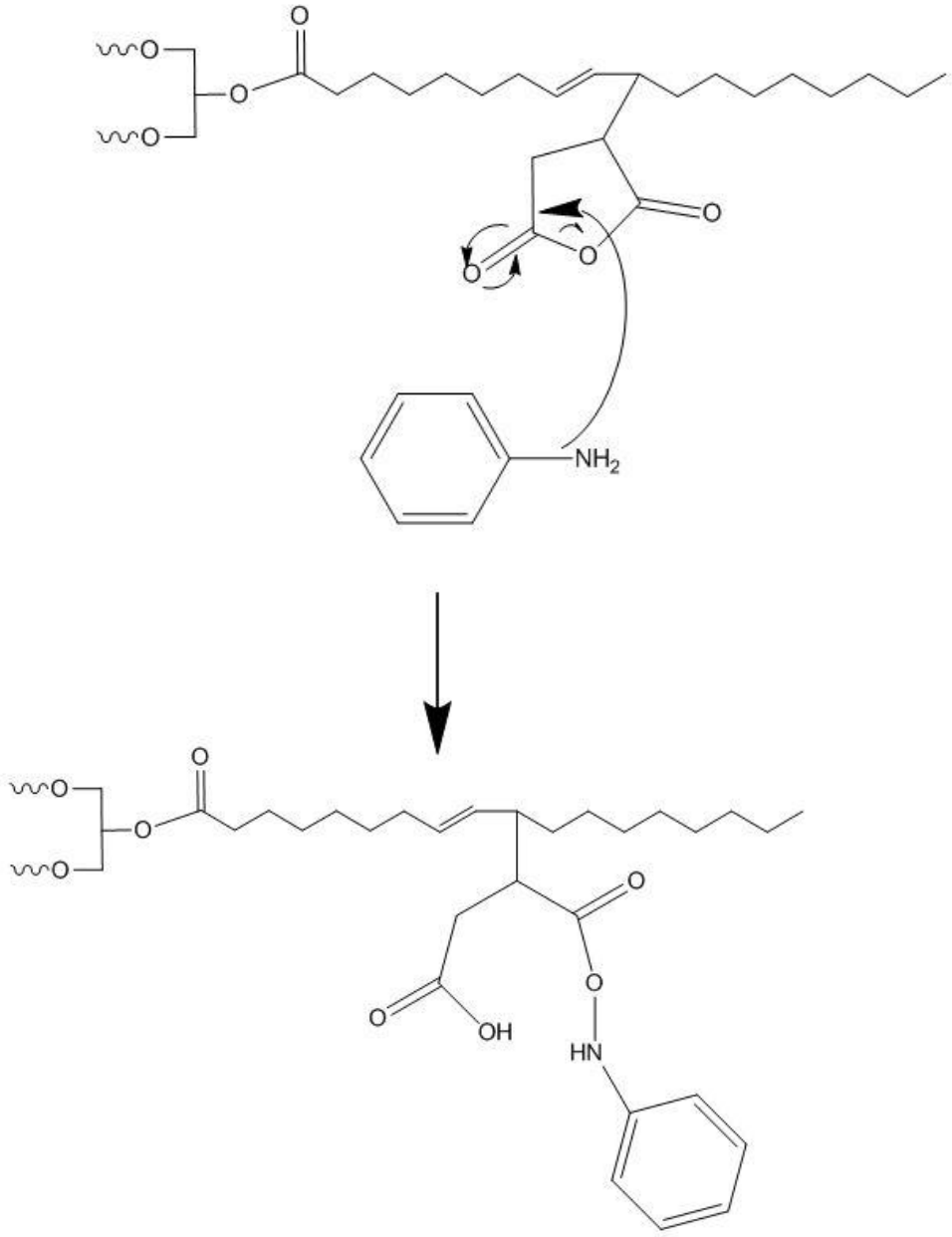


Figure 4.32. Succinic Anhydride Ring Opening With Aniline.

