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INVESTIGATION INTO THE ADDITION OF BENZOIC ACID
AND STYRENE OXIDE & EFFECT OF PHOSPHONIUM SALTS
FOR FLAME RETARDANCY IN POLYURETHANE FILMS

A Thesis Submitted to the Graduate School
in Partial Fulfillment of the Requirements
for the Degree of
Master of Science

Salehin Mahbub

Pittsburg State University

Pittsburg, Kansas

June, 2020

INVESTIGATION INTO THE ADDITION OF BENZOIC ACID AND STYRENE
OXIDE & EFFECT OF PHOSPHONIUM SALTS FOR FLAME RETARDANCY IN
POLYURETHANE FILMS

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INVESTIGATION INTO THE ADDITION OF BENZOIC ACID AND STYRENE OXIDE & EFFECT OF PHOSPHONIUM SALTS FOR FLAME RETARDANCY IN POLYURETHANE FILMS

An Abstract of the Thesis by
Salehin Mahbub

The thesis will be divided into two sections. First, the synthesis of a 1,2-hydroxy ester was performed using styrene oxide and benzoic acid using several different catalysts and solvents. This project was chosen because there is a limited number of studies concerning this reaction in literature and they have not addressed the ratio of stereoisomers as a function of catalyst or solvent. It was anticipated that one isomer could be obtained or an enrichment of one isomer obtained. Various catalysts will be used in this study such as tetrabutylammonium bromide, tetrabutylammonium chloride, tetrabutylammonium fluoride, tetrabutylammonium iodide to determine the effects of the halide on the reaction. The solvents chosen for this research were toluene, isopropanol, butanol and THF to determine solvents effects. Samples were analyzed by Fourier-transform infrared (FT-IR) spectroscopy and Nuclear magnetic resonance (NMR) spectroscopy. FTIR was used to determine reaction completion and NMR was used to determine the ratio of the regioisomers.

The second part of the research is the study of the effects of novel phosphonium salts on flame retardancy. New flame resistant materials are required industrially to replace halogenated flame retardants since these compounds have a negative environmental impact. In this study, phosphonium salts and triphenyl phosphate were incorporated into polyurethane films. FT-IR was used to characterize the polymer. Polyurethane films containing phosphonium salts and triphenyl phosphate were

characterized by a burn test and thermogravimetric analysis (TGA) to determine their effect on flame retardancy and thermal stability.

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LIST OF ABBREVIATION

TBAF- Tetrabutylammonium fluoride

TBAC- Tetrabutylammonium chloride

TBAB- Tetrabutylammonium bromide

TBAI- Tetrabutylammonium iodide

TEATs- Tetraethylammonium p-toluenesulfonate

THF- Tetrahydrofuran

MeCN- Acetonitrile

^1H -NMR- Proton Nuclear Magnetic Resonance

FT-IR- Fourier-Transform Infrared Spectroscopy

Chapter I

1. Introduction

1.1 Introduction of Regioisomers

1.1.1 Esters

Esters are chemical compound which are derived from a carboxylic acid and an alcohol where a hydroxyl group is replaced by an alkoxy group.¹⁷ In biology, glycerides (fatty acid esters of glycerol) are one of many main classes of lipids. Several esters which are low molecular weight can be used as perfumes and colognes and some of them are also present in pheromones and essential oils. Esters are studied as high-quality solvents for lacquers, resins, plastics and plasticizers because of their appealing smell.¹⁸ In DNA molecule, phosphorus esters form the backbone. Polyesters are used for plastics, whereas nitrate esters are popular for having explosive properties. Commercially esters are one of the largest classes of synthetic lubricant.¹⁹

Esters are less polar than alcohols but more polar than ethers. In hydrogen bonds, an ester act as hydrogen bond acceptor but cannot participate as the hydrogen bond donor as their parent alcohol. Therefore, carboxylic acids with similar or same molecular weight are less volatile than esters.²¹ FT-IR spectra of ester show band in the range of 1700-1750 cm^{-1} as $\text{C}=\text{O}$. The peak can change due to the functional groups attached to the $\text{C}=\text{O}$. The

FT-IR spectrum band of carboxylic acid is at 1680 cm^{-1} and shifts to the $1700\text{-}1750\text{ cm}^{-1}$ forming C=O as the reaction progresses.

Structurally esters are quite flexible functional groups and have low polarity, therefore they are more volatile and less rigid than amides.²¹ Esters can be stereoisomer where they embrace to be cis conformation rather than trans conformation because of a Anomeric effect.^{22,23} Normally, when cis-trans is explained, it is the two substituents on a ring or an alkene not the ester, but the relationship of R group of the ester through carbonyl usually turns out to be cis conformation. Though some cyclic structure ester tends to be trans conformation, for example small rings Lactones.

1.1.2 Reaction of Ester

A common synthesis of an ester is a Fisher-esterification where an alcohol and an acid react to ester. Esters are commonly used in biological materials and organic chemistry. It is common in industries due to its wide use in fragrances and flavor, as well as, polyester. Several esterifications are well known in industry and chemistry labs, for example esterification of carboxylic acids with epoxides, esterification of carboxylic acids with alcohol, alcoholysis of acyl chlorides and acid anhydrides, alkylation of carboxylate salts, transesterification, carboxylation, addition of carboxylic acids to alkenes and alkynes, etc. Many reactions of esters involve the addition of nucleophiles at the carboxyl carbon. In the reaction strong nucleophiles attack the carboxyl because it is weakly electrophilic, for example alkoxide, amines etc. There are several additional types of reactions of esters, for example hydrolysis and saponification, reduction, etc.

1.1.3 Epoxides

Epoxides are cyclic ethers consisting of three-atom rings. Epoxides are more reactive than other ethers due to ring strain. Epoxides have many applications and are usually produced on large scale. Epoxides which have low molecular weight are volatile, colorless and nonpolar.¹ Ethoxylation method is used for ethylene oxide to produce surfactants and detergents. Ethylene glycol is made by hydrolysis after ethoxylation which is used for sterilization (mostly medical instruments). When an amine is added to epoxides, epoxy glues and structural materials are made. In common household items epoxy is also found, for example Bisphenol A diglycidyl ether. A commercially important plasticizer, ESBO consist of epoxidezel linolein. There are naturally occurring epoxides, for example epothilones.

An epoxide containing compound are referred to by a variety of names: oxirane, ethoxyline, epoxy, epoxide, axial oxides. For example, epoxides of propylene is propylene oxide (C_3H_6O) or methyl oxirane (common name). When a polymer is synthesized from epoxide monomers, it is then called epoxy, though epoxide group are not present in the material.

1.1.4 Reaction of Epoxides

The main reactions of epoxides are ring-opening reactions. Epoxides go through several different types of reaction. Hydrolysis and addition of nucleophile where several reagents such as water, thiols, amines, alcohol, etc add to the epoxide, and this reaction basically has two commercial applications which are glycols and epoxy glues.²⁴ By hydrolysis, glycol is produced when an acid catalyst is used. Polyethers are formed when

epoxides are polymerized, for example polymerization of ethylene oxide produces polyethylene glycol or polyethylene oxide. Ethoxylation (ethylene oxide reacted with phenol or alcohol) is used to make surfactants.²⁵ Epoxides produce polyester when reacted with anhydrides.²⁶ Oxophilic reagents can deoxygenate epoxides, which can proceed with loss or retention of configuration.²⁷ Epoxides can also go through ring expansion reaction where it produces cyclic carbonates by injecting of carbon dioxide.

Ethylene oxide and propylene oxide are the most prominent and major epoxides in the industry which are produced on a large scale.²⁸ There are several syntheses of epoxides which are most often used, such as heterogeneously catalyzed oxidation of alkenes,²⁹ olefin oxidation using organic peroxides and metal catalyst,³⁰ olefin peroxidation using peroxy carboxylic acids,³¹ homogeneously catalyzed asymmetric epoxidation,³² biosynthesis,³³ intramolecular SN2 substitution³⁴ and nucleophilic epoxidation. The SN2 substitution includes dehydrohalogenation, where the chloride is intramolecularly displaced by an alkoxide ion and the parent compounds are called halohydrins. This can be produced by halohydrate of an alkene.³⁴ In nucleophilic epoxidation, an electron-deficient olefin is epoxidized by nucleophilic oxygen compounds, for example peroxides. This reaction has a two-step mechanism, a stabilized carbanion is formed by oxygen carrying out a nucleophilic conjugate addition and the epoxide ring closes when the carbanion attacks the oxygen atom replacing the leaving group.

1.1.5 Addition of Carboxylic Acid to Epoxides

Epoxides are intermediates which are easily synthesized in organic synthesis and can undergo ring-opening reaction with several nucleophiles. The ring opening reactions

of epoxides with catalyst and carbon dioxide forms cyclic carbonates. Also ring opening reaction of epoxides with oxygen nucleophiles (for example phenols and carboxylic acids) are used for the synthesis of ethers and beta-hydroxy esters. For ring opening reactions of epoxides, strong acids and bases are often used as the catalyst for both carbon dioxide and oxygen nucleophiles.³⁵

The ring-opening reactions of epoxides with carboxylic acids has been carried out using various reagents and conditions. Research at Yeungnam University showed new conditions developed for these processes. The results of their study showed that a variety of quaternary onium halides promote these processes and that tetrabutylphosphonium bromide was the most efficient catalyst due to the high percentage yield.³⁵ Another research at Ohio State University showed homopolymerization of propylene oxide and the copolymerization of propylene oxide and carbon dioxide by porphyrin aluminum(III) complexes was first order in aluminum. This research was one of the first stereochemical consequences of ring-opening of SO by a coordinate metal catalyst and was effective.³⁸ Two researches at Shiraz University of Technology showed TBAB as a catalyst for the ring opening of epoxides with benzoic acid derivatives in anhydrous MeCN to afford benzoylated 1,2-diols and the quantity of TBAB affected the reaction progress.³⁹ Another process where synthesis of 1,2-diol mono-esters via ring opening of epoxides was reported with structurally diverse carboxylic acids as well as amino acids using [bmim]Br as a room temperature ionic liquid.⁴⁰

1.1.6 Project Rationale of Regioisomers:

Epoxides are a versatile-intermediates in organic synthesis and many are commercially available. The addition of carboxylic acid to an asymmetric epoxide gives

two regioisomers which is often undesirable in synthesis. The main goal of this research was to obtain one isomer or improve upon the ratio of the regioisomers by changing reaction conditions. For this study various solvents were used from protic or polar aprotic solvents. In addition various catalyst were used to determine their effects on the reaction.. This research could help achieve one product instead of two regioisomers.

1.2 Introduction of Flame Retardants

The use of polymeric materials is growing continuously, and many polymeric materials require flame retardant properties, depending on application.² Most polymers are carbon based and therefore inherently flammable.³ Industries prefer flame retardant materials to be ecological and to combat combustion to a higher degree. The type of flame retardant required varies with application: automotive industries require more time after the ignition for the person to escape the situation. Home furnishing and appliances focus on fire resistance. The initial goal for building materials and trains are to restrain or to slow the fire.

1.2.1 Flame Retardants

There has been a major change in the flame retardants material sciences; halogenated flame retardants have issues with toxicity and other biohazards. Therefore, a replacement for halogen-based flame retardants is needed.¹ Non-halogenated flame retardants have appeared as the effective additive system used in engineering plastics. Even though several commercial flame retardants still use halogenated flame retardants, currently industry is seeking non-halogenated flame retardants due to their lower toxicity and environmental considerations.¹ Halogenated flame retardants are toxic and harmful to the ecological system which requires a shift from halogenated flame retardants to non-halogenated flame retardants.

The four basic flame retardant mechanisms are endothermic degradation, thermal shielding (solid phase), dilution of gas phase and gas phase radical quenching. In endothermic degradation, when heated to high temperature some compounds break apart

endothermically. For example, magnesium and aluminum hydroxides when heated along with carbonates and hydrates, heat is removed from the surface and cools the material.^{6,8,9} Since, hydroxides and hydrates have a low decaying temperature, it helps the polymer to not reach its melt temperature, such as polyolefins for wire and cable applications. Thermal shielding creates a thermal insulation barrier between the burning surface and the unburned portions of the material to prevent the spreading of fire. The surface of the polymer is charred which creates a separation between the fire and the material. Phosphate-based flame retardants usually fall under thermal shielding by creating a charred phosphoric acid polymer layer.¹⁰ Dilution of gas phase lowers the inert gases pressure created by thermal degradation and the pressure of oxygen which helps to delay the combustion.^{4,5} In gas phase radical quenching, halogenated materials (chlorinated or brominated) thermally degrade to create HCl or HBr which reacts with H and OH radicals in the flame to make it inactive which helps to delay or prevent the combustion.^{7,8g}

The health concerns by the earliest flame retardants, polychlorinated biphenyls (PCBs), were detected during mid-1970s, and in 1977 it was banned in the United States when found to be toxic.¹¹ Therefore industries started using brominated flame retardants. However, under closer scrutiny. Several types of polybrominated diphenyl ethers (PBDEs) were banned in the European Union in 2004 and 2008.¹² When flame retardant products are thermally degraded, the degradation products are toxic. For instance, when a halogenated compound is heated, it can degrade into dioxins and dioxin-like compounds.¹³ This can happen during a fire, recycling, production or when exposed to sunlight. One of the highly toxic compounds listed by the Stockholm Convention on

Persistent Organic Pollutants is chlorinated dioxins. In addition, a higher number of bromine atoms in polybrominated diphenyl esters can be more toxic to the environment.^{14,15} When PBDEs are metabolized they can create hydroxylated metabolites which can be more toxic than the original compound.