4.5.4. SOMA – Jeffamine T-403 Adduct

One of the molecules which has primary amino functional groups and fits our criteria is Jeffamine. Jeffamine used in this work is, poly(propylene glycol)bis 2-(aminopropyl) ether, and it contains primary amino groups attached to the terminus of a polyether backbone.

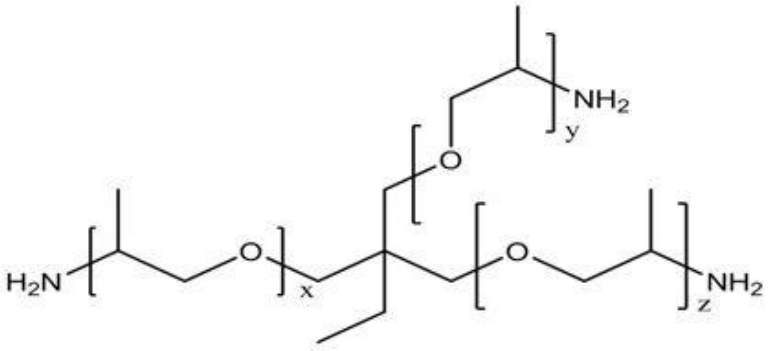


Figure 4.33. Jeffamine Molecule.

Although Jeffamines are hydrophilic molecules and have mixing problems with triglycerides, they are liquid and its possible to stir this reaction vigorously and dispers the two liquids in each other. In this thesis Jeffamine T-403 has been preferred. The letter following the Jeffamine (D or T) represents the functionality (di- or tri-) of the molecule while the number designates the approximate molecular weight [17]. Thus, a tri-functional (three amine molecules per molecule) polyether with molecular weight around 403 gram is reacted with di-functional SOMA molecule and a cross-linked product should be obtained. Although Jeffamine is not edible or renewable, it is used in the production of heart valve implants and is histocompatible.

The cross linking reaction between the SOMA and Jeffamine T-403 occurs so fast that it is not possible to manage this reaction properly and get homogeneous products at room temperature. A suitable method for achieving better control of the reaction and get

homogeneous product is to dissolve both of the reactants in a suitable solvent to decrease concentration and mix them at colder temperature to slow down the reaction. After they have been dissolved in acetone at 4°C, the mixture was left in the hood at room temperature to remove acetone. Then the mixture was kept in vacuum oven to be sure that there is no acetone left in the product. Reaction is followed by FT-IR spectrum as it is seen in Figure 4.36. The non-existence of peaks allocated to anhydride rings at 1788.61 cm^{-1} and 1849.80 cm^{-1}confirms that reaction takes place. The new peak at 1711.66 cm^{-1} indicates carbonyl's stretching in newly formed amide linkage.

The product is a soft transparent brown solid. Fracture toughness of SOMA products could be changed by changing the equivalent weight of Jeffamine. Although jeffamines are water soluble and it is expected to produce a surfactant, the final product does not dissolve in water due to its cross-linked structure. So, it could not be used as a solubilizing agent or emulsifier etc. In cross-linked molecules, evaluating swelling ability rather than HLB value gives more information about the product. Swelling is a process by which a material expands by absorbing a solvent, and increase in mass and volume. Number and the location of amino groups on PEG chain and chain length of PEG have influence on swelling properties of final products. The degree of weight average swelling ability is calculated as:

$$\text{Degree of water uptake} = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \text{ x } 100 \text{ [18]} \qquad (4.10)$$

Two samples of dried adduct were swollen in deionized water at room temperature for 1 day to achieve equilibrium. Degree of water uptake capacity of the SOMA -Jeffamine T-403 is around 12%. It is not enough to be used as a hydrogel. SOMA having a lower anhydride functionality or Jeffamine with a lower amino functionality could be used to obtain a hydrogel. Solvent uptake test could not be run at ethanol and methanol because of the fact that the product is disintegrated and dissolved in those solvents. So, it could be said that attaching Jeffamine molecules on SOMA makes it more polar. Solubility brings the advantage of getting NMR data of the product which is shown in Figure 4.36.

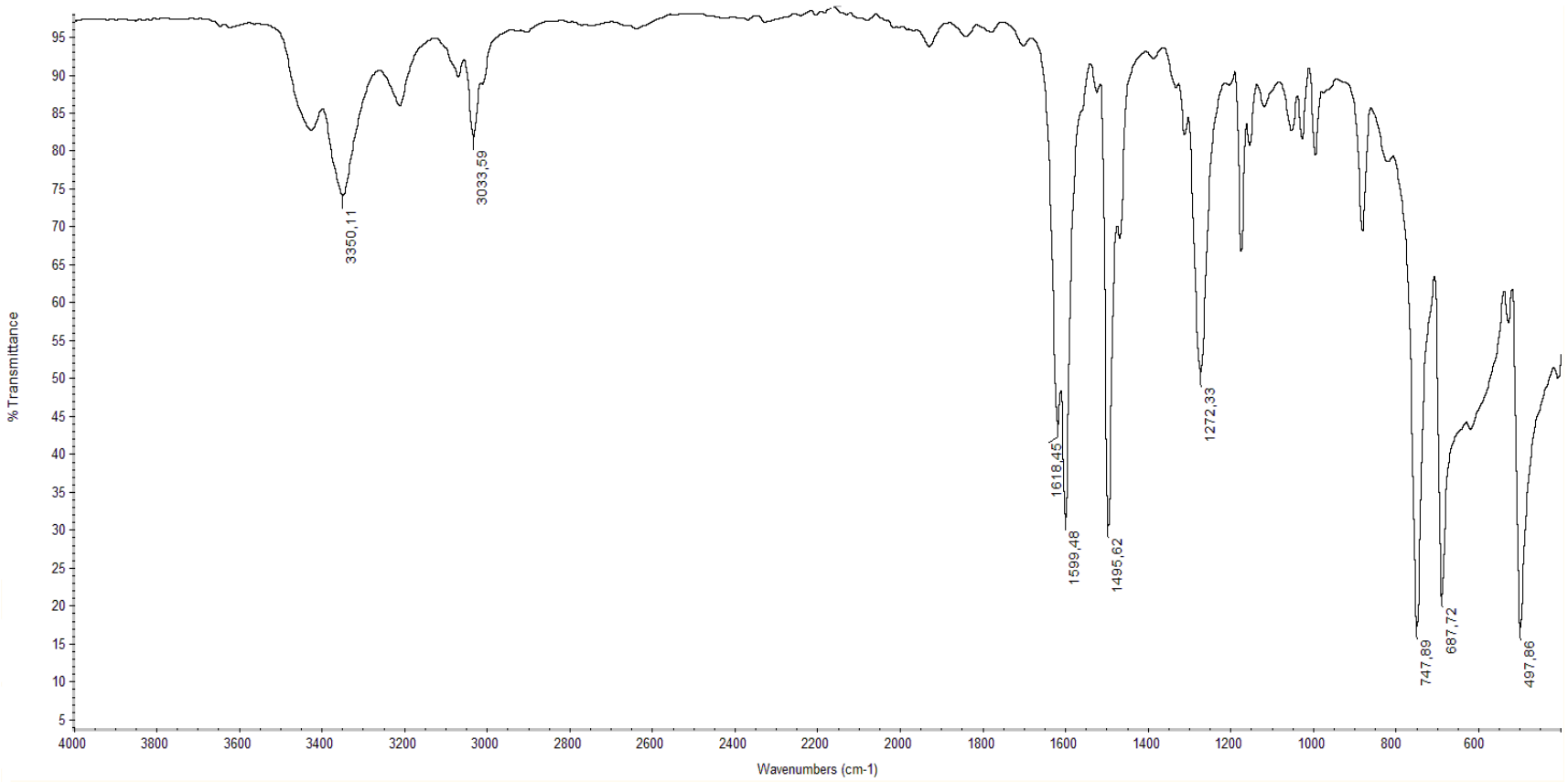


Figure 4.34. FT-IR spectrum of Jeffamine T-403.