1.2.2 Polyurethanes

Polyurethanes are commonly used in daily life in various application. Polyurethanes are produced as rigid foams, flexible foams, surface coating and elastomers. They are used as furniture coating, cushions and carpet backing, sealants, hardwood floor coating and thermal insulation in building and transportation. However, polyurethanes are very flammable and creates a huge amount of smoke while burning. For their use, it is important to prevent or delay the combustion progress and also the combustion byproducts to be non-toxic during an incident for a human while egressing a fire.

In the current studies of polyurethane both halogenated and non-halogenated flame retardants are used for polyurethane foams and films. Phosphorus-based compounds are a very common additives to polyurethane films in terms of non-halogenated flame retardants. Many of these phosphorus-based flame retardants are commercialized. For polyurethane foams, halogenated compounds are more common even though both halogenated and non-halogenated flame retardants are used.

1.2.3 Phosphorus Containing Flame Retardants

The use of phosphorus-based flame retardants is growing fast due to its efficiency, lower density, toxicity, environmental considerations and good light stability.

Phosphorus flame retardants are more effective in oxygen or nitrogen containing polymers due to heterochain polymers or polymers with oxygen or nitrogen in the pendant group. These phosphorus flame retardants react with the polymer to produce charring, making it a good charring agent. The char prevents or delays the heat flow to the polymer surface and blocks the heat progress of the volatile thermal decomposition products to the flame.^{4,5}

Phosphorus-based flame retardants modes can be either condensed-phased or vapor-phased. Though, several phosphorus-based flame retardants were observed to contain both condensed and vapor phase modes of action. In condensed-phase mode, the phosphorus-based flame retardant affects the physical character and amount of the char in a urethane foam. Due to phosphorus-containing flame retardant, the rigid urethane foam forms a more coherent char from pyrolyzed but unburned material, which acts as a barrier for combustion process. There is evidence that a portion of the phosphorus is retained in the char. The inhibition of glowing combustion of char by phosphorus compounds is explained partly by this barrier action. Flexible urethane foams do not yield much char on burning, but often form a decomposition product layer. Vapor-phased mode is often found to be effective in phosphorus-based flame retardants in a non-charring polymer, also where capability of being vaporized at the temperature of the pyrolyzing surface of the flame retardant or phosphorus-containing products. In the engineering thermoplastic Noryl (SABIC), incorporate a mixture of a charrable poly(phenylene oxide) and a poorly charrable polystyrene, analysis shows that effective flame retardants, for example triphenyl phosphate react in the vapor phase to suppress the flammability of the polystyrene pyrolysis products.¹⁶

Phosphorus-based flame retardants are divided into three large classes:¹ Inorganic characterized by ammonium phosphates, metal hypophosphates and red phosphorus. Semi-organic characterized by phosphonium salts, amine and melamine salts of phosphoric acid and metal salts of organophosphinic acids. Phosphate and phosphonate esters. Phosphorus-based flame retardants can be both water-soluble and water-insoluble. Water-soluble phosphorus-based flame retardants are mainly used for restoring exterior of textile and wood products. Water-insoluble phosphorus-based flame retardants can be applied in synthetic foams, coating, thermoplastics and thermosetting resins.

Phosphorus based flame retardants have many advantages.¹ They are biodegradable which makes the combustion to stop. In comparison to halogen flame retardants it creates less acidic smoke and the tendency of creating toxic smoke is less. Compared to halogen flame retardants it gives better UV stabilization. It has a low specific gravity which helps to achieve light plastic parts. For charrable polymers it is efficient at creating char barrier. Compared to halogen content it needs less phosphorus content for flame retardancy.

1.2.4 Project Rationale of Flame Retardants:

Halogenated flame retardants are used commonly in many application for various materials, but it has ecological and toxic byproduct issues when burning. Non-halogenated flame retardants have evolved as the newer flame retardants option which shows less environmental issues including less toxic byproducts. The goal of this research was to incorporate novel phosphonium salt compounds into a standard polyurethane film and determine their potential as flame retardants using FT-IR, burn test and thermogravimetric analysis.

Chapter II

2. Experimental

2.1 Addition of Benzoic Acid to Styrene Oxide

All starting materials were commercially available unless specified otherwise. Solvents used for this reaction were tetrahydrofuran, toluene, isopropanol and 1-butanol. The catalysts used in this reaction were in different ratios; TBAB (0%, 10% & 15%), TBAF (15%), TBAC (15%), TBAI (15%) and TEATs (15%). The amount of catalyst was based on benzoic acid. The infrared spectra were taken on Perkin-Elmer Spectrum Two™ FT-IR L1600400 spectrometer, and the ratios of monomer products were found using Bruker-Spectrospin UltraShield™ 300 MHz NMR spectrometer for ¹H-spectra. Each reaction was performed under the same conditions and a general procedure is given below:

To a 50mL round bottom flask with a stir bar was added benzoic acid (0.50g, 4mmol) and styrene oxide (0.49g, 4mmol). TBAB (0.075g, 15%) was added to the flask. Toluene (10mL) was then added to the flask. The reaction was heated to reflux and stirred. Aliquots were periodically collected, and the solvent was removed to monitor the reaction by FT-IR spectroscopy. Once the reaction was complete the solvent was removed and a ¹H-NMR spectrum was collected to determine the ratio of regioisomers.

2.2 Flame Retardants

All starting materials were commercially available unless specified otherwise. Polyol mixture and isocyanate for the polyurethane films were provided by ETCO-Specialty Products Inc. in Girard, Kansas. Phosphonium salt 1 and phosphonium salt 2 were provided by Bruce Atwater from Fort Hays State University. Different ratios of triphenyl phosphate (0%, 5%, 10% & 20%), phosphonium salt 2 (2.8%) and phosphonium salt 1 (2.8% & 10%) were used. The amount of phosphorus compound was based on the weight of polyol and isocyanate. All polyurethane films were cast with an 8:2 ratio (m/m) of polyol and isocyanate mixture to the different ratios of phosphate and phosphonium salt. For triphenyl phosphate, a mortar and pestel were used prior to mixing. The infrared spectra were taken on Perkin-Elmer Spectrum TwoTM FT-IR L1600400 spectrometer. The burn tests were performed in an SDL-AtlasTM horizontal flame chamber, M223M. The burn test involved igniting one end of the film with a Bunsen burner and holding the fire for 10 seconds to let the film start burning, letting the sample to burn completely, and recording the burn time and as well as the weight of the burned sample. The thermogravimetric analysis was carried out on a TGA-Q500 Discovery. Each reaction was performed under same conditions and general procedure is given below:

Polyol (8g) and triphenyl phosphate (2g, 20%) was added to a disposable cup and stirred with a wooded stick for about one minute to dissolve. Once the phosphate was dissolved, isocyanate (2g) was added to the cup and stirred for another minute. The mixture was then poured onto the glass plate and casted using a doctor's blade at 0.15mm thickness. Once casted, the sample was allowed to cure for 24 hours. The film was cut

using scissors into strips of 3.5 inches x 1.5 inches and the excess used as TGA testing.

The burn test was carried out on the films.

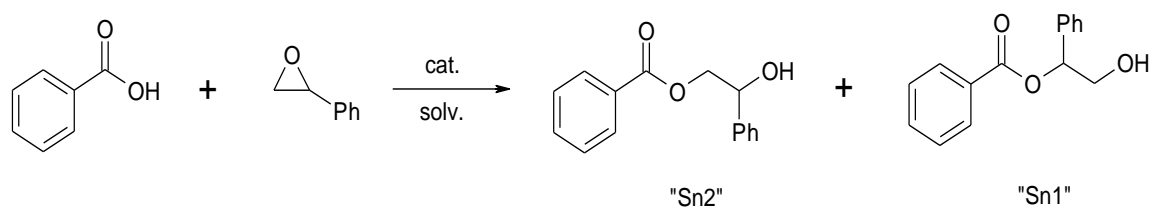
Chapter III

3. Results & Discussion

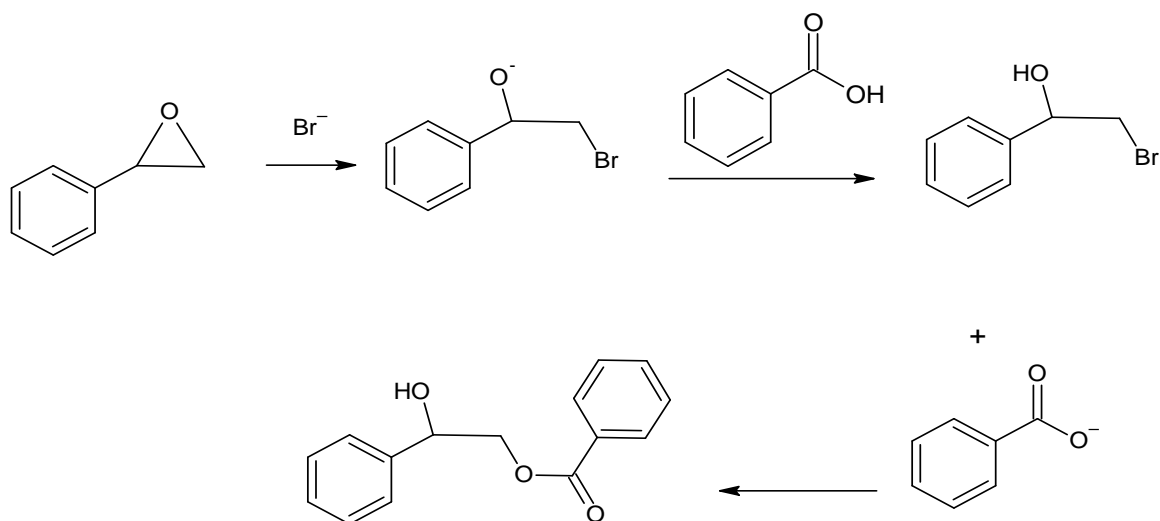
3.1 Results and Discussion of Regioisomers

The synthesis of 1,2-hydroxy esters is shown in Scheme 1. Benzoic acid and styrene oxide were mixed in the presence of an ammonium salt catalyst and solvent, and 1,2-hydroxy esters was formed via a Sn1 and Sn2 mechanism.

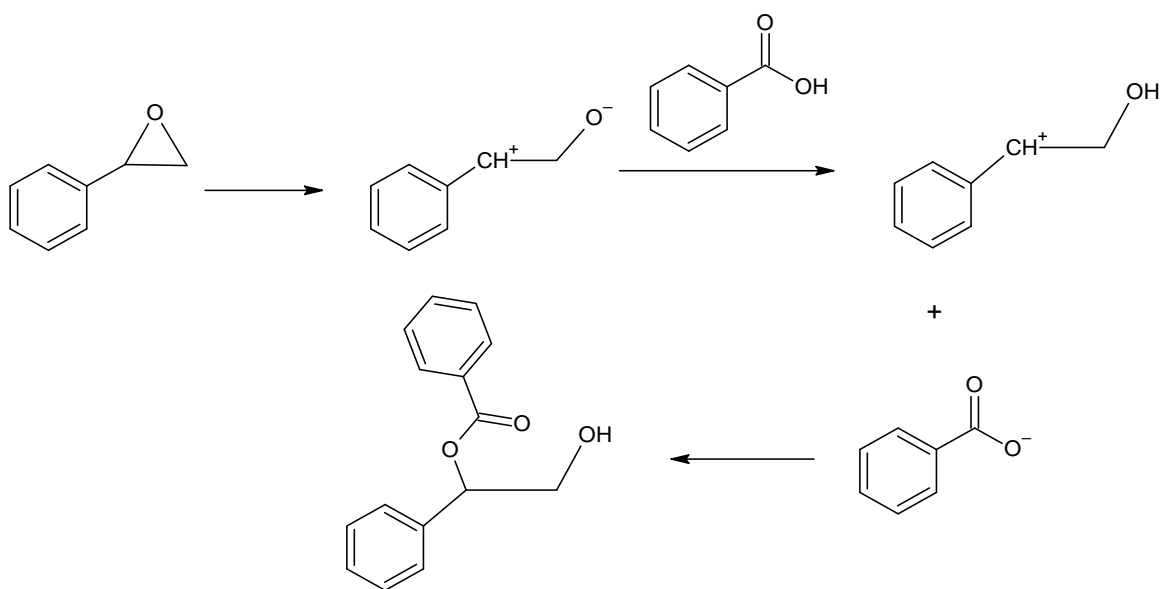
The Sn2 mechanism is shown in Scheme 2. The initial step is a nucleophilic attack of the bromide on the least substituted carbon, opening the epoxide. The second step is proton exchange between the carboxylic acid and alkoxide. The final step is the nucleophilic attack by the carboxylate on to the alkyl bromide which produces the Sn2 product. The Sn1 mechanism is shown in Scheme 3. The initial step is ring opening the epoxide to form a zwitter ion. The second step is protonation of the alkoxide by the carboxylic acid. The final step is a nucleophilic attack of carboxylate onto the carbocation which produces the Sn1 product.



Scheme 1. Synthesis of 1,2-Hydroxy ester.



Scheme 2. Sn2 mechanism.



Scheme 3. Sn1 mechanism.

Catalysts used in this reaction were TBAB, TBAF, TBAC, TBAI and TEATs and solvents used were tetrahydrofuran (THF), toluene, isopropanol and 1-butanol. THF and toluene were polar aprotic solvents, and isopropanol and 1-butanol were polar protic solvents. The boiling points of polar aprotic solvents were 66°C (THF, 0.207)³⁷ and 110°C (toluene, 0.099)³⁷ respectively. The boiling points of polar protic solvents were 83°C (isopropanol, 0.546)³⁷ and 118°C (1-butanol, 0.552)³⁷. The initial hypothesis was that the reaction rate would increase when the reaction temperature increases. Also, the ratio of product was expected to change due to the solvent boiling point and polarity.

All samples were characterized by FT-IR spectroscopy and the 15% TBAB with toluene spectrum is shown as an example in Figure 1. The FT-IR spectra of the remaining samples are in the appendix. The FT-IR spectrum at the beginning of the reaction showed a peak at 1680 cm⁻¹ indicative of carboxylic acid carbonyl. The FT-IR spectrum was used to monitor the reaction progress. The OH stretch shifted from 3400-2500 cm⁻¹ to 3400 cm⁻¹ and the C=O stretch shifted from 1680 cm⁻¹ to 1700 cm⁻¹ as the reaction progressed. The shift in absorbencies were consistent with the carboxylic acid converting to an ester.

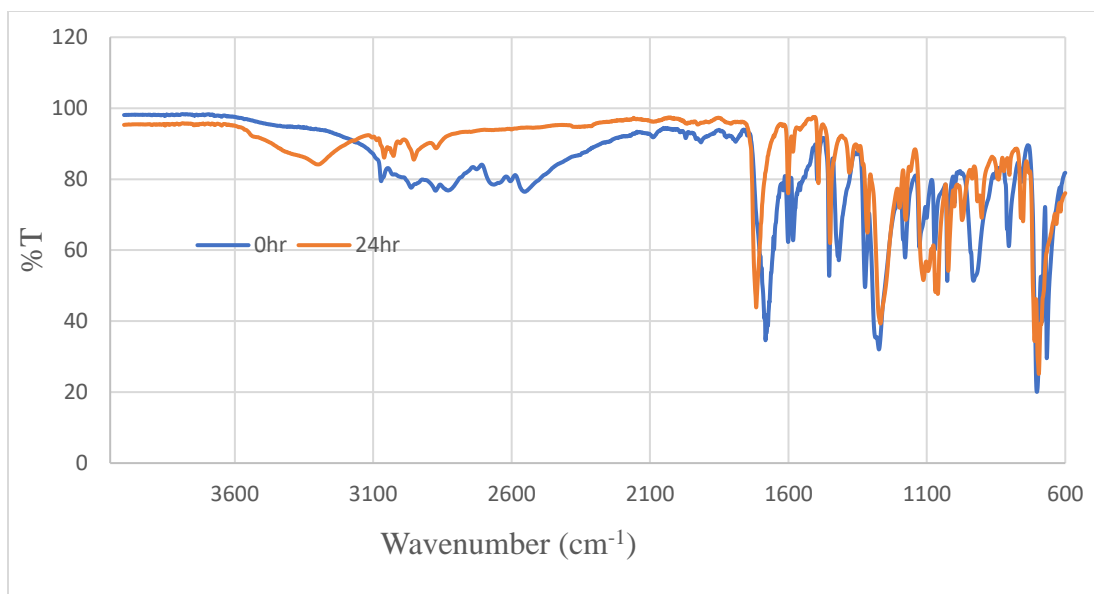


Figure 1. FT-IR spectrum of addition of benzoic acid to styrene oxide using 15% TBAB in toluene solution.

$^1\text{H-NMR}$ spectra were obtained for each of the samples and 10% TBAB with toluene spectrum is shown as an example in Figure 2. The $^1\text{H-NMR}$ spectra for the remaining samples are listed in the appendix. The $^1\text{H-NMR}$ spectra were used to determine the product ratio. Predicted $^1\text{H-NMR}$ spectra for Sn2 and Sn1 of 1,2-hydroxy ester are shown in figure 3 and figure 4, respectively.³⁶ Predicted $^1\text{H-NMR}$ spectrum for Sn2 shows a signal at 4.94 ppm (1H, t, $J=4.5$ Hz) and Sn1 shows a signal at 5.51 ppm (1H, t, $J=5.4$ Hz) for the benzyl proton of each product. For the Sn2 process the chemical shift of the benzyl proton was predicted to be 5.1 ppm and the Sn1 process the chemical shift of the benzyl proton was predicted to be 6.1 ppm. The integration ratio of these peaks were used to determine the product ratio.

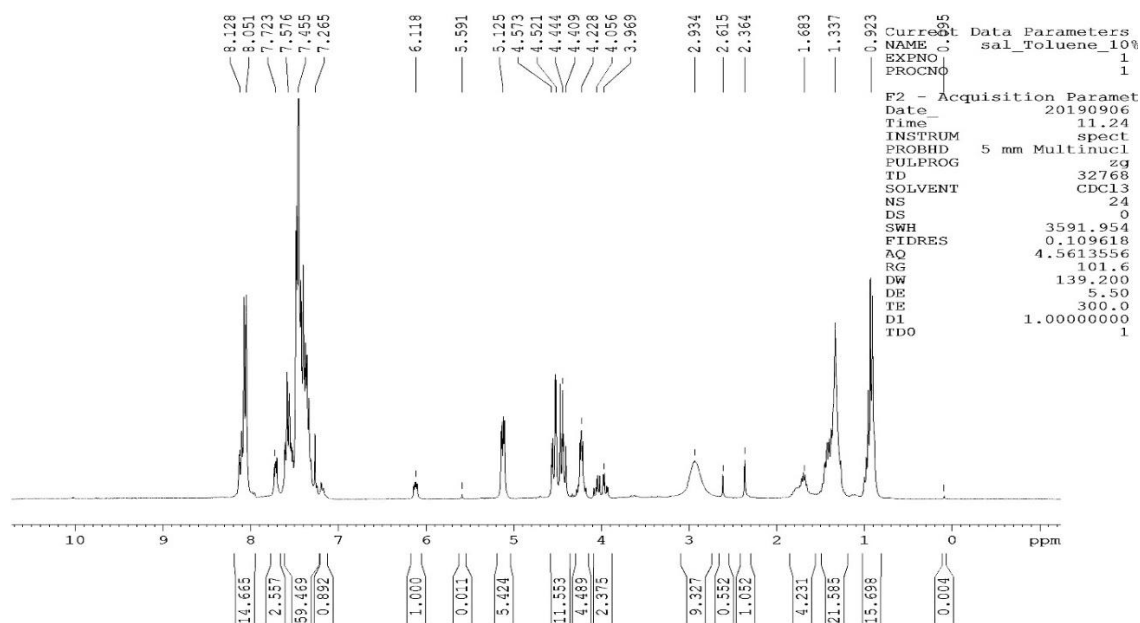


Figure 2. ^1H -NMR spectrum of addition of benzoic acid to styrene oxide using 10% TBAB in toluene solution.

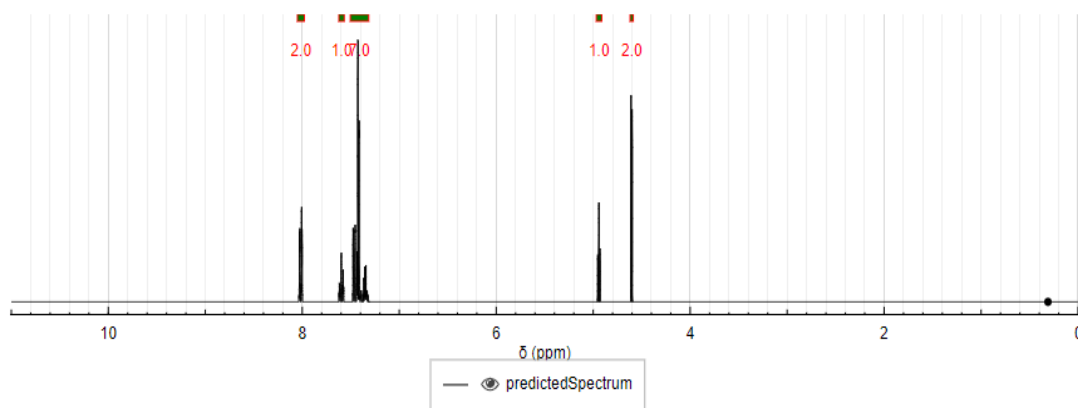


Figure 3. Sn2 1,2-hydroxy ester predicted ^1H -NMR spectrum.³⁶

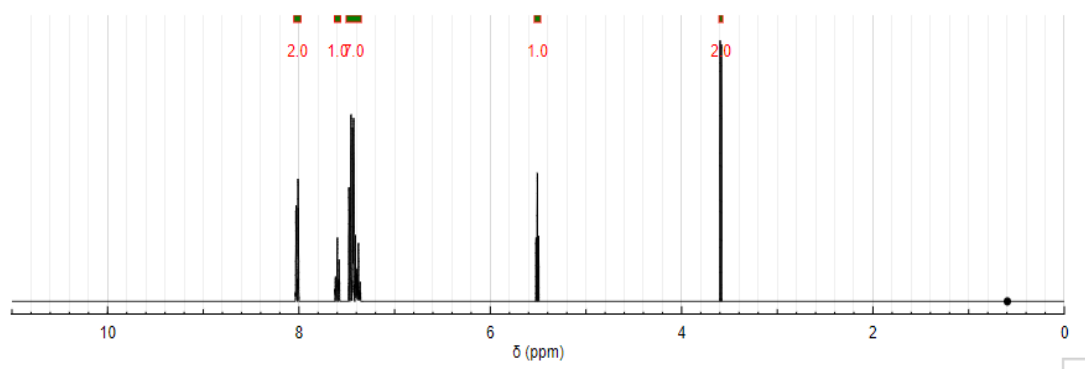


Figure 4. Sn1 1,2-hydroxy ester predicted ^1H -NMR spectrum.³⁶

The ratios of Sn2: Sn1 products and reaction time of the samples are shown in Table 1. Various solvents were studied because it was anticipated that protic solvents would stabilize the intermediates and increase the reaction rate. Isopropanol and 1-butanol were used because the higher polar protic solvents favor the Sn1 mechanism because it helps to stabilize the charges during the formation of epoxides. THF and toluene were used because the less polar solvents favor Sn2 mechanism because there are fewer charges within the mechanism.

Reactions using 1-butanol showed product ratios and reaction times which were inconsistent in terms of the product ratios compared to the other solvents as the catalyst loading was increased there was no significant increase in Sn2 product, TBAB (15%) 3.7:1 (5 days), TBAB (10%) 3.3:1 (6 days) and TBAB (0%) 4.0: 1 (5 days). Reactions with isopropanol showed product ratios as TBAB (15%) 4.1:1 (1 day), TBAB (10%) 3.0:1 (3 days) and TBAB (0%) 0.9: 1 (5 days). Isopropanol with TBAB (0%) showed a higher Sn1 product which was not observed for any other reactions. The polar aprotic solvent, toluene with TBAB, 3.7: 1 (0%), 5.4: 1 (10%) and 6.3:1 (15%) showed a consistent higher product ratio than the other solvents. Reactions with THF showed

product ratios as TBAB (15%) 4.4:1 (2 day), TBAB (10%) 3.2:1 (4 days) and TBAB (0%) 3.2: 1 (5 days). THF with TBAB 0% and 10% showed same ratio and also showed a lower ratio in comparison with toluene with TBAB. The polar aprotic solvents showed a higher Sn2 product ratio than the polar protic solvents. The least polar solvent, toluene yielded the highest Sn2 product and the most polar solvents, isopropanol and 1-butanol yielded the least Sn2 product.