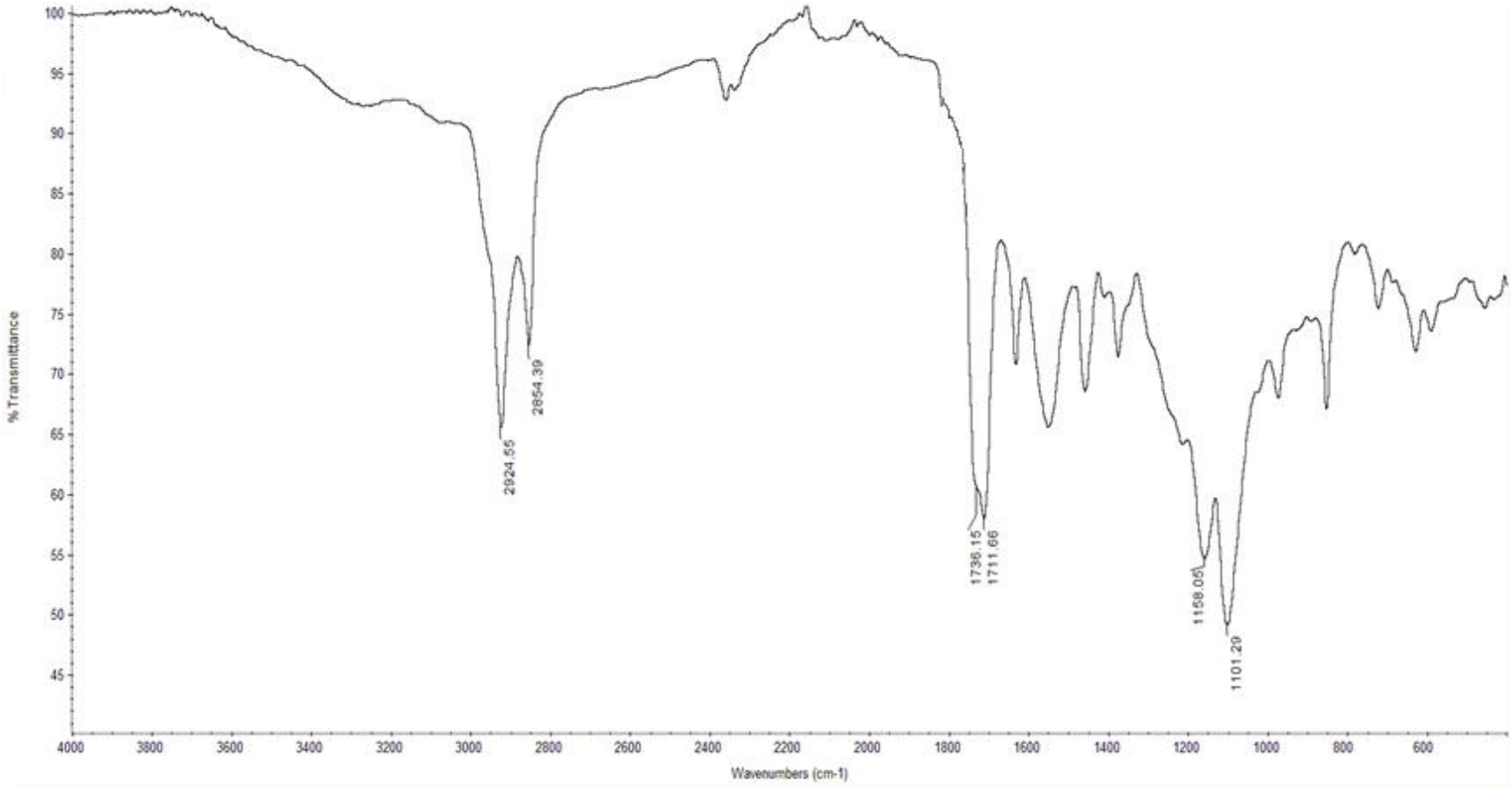


Figure 4.35. FT-IR Spectrum of SOMA - Jeffamine T-403 Adduct.