The catalyst percentage loading affected the product ratio which can be seen in Table 1. THF, toluene and isopropanol showed lesser amount of catalyst loading yielded less Sn2 product and a higher amount of catalyst loading yielded with higher Sn2 product because the higher loading of catalyst favors Sn2 mechanism. Also, the lesser amount of catalyst loading showed higher reaction time.

TBAB, TBAF, TBAC and TBAI were used as the catalyst to study the halide effect on the reaction due to their different nucleophilicity. Toluene was used as the solvent for the synthesis carried out with TBAF, TBAC, TBAI and TEATs at 15% ratio. In literature, the nucleophilicity of the halides follows the trend of Fluorine < Chlorine < Bromine \approx Iodine.²⁰ TBAF (15%) yielded 3.8:1, TBAC (15%) yielded 4.7:1, TBAB (15%) yielded 6.3:1 and TBAI (15%) yielded 5.4:1. TBAB and TBAI showed the highest Sn2 product which suggests the greater nucleophilicity of the anion did increase the amount of Sn2 product.

Toluene with TEATs (15%) was also used because it is a non-nucleophilic anion and theoretically should not catalyze the reaction. The FT-IR spectrum at the beginning of the reaction showed a peak at 1680 cm^{-1} indicative of carboxylic acid carbonyl. The OH stretch shift was observed from $3400\text{--}2500\text{ cm}^{-1}$ to 3400 cm^{-1} at 96th hour but at 144th

hour it was not observed at all. The C=O stretch shifted from 1680 cm^{-1} to 1700 cm^{-1} was observed to be completed. The shift in absorbencies cannot confirm carboxylic acid converting to an ester. The ^1H -NMR spectrum yielded a product ratio of 3.2:1. TEATs (15%) with toluene product ratio indicates a lower $\text{Sn}2$ product in comparison with toluene with TBAB (15%). TEATs (15%) data suggest that it is necessary for nucleophile to be present for the reaction to obtain higher $\text{Sn}2$ product. The reaction was not observed to be completed within 6 days, indicating that the TEATs was not a good catalyst for this reaction as anticipated.

Table 1. Solvents, catalyst percentage, product ratio and reaction time for addition of benzoic acid to styrene oxide.

Solvent	Catalyst (%)	Sn2: Sn1	Reaction Time (days)
THF	(0)	3.2: 1	5
THF	TBAB (10)	3.2: 1	4
THF	TBAB (15)	4.4: 1	2
Toluene	(0)	3.7: 1	5
Toluene	TBAB (10)	5.4: 1	2
Toluene	TBAB (15)	6.3: 1	1
Isopropanol	(0)	0.9: 1	5
Isopropanol	TBAB (10)	3.0: 1	3
Isopropanol	TBAB (15)	4.1: 1	1
Butanol	(0)	4.0: 1	5
Butanol	TBAB (10)	3.3: 1	6
Butanol	TBAB (15)	3.7: 1	5
Toluene	TBAF (15)	3.8: 1	1
Toluene	TBAC (15)	4.7: 1	3
Toluene	TBAI (15)	5.4: 1	1
Toluene	TEATs (15)	3.2: 1	6

3.2. Results and Discussion of Flame Retardants

All samples were characterized by FT-IR spectroscopy and the polyurethane with 10% phosphonium salt 1 spectrum is shown as an example in Figure 5. The FT-IR spectra of the remaining samples were similar and are in the appendix. Absorbances were observed at 1050 cm^{-1} indicative of a C-O stretch and at 1700 cm^{-1} indicative of a C=O stretch. Additional peaks at 3300 cm^{-1} and 3050 cm^{-1} indicated to be N-H and $\text{sp}^3\text{ C-H}$ stretching, respectively. These peaks were consistent with the polyurethane.

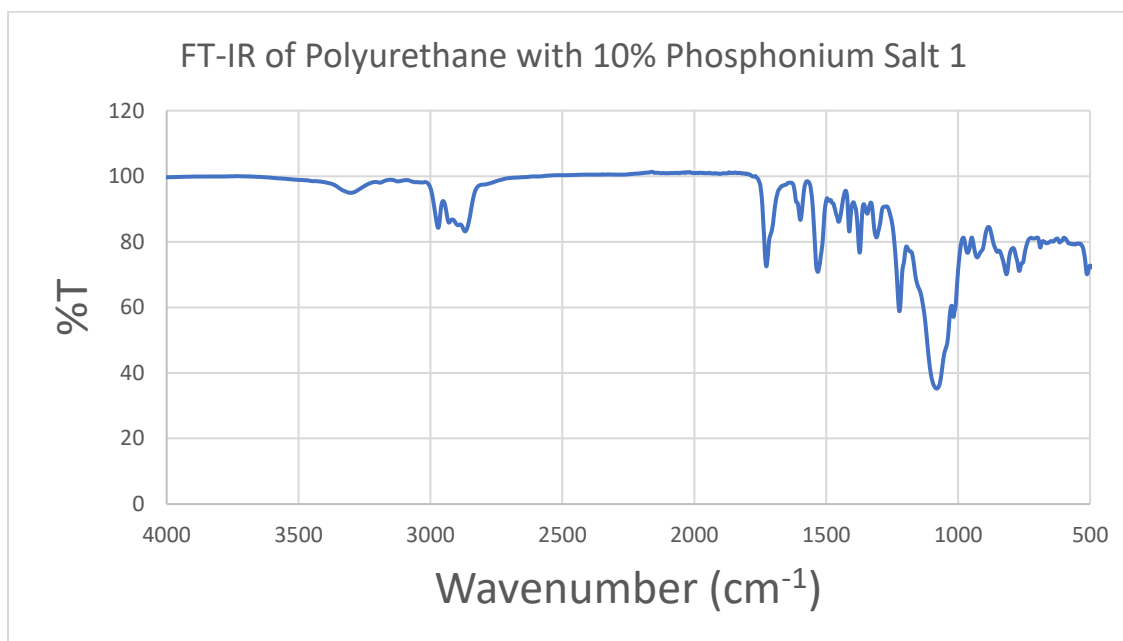


Figure 5. FT-IR spectrum of polyurethane with 10% phosphonium salt 1.

Polyurethane samples were subjected to a burn test and results are shown in Table 2. Triphenyl phosphate was used as the standard because it is one of the most common flame retardants for many polymers and compares well with halogenated FRs.¹ The polyurethane without a flame retardant had a short burn time of 132s. Polyurethane with

triphenyl phosphate samples had consistent burn times ranging from 240-262 seconds which was higher than polyurethane sample without a flame retardant in it. Polyurethane 20% triphenyl phosphate had the least burn time because of higher percentage of triphenyl phosphate. Polyurethane 10% triphenyl phosphate had a longer burn time due to the sample size. The polyurethane phosphonium salt 1 and phosphonium salt 2 had burn times less than polyurethane with triphenyl phosphates ranging from 163-214 seconds but greater than polyurethane sample without flame retardant showing flame retardant properties. The remaining weight after burning of the polyurethane and polyurethane with triphenyl phosphate samples were similar ranging from 0.6081-0.6938g indicating that triphenyl phosphates are similar to polyurethane sample which suggests that the triphenyl phosphate is volatilizing into the flame acting as a flame inhibitor. The polyurethane with phosphonium salt samples remaining weight after burning ranged from 1.0194-1.2060g which was higher than the polyurethane and polyurethane with triphenyl phosphate samples indicating that the phosphonium salts are charring agent.

Table 2. Burn time and remaining weight after the burn tests of the samples.

Sample	Sample weight before burn test (g)	Burn time (s)	Remaining sample weight after burn test (g)
Polyurethane	4.42	132	0.6893
Polyurethane 5% Triphenyl phosphate	5.35	248	0.6938
Polyurethane 10% Triphenyl phosphate	6.36	262	0.6858
Polyurethane 20% Triphenyl phosphate	4.67	240	0.6081
Polyurethane 10% Phosphonium salt 1	5.06	214	1.2060
Polyurethane 2.8% Phosphonium salt 1	4.45	163	1.0439
Polyurethane 2.8% Phosphonium salt 2	5.32	190	1.0194

TGA was used to determine the char yield and thermal stability. The TGA for polyurethane, polyurethane with triphenyl phosphate and polyurethane with phosphonium salts are shown in Figure 6 and Figure 7. The thermal stability and char yield are shown in Table 3. Thermal stability was determined at 10% weight loss and the char yield was determined by weight percentage at 600 °C from the TGA data. The polyurethane with triphenyl phosphate samples at 5% and 10% loading showed thermal stabilities of 268 and 263 °C, respectively. These thermal stabilities were consistent with the polyurethane sample. The lower thermal stability of 230 °C of polyurethane 20% triphenyl phosphate suggested that the loading was excessive and interfered with the polymerization to form polyurethane. Both polyurethane with phosphonium salt 1 and phosphonium salt 2 samples showed thermal stabilities ranging from 281-313 °C, which were higher thermally stable than the polyurethane triphenyl phosphate samples. The

phosphonium salts may be enhancing the polymerization or it could also increase the organization of the polymer which increases the thermal stability. The catalyst used in making the phosphonium salts probably surpass the polymerization organization. The char yield of polyurethane with triphenyl phosphate samples were consistent ranging from 16.6-18.3%. The polyurethane with phosphonium salts char yields were ranged from 19-27% showing a higher char yield than the polyurethane triphenyl phosphate samples. The increase in char yield suggests that the phosphonium salts behave as a charring agent and was consistent with the results from the burn test.

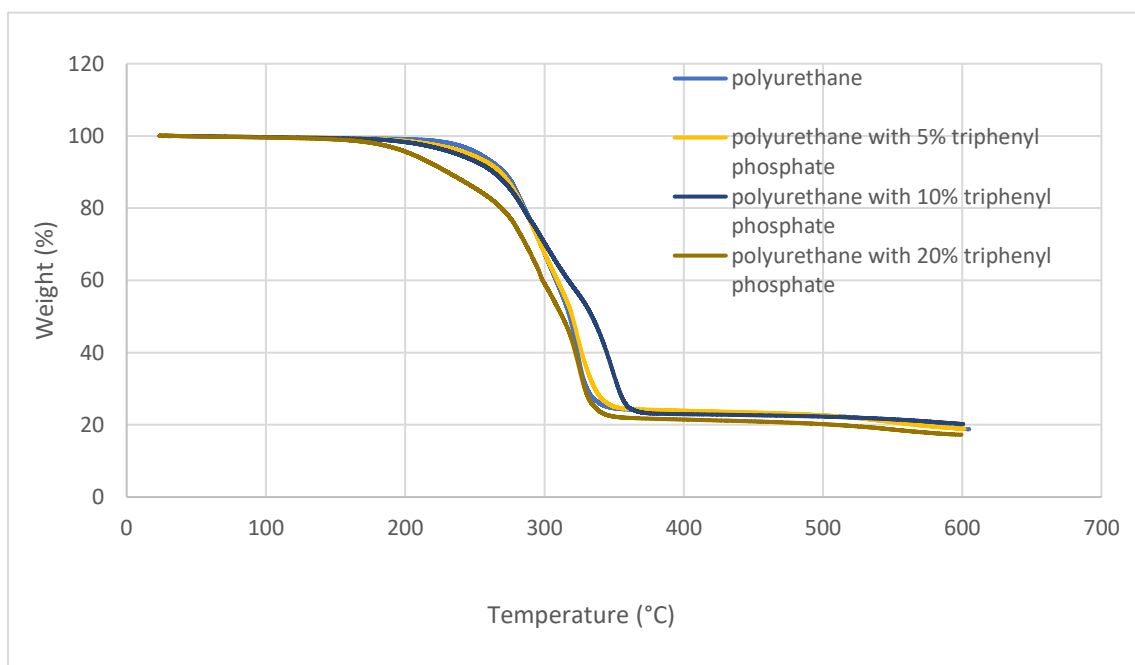


Figure 6. TGA graph of polyurethane with triphenyl phosphate samples.

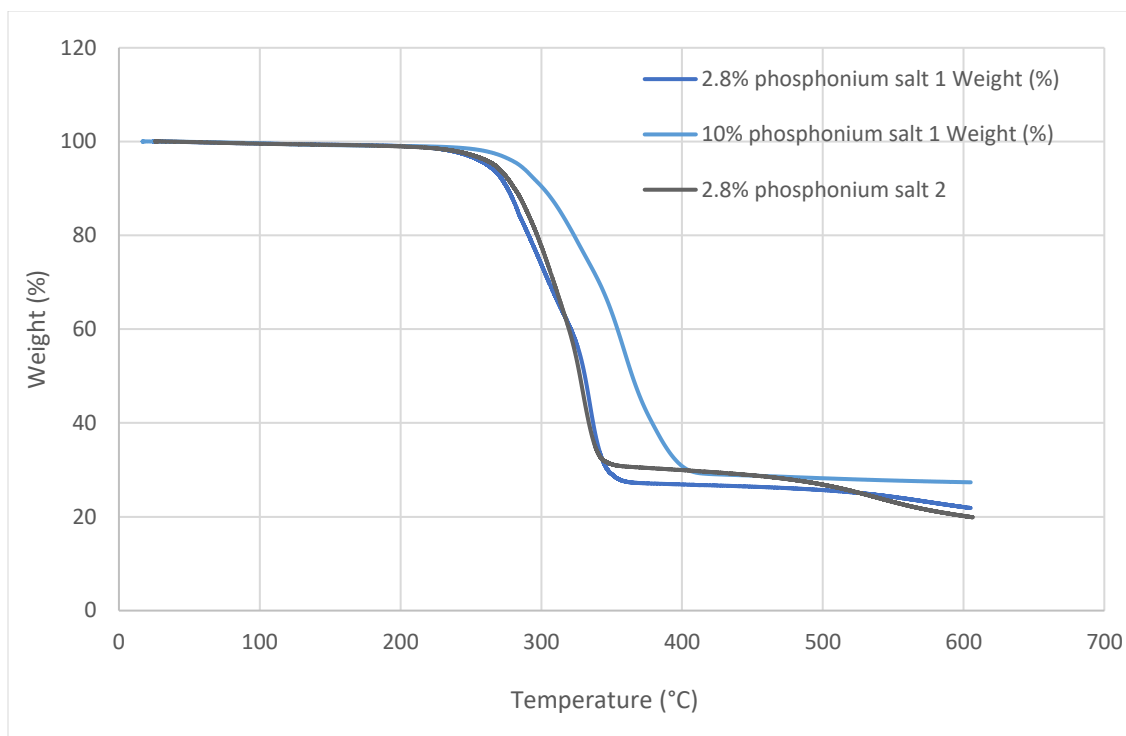


Figure 7. TGA graph of polyurethane with phosphonium salt samples.

Table 3. Thermal stability and char yield of flame retardants samples.

Sample	Temperature (°C) at 10% wt. loss	Char yield (%)
Polyurethane	271	17.8
Polyurethane 5% triphenyl phosphate	268	18.3
Polyurethane 10% triphenyl phosphate	263	18.3
Polyurethane 20% triphenyl phosphate	230	16.7
Polyurethane 10% phosphonium salt 1	301	27
Polyurethane 2.8% phosphonium salt 1	313	21
Polyurethane 2.8% phosphonium salt 2	281	19

Chapter IV

4. Conclusion

4.1 Conclusion of Regioisomers

All regioisomer samples were studied using ATR FT-IR and H-HMR spectroscopy. FT-IR spectroscopy was used to characterize the samples and each sample were consistent with 1,2-hydroxy ester. It was also used to determine the reaction end point. Initial absorbencies were observed at 1680 cm^{-1} and $3400\text{-}2500\text{ cm}^{-1}$ indicative of carboxylic acid and final absorbencies were observed at 3450 cm^{-1} and 1700 cm^{-1} indicative of the hydroxy ester indicating the completion of the reaction.

The ^1H -NMR spectroscopy was performed to determine the product ratio using the integration ratio of benzyl protons of the Sn2 and Sn1 products. For the Sn2 and Sn1 products the chemical shift of the benzyl proton was predicted to be 5.1 ppm and 6.1 ppm respectively. Sn2 product yields were higher than Sn1 product for all the samples except TBAB (0%) with isopropanol.

TBAB, TBAF, TBAC and TBAI were used as the catalyst to study the halide effect on the reaction due to their different nucleophilicity. TBAF (15%) yielded 3.8:1, TBAC (15%) yielded 4.7:1, TBAB (15%) yielded 6.3:1 and TBAI (15%) yielded 5.4:1 with polar aprotic solvent toluene, which was consistent with the nucleophilicity of the

halides. The catalyst percentage loading affected the product ratio. For each solvent, a lower amount of catalyst yielded with less Sn2 product. Also, a lower amount of catalyst loading showed higher reaction times.

The polar aprotic solvents showed a higher product ratio than the polar protic solvents. The polar protic solvent 1-butanol showed product ratios and reaction times which were not consistent. The polar aprotic solvent, toluene with TBAB showed a consistent higher product ratio than the other solvents. The product ratio of TEATs (15%) with toluene was 3.2:1 which is low in comparison with TBAB (15%) with toluene. The reaction was not observed to be completed and can be concluded as a slow reaction.

Overall, conditions did have an effect on the ratio of stereoisomers. Using IPA without catalyst showed ca. 53% of the Sn1 product while using toluene with TBAB (15%) showed an increase of the Sn2 product to 86%. While the roles of the solvent and the catalyst are not completely understood, further studies may improve upon these results.

4.2 Conclusion of Flame Retardants

All polyurethane sample were studied using TGA and ATR FT-IR. FT-IR spectroscopy was used to characterize the samples and each sample was consistent with polyurethane. Absorbances were observed at 1050 cm^{-1} indicative of a C-O stretch and at 1700 cm^{-1} indicative of a C=O stretch. Additional peaks at 3300 cm^{-1} and 3050 cm^{-1} indicated N-H and sp^3 C-H stretching, respectively which were consistent with polyurethane. Horizontal burn test was performed where burn time and remaining sample weight after burn test were recorded. The polyurethane phosphonium salt 1 and

phosphonium salt 2 had burn times less than polyurethane with triphenyl phosphate ranging from 163-214 seconds but greater than polyurethane sample without flame retardant showed flame retardant properties. The remaining weight after burning of the polyurethane and polyurethane with triphenyl phosphate samples were similar and ranged from 0.6081-0.6938g indicative of triphenyl phosphates are similar to polyurethane sample which suggests that the triphenyl phosphate is volatilizing into the flame acting as a flame inhibitor.

TGA was used to determine the char yield and thermal stability of the polyurethane, polyurethane with triphenyl phosphate and polyurethane with phosphonium salt samples. The polyurethanes with phosphonium salts showed higher thermal stability than polyurethane and polyurethane with triphenyl phosphate samples. This may be due to phosphonium salt may be enhancing the polymerization or increasing the organization of the polymer. The polyurethane with phosphonium salts showed a higher char yield than polyurethane and polyurethane with triphenyl phosphate samples suggesting that the phosphonium salts act as a charring agent which was also consistent with the results from the burn test.

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APPENDIX

Part I. FT-IR Spectra of Addition of Benzoic Acid to Styrene Oxide

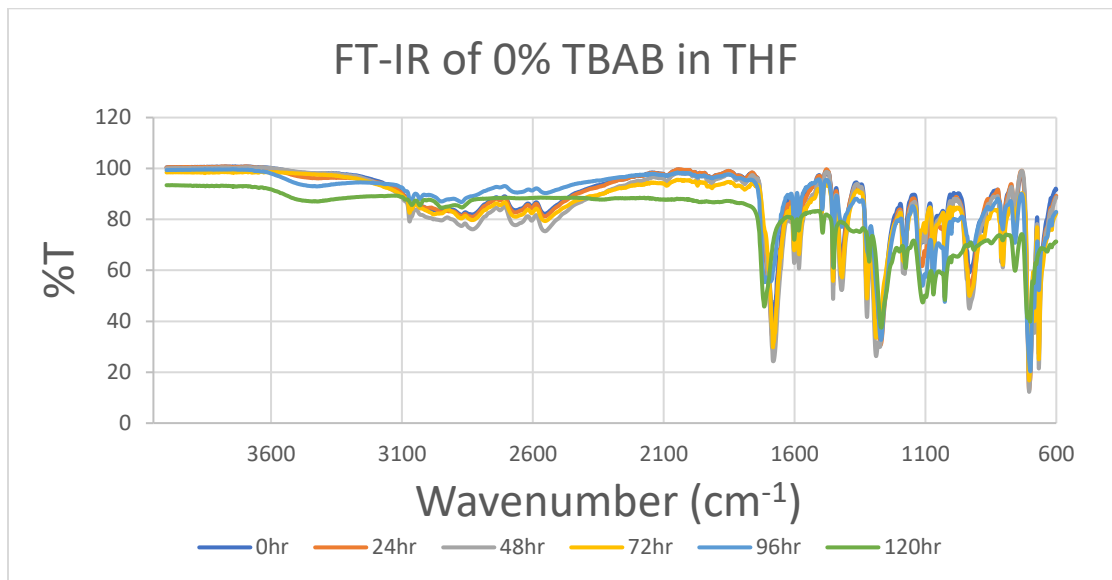


Figure 1. FT-IR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 0% Tetrabutylammonium Bromide in Tetrahydrofuran Solution.

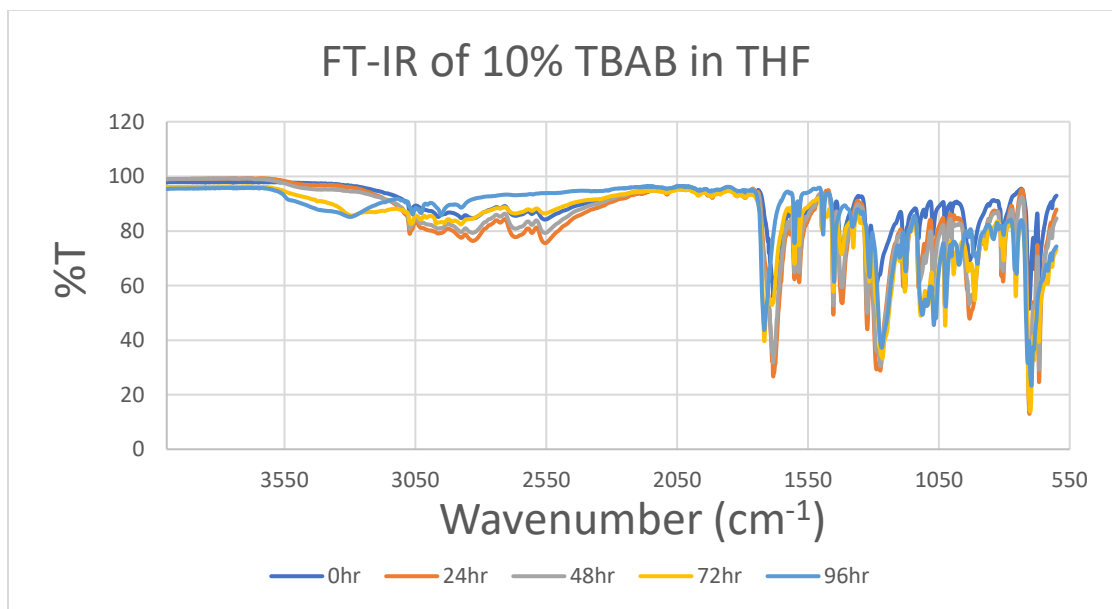


Figure 2. FT-IR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 10% Tetrabutylammonium Bromide in Tetrahydrofuran Solution.