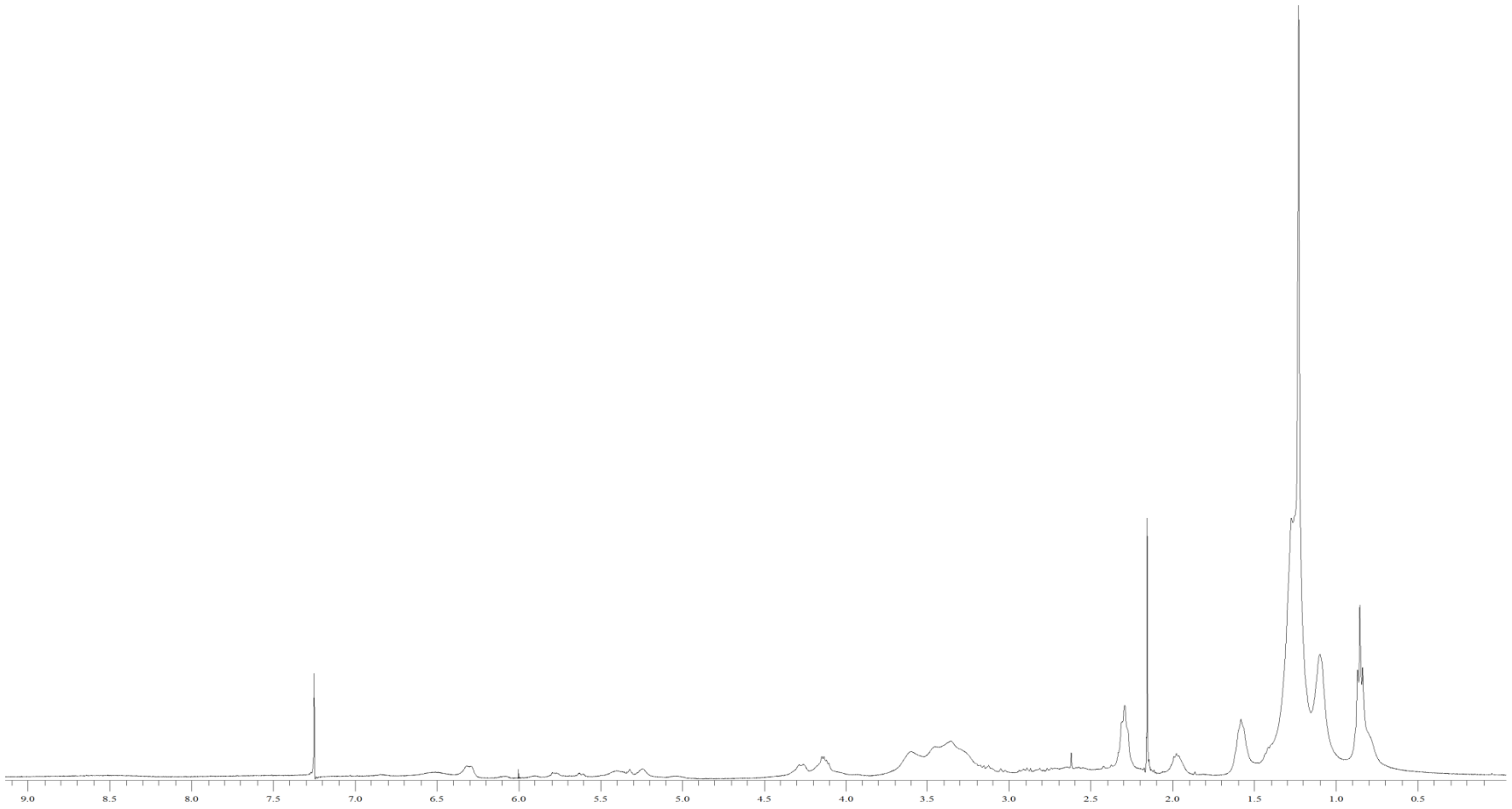


Figure 4.36. ^{1}H NMR Spectrum of SOMA - Jeffamine T-403 Adduct.

The proposed mechanism for this reaction is:

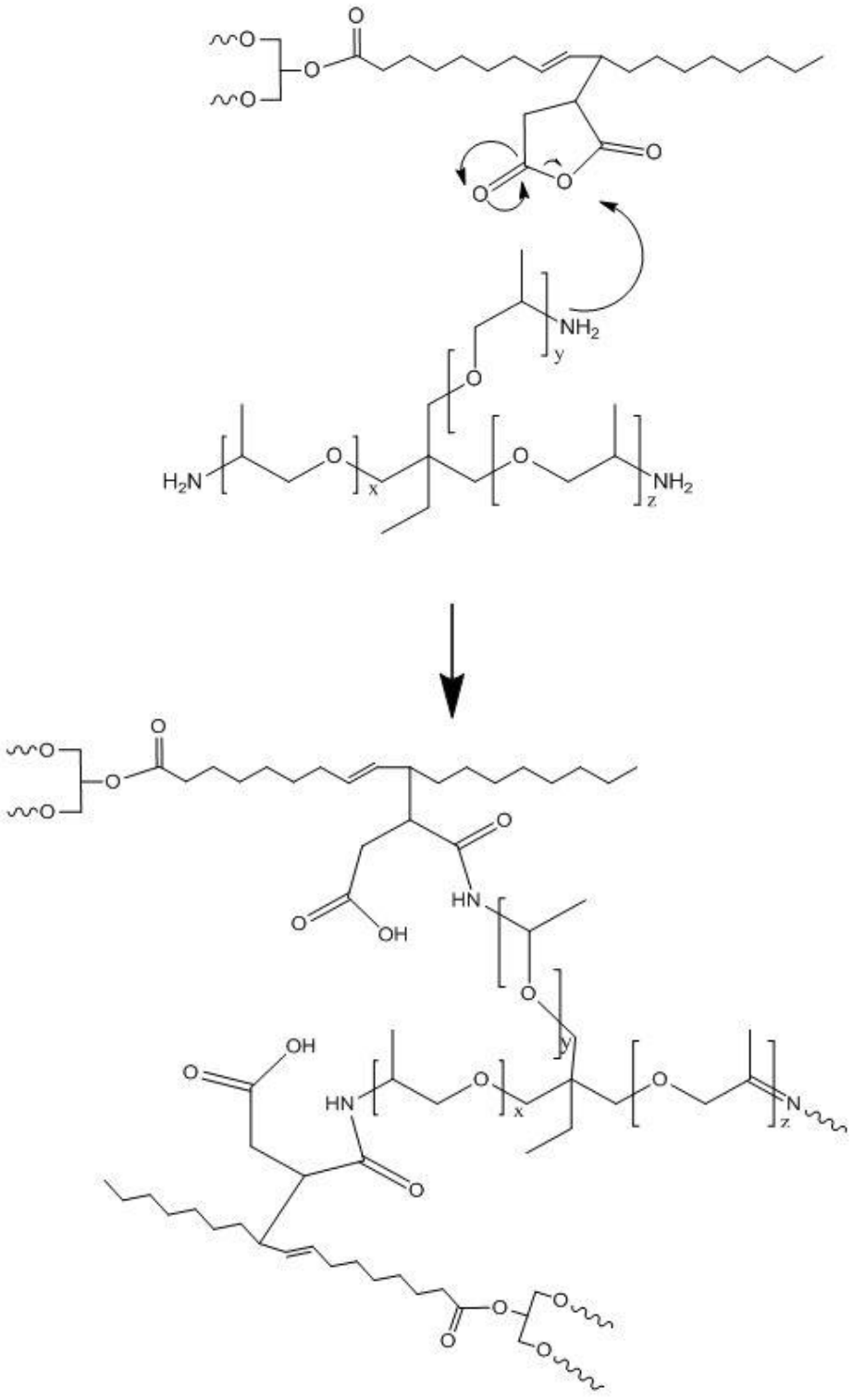


Figure 4.37.Succinic Anhydride Ring Opening With Jeffamine T-403.

5. CONCLUSION

The vigorously growing demand for biodegradable monomers and polymers from renewable resources as an alternative to petroleum oil based materials make them attractive research topics. This thesis discusses the synthesis and characterization of novel bio-active and surface active soybean oil based bio-degradable materials, including various monomers and a polymer.

In the first part of this thesis, maleic anhydride is reacted with soybean oil triglyceride and SOMA is obtained. Then, different biologically important molecules have been attached on soybean oil via succinic anhydride functional groups to produce new bio-active materials. The products contain an oleophilic triglyceride attached to a hydrophilic bioactive molecule. Such combinations are quite rarely found in nature or by synthesis.

The successful opening of succinic anhydride rings on SOMA by benzyl alcohol heralds that various biologically active molecules which have primary hydroxyl functional groups could be attached on soybean oil triglyceride. Using this chemistry, 3 different bio-active plant oil based monomers, SOMA – glucose adduct, SOMA – cholesterol adduct and SOMA – riboflavin adducts were synthesized. These syntheses suffered from lack of suitable solvent and the fact that the products were insoluble and could not be fully characterized.

Synthesis of surface active derivatives of SOMA was more successful. 2 different surface-active plant oil based molecules, SOMA – MPEG 450 adduct and SOMA – MPEG 5000 adduct were synthesized and characterized. Also SOMA – aniline adduct was efficiently prepared to confirm that succinic anhydride rings which are attached on a soybean oil molecule could be opened by primary amines. The positive outcome gives us encouragement to widen the scope of this thesis to amines and by using this chemistry a

new plant oil based surface active polymer, SOMA – Jeffamine T-403 adduct was synthesized.

Over the course of all these experiments, lots of challenging problems comes out. 4 important points can be concluded about the synthesis of novel soybean oil based bio-active and surface active molecules:

(i) If a hydrophilic molecule which is organic insoluble is tried to be reacted with SOMA, it must be liquid at the reaction temperature due to stirring problems.
(ii) If a solid hydrophilic molecule is to be reacted with SOMA, thermal energy is not enough to run these reactions. A Lewis acid catalyst must be used.
(iii) If the reactant is hydrophilic, its hydroxyl functional group must be a primary hydroxyl. Secondary or tertiary alcohols could not open succinic anhydride rings on SOMA due to the fact that primary alcohol reactions are much faster than secondary and tertiary alcoholic reactions.
(iv) If the reactant is lipophilic, its hydroxyl functional groups do not have to be primary. Secondary hydroxyl functional groups could also open succinic anhydride rings on SOMA due to the fact that it is soluble in the triglyceride.

Under the light of all data and experiments those are discussed in this thesis, it can be concluded up that new plant oil based monomers could be synthesized and characterized as an environment friendly alternative to petroleum oil based polymers. Continuously increasing demand for bio-degradable materials and decreasing cost of plant oils by cultivation of genetically modified organisms shows that more exotic plant oil based materials will be developed in near future.

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