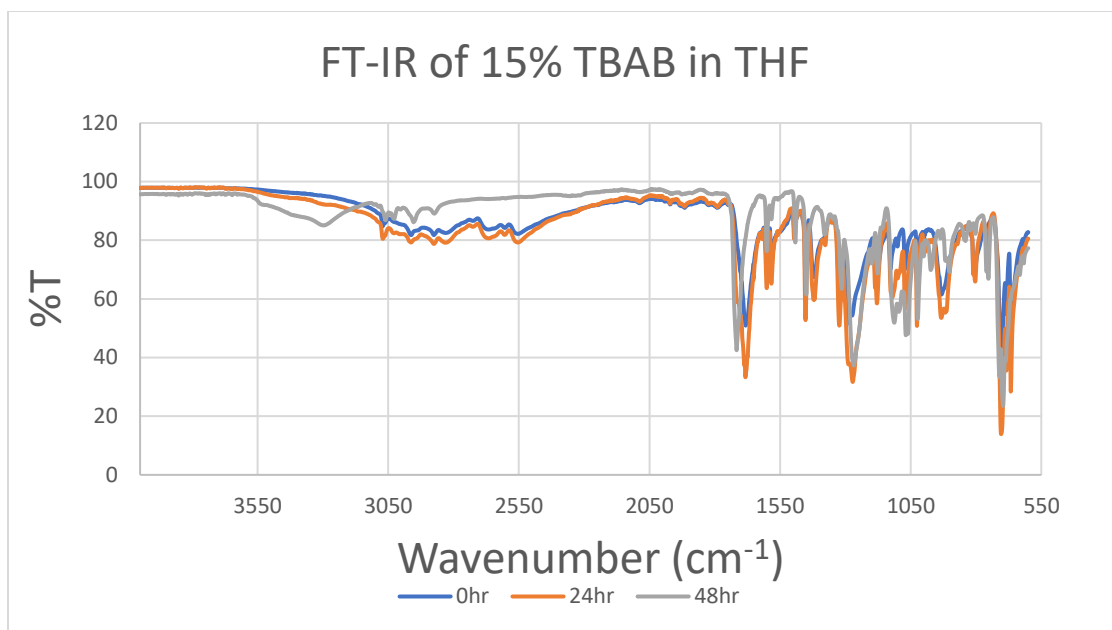


Figure 3. FT-IR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 15% Tetrabutylammonium Bromide in Tetrahydrofuran Solution.

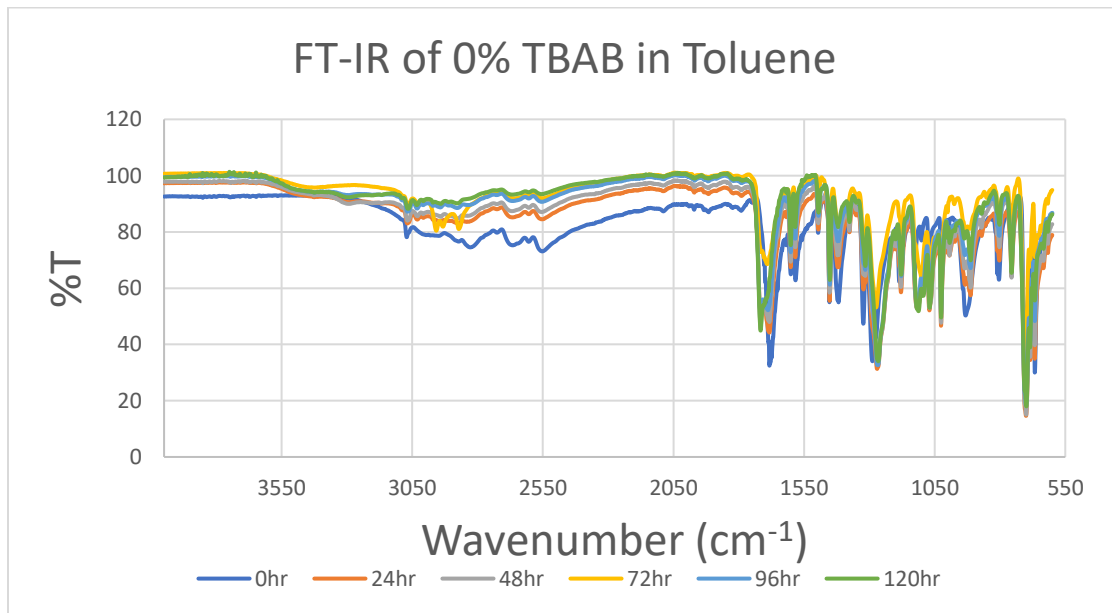


Figure 4. FT-IR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 0% Tetrabutylammonium Bromide in Toluene Solution.

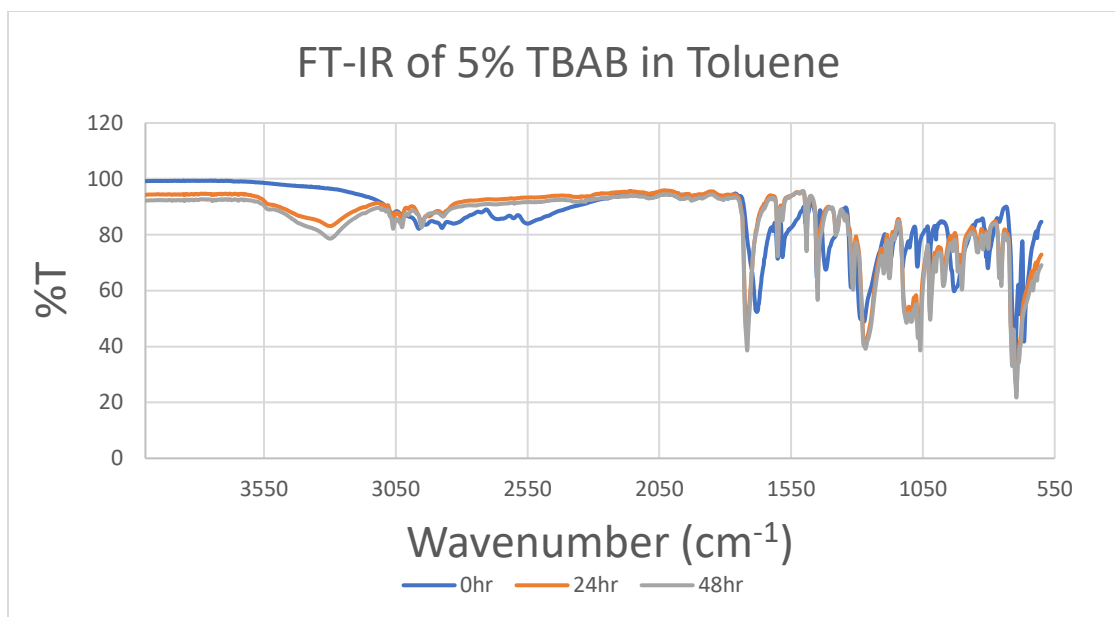


Figure 5. FT-IR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 10% Tetrabutylammonium Bromide in Toluene Solution.

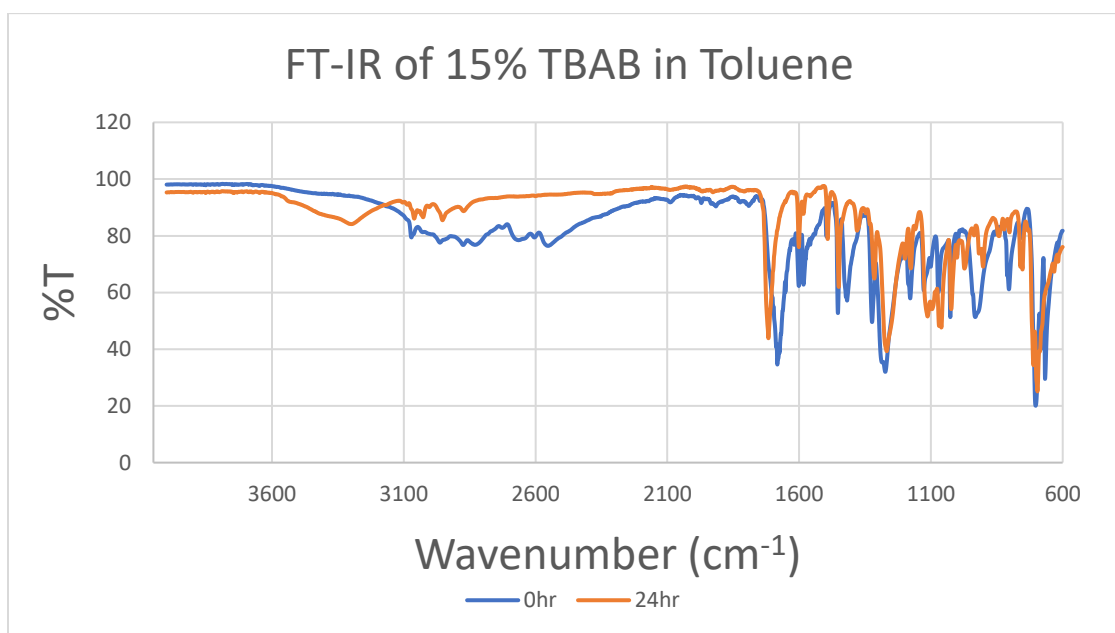


Figure 6. FT-IR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 15% Tetrabutylammonium Bromide in Toluene Solution.

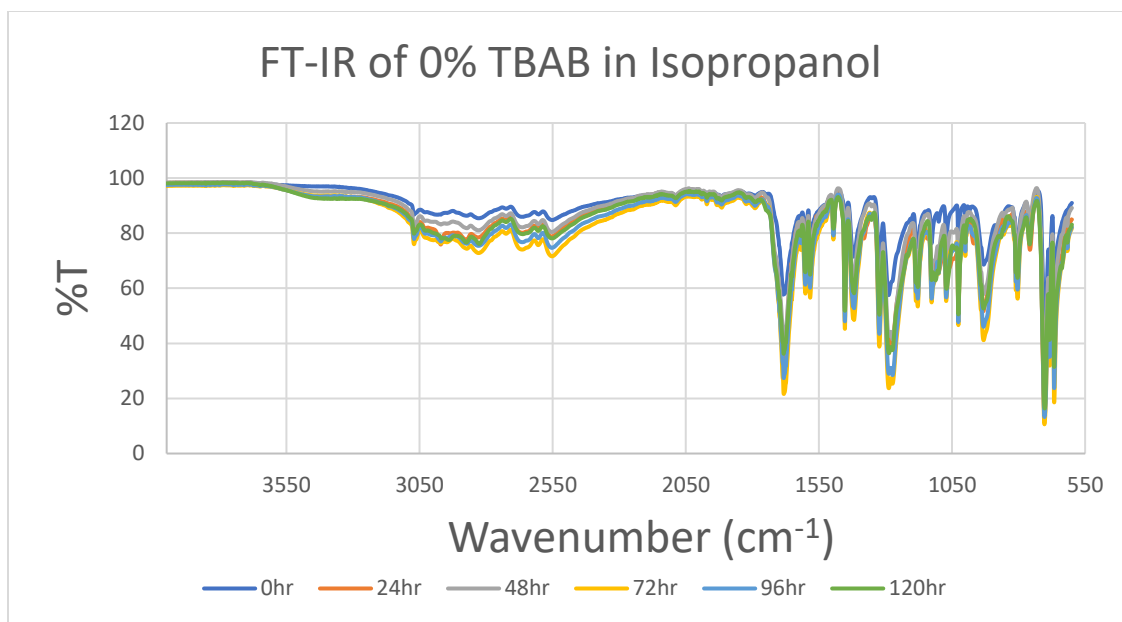


Figure 7. FT-IR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 0% Tetrabutylammonium Bromide in Isopropanol Solution.

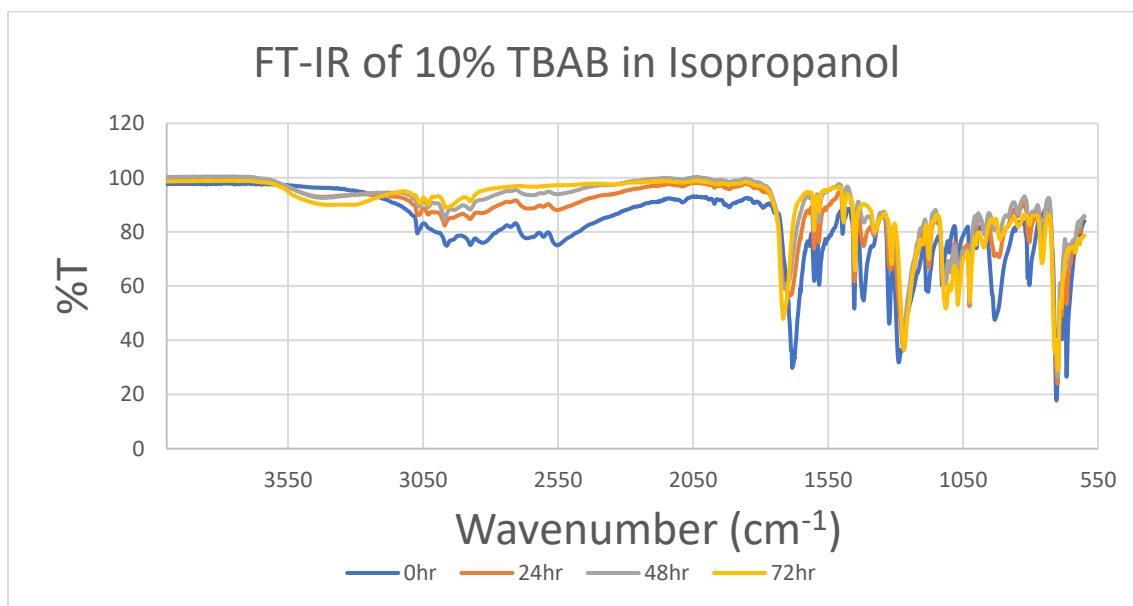


Figure 8. FT-IR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 10% Tetrabutylammonium Bromide in Isopropanol Solution.

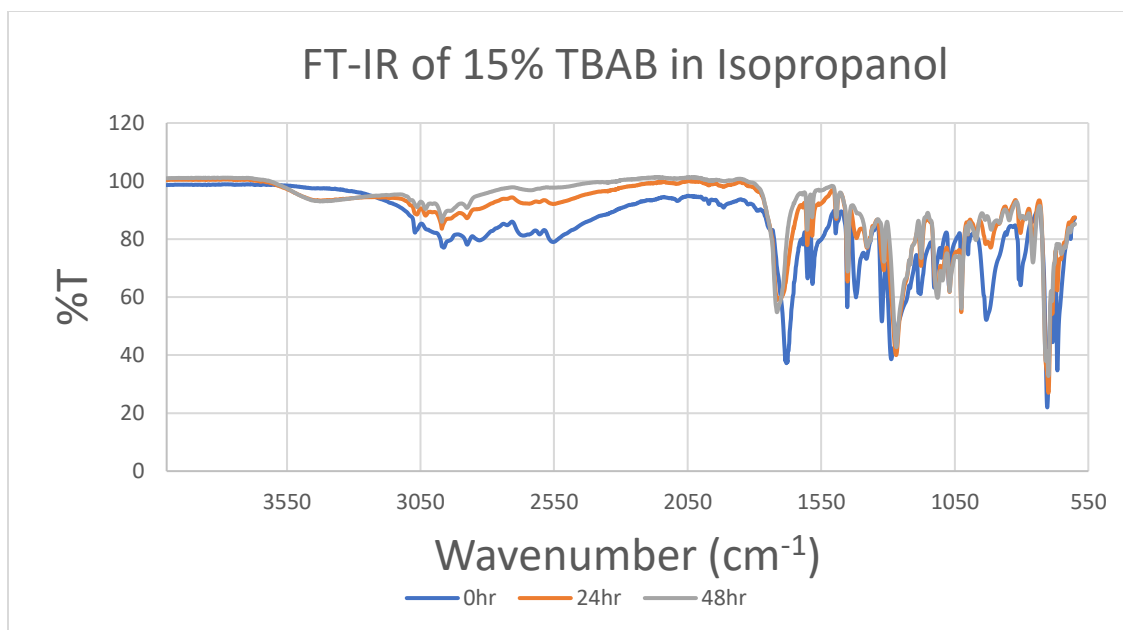


Figure 9. FT-IR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 15% Tetrabutylammonium Bromide in Isopropanol Solution.

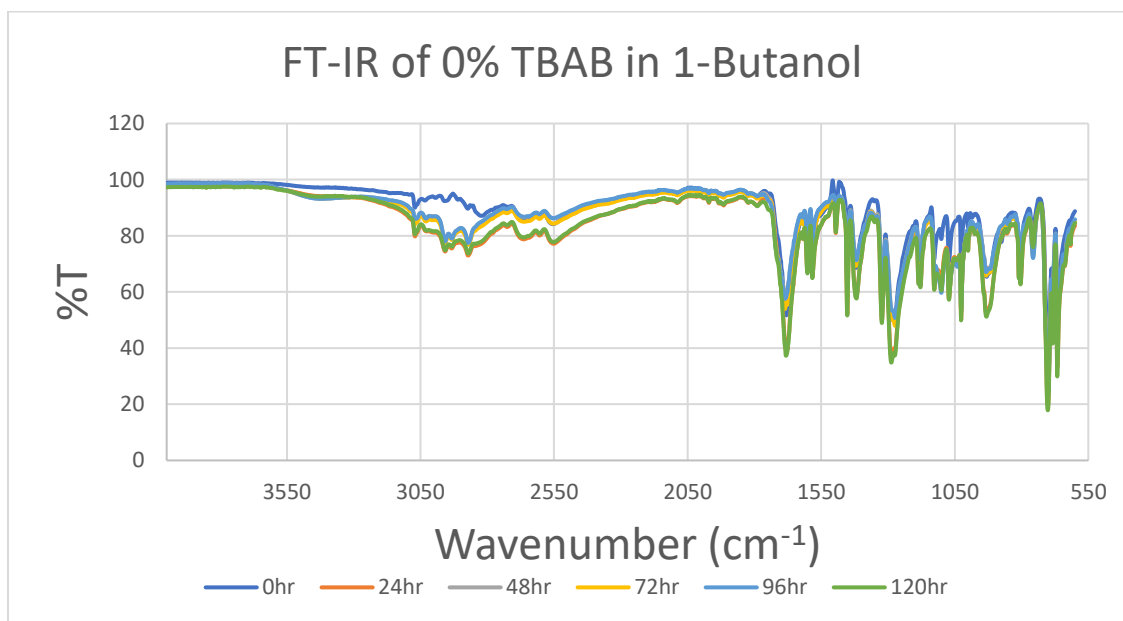


Figure 10. FT-IR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 0% Tetrabutylammonium Bromide in 1-Butanol Solution.

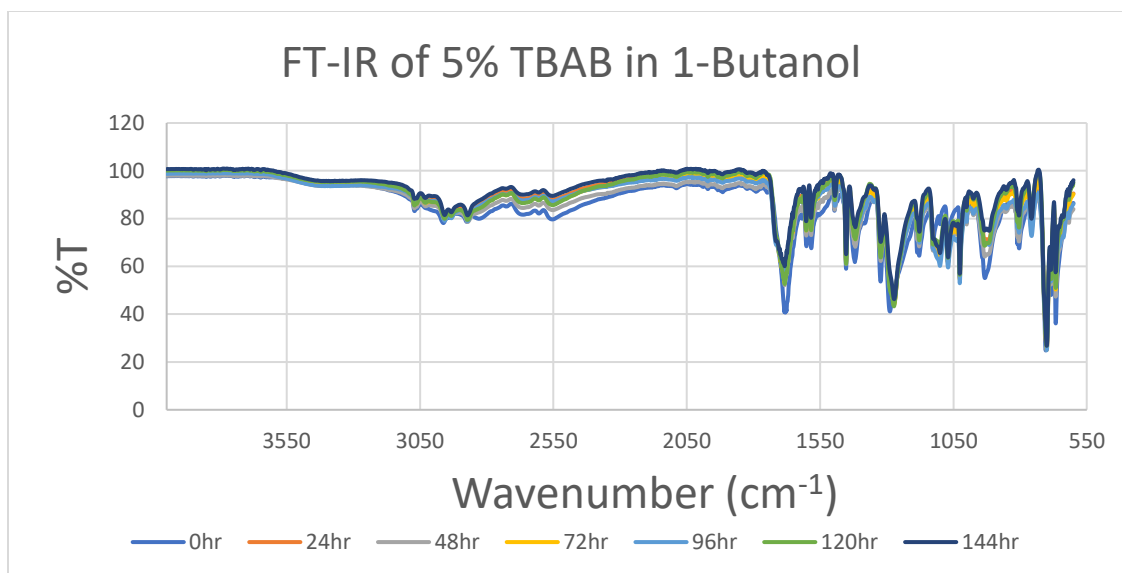


Figure 11. FT-IR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 10% Tetrabutylammonium Bromide in 1-Butanol Solution.

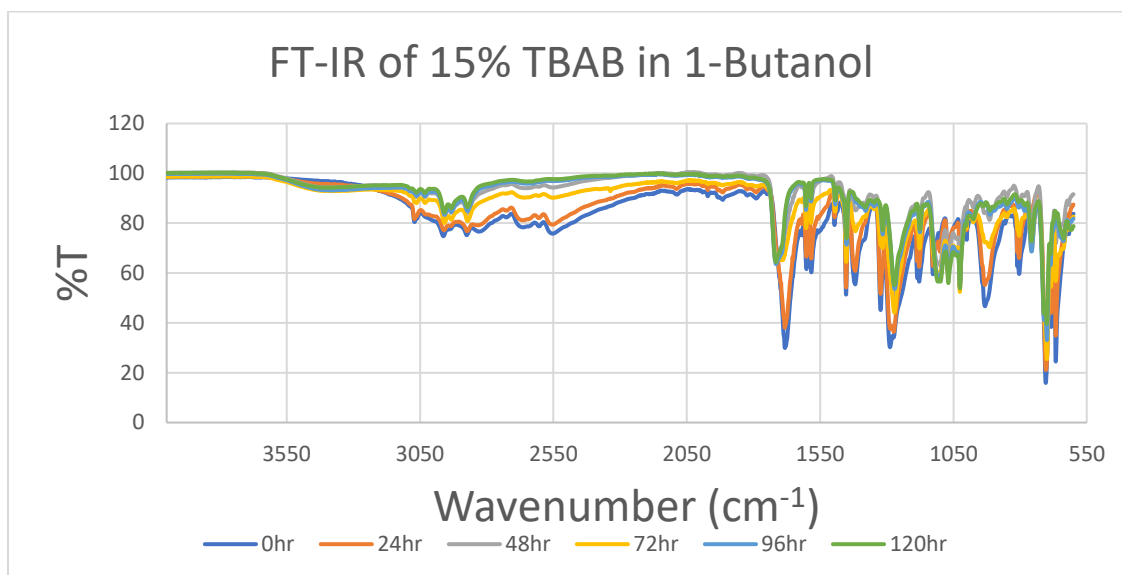


Figure 12. FT-IR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 15% Tetrabutylammonium Bromide in 1-Butanol Solution.

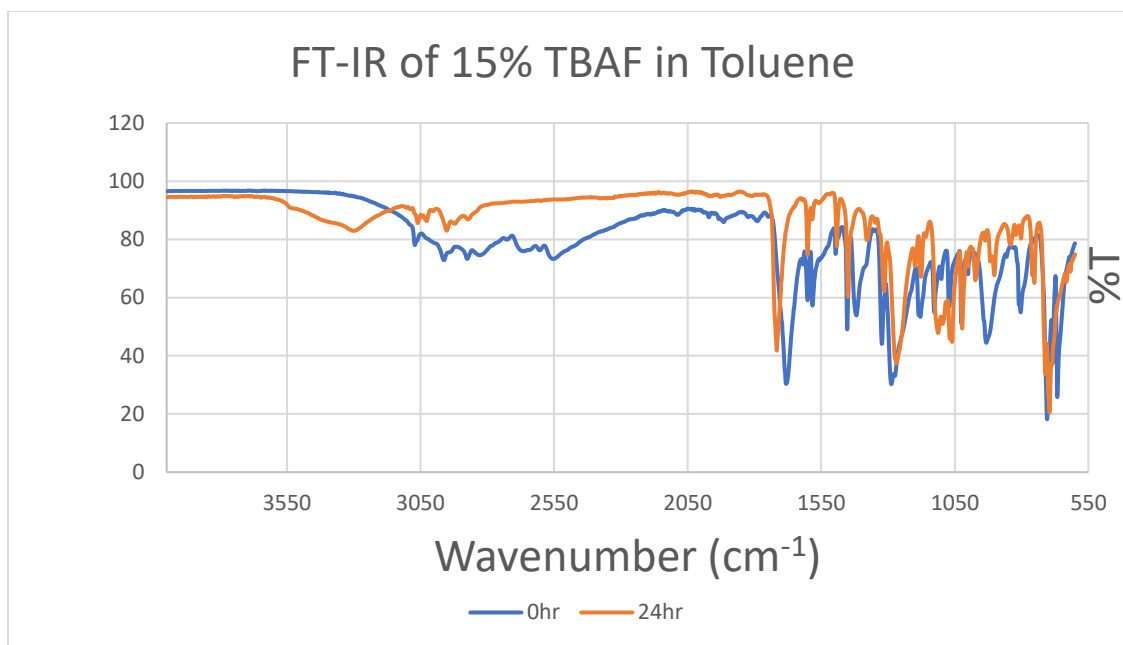


Figure 13. FT-IR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 15% Tetrabutylammonium Fluoride in Toluene Solution

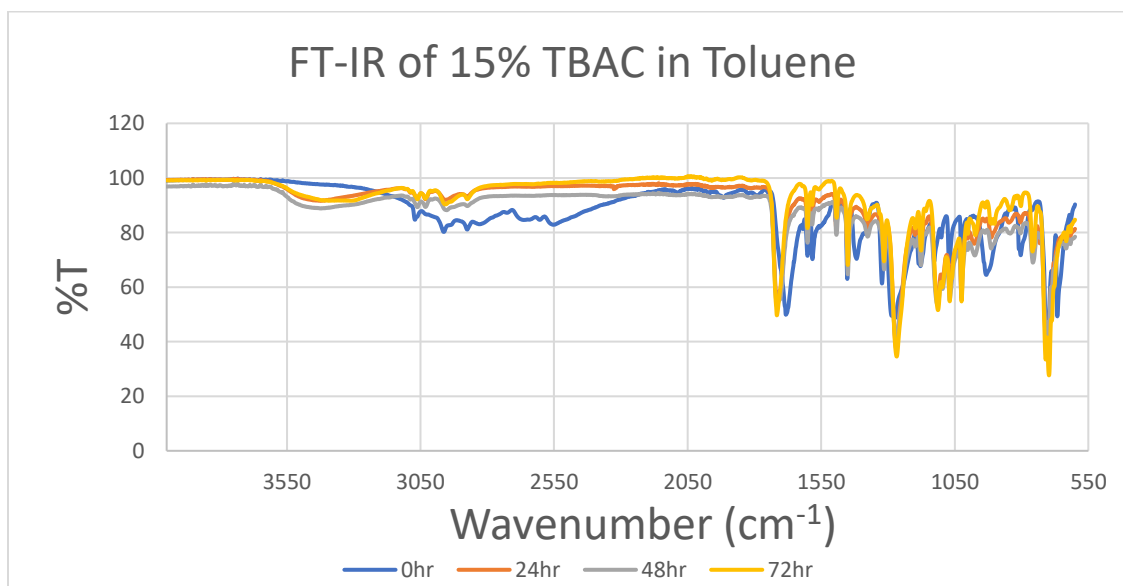


Figure 14. FT-IR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 15% Tetrabutylammonium Chloride in Toluene Solution.

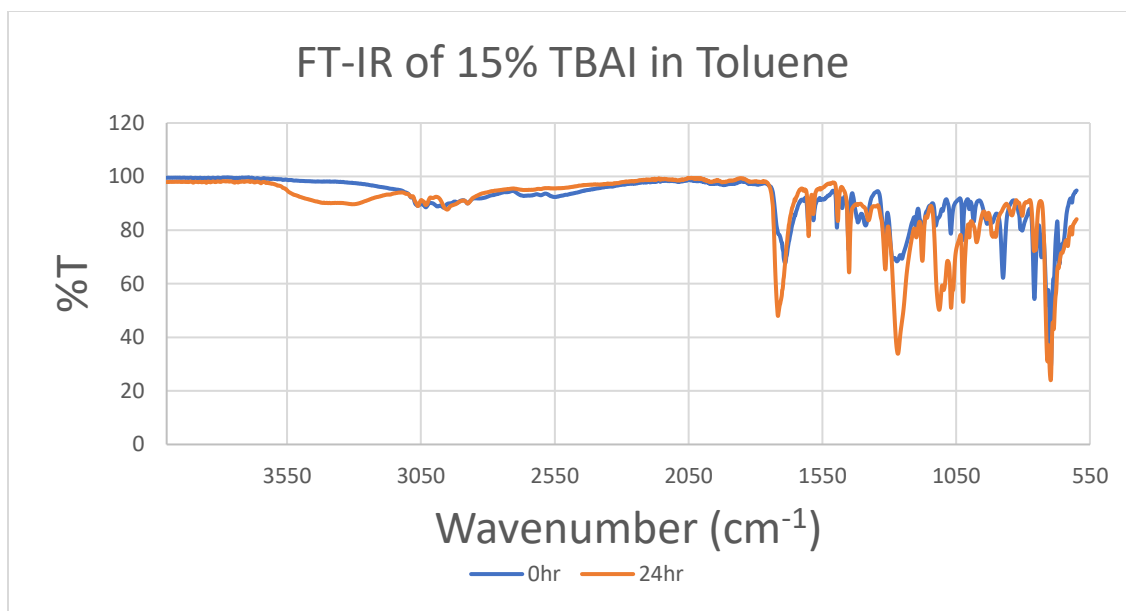


Figure 15. FT-IR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 15% Tetrabutylammonium Iodide in Toluene Solution.

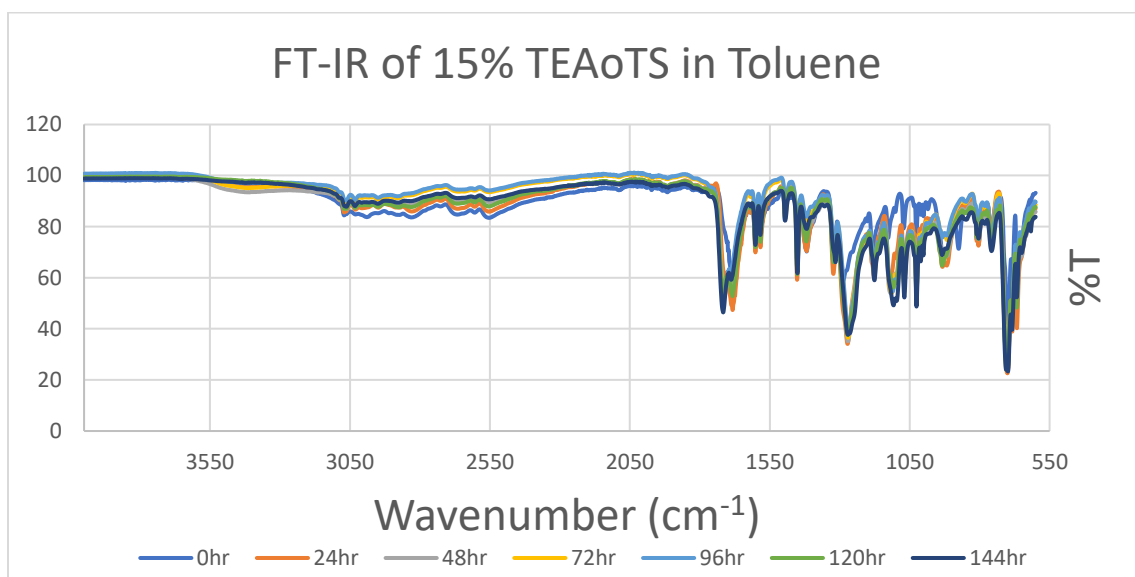


Figure 16. FT-IR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 15% Tetraethylammonium p-Toluenesulfonate in Toluene Solution.

Part II. Addition of Benzoic Acid to Styrene Oxide ^1H -NMR

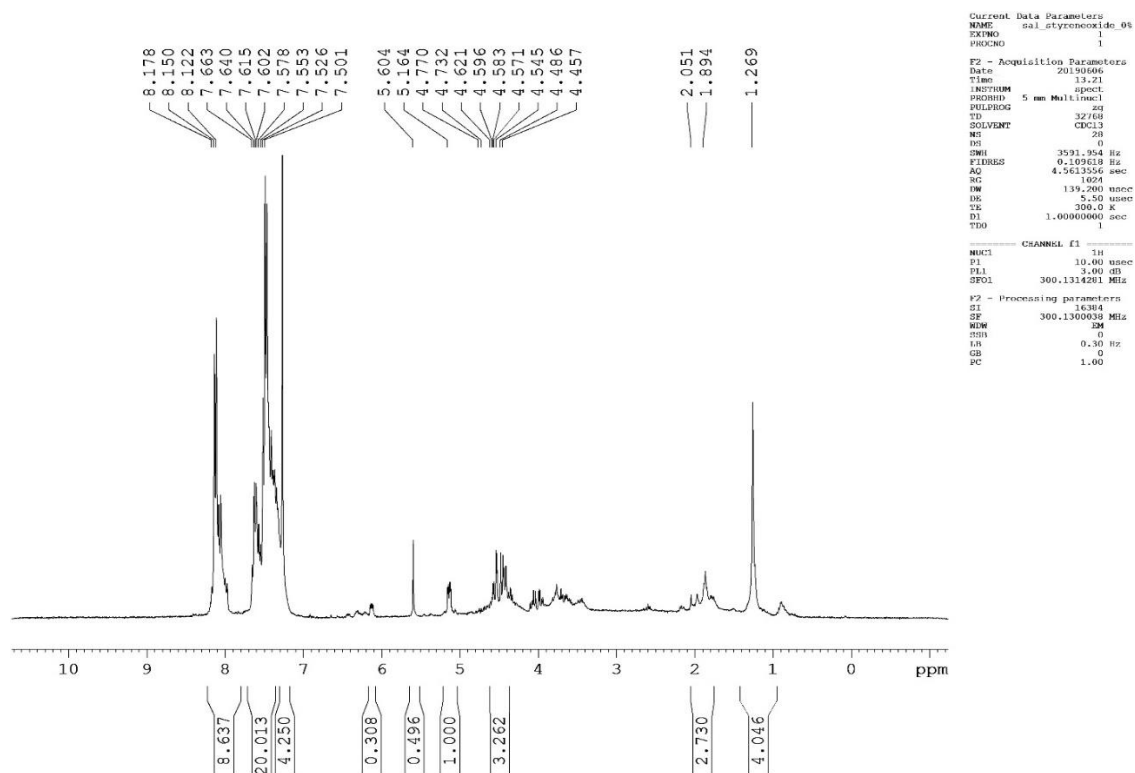


Figure 17. ^1H -NMR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 0% Tetrabutylammonium Bromide in Tetrahydrofuran Solution.

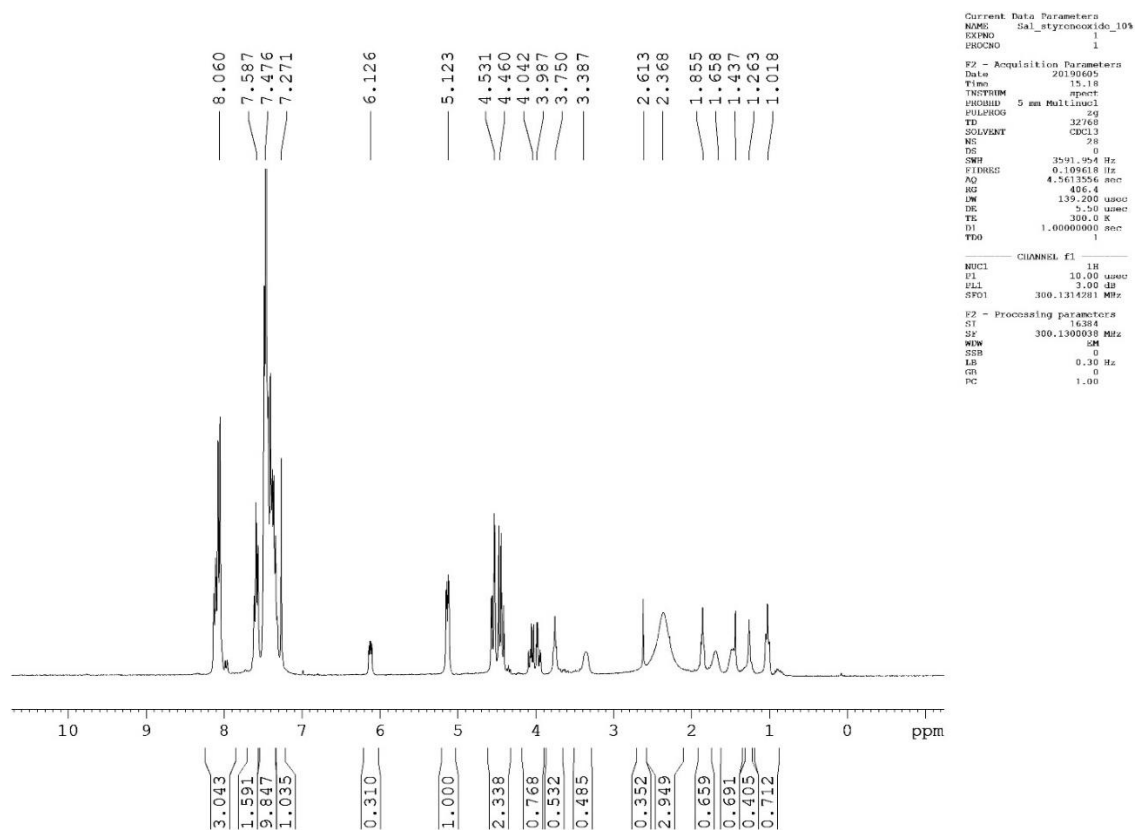


Figure 18. ^1H -NMR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 10% Tetrabutylammonium Bromide in Tetrahydrofuran Solution.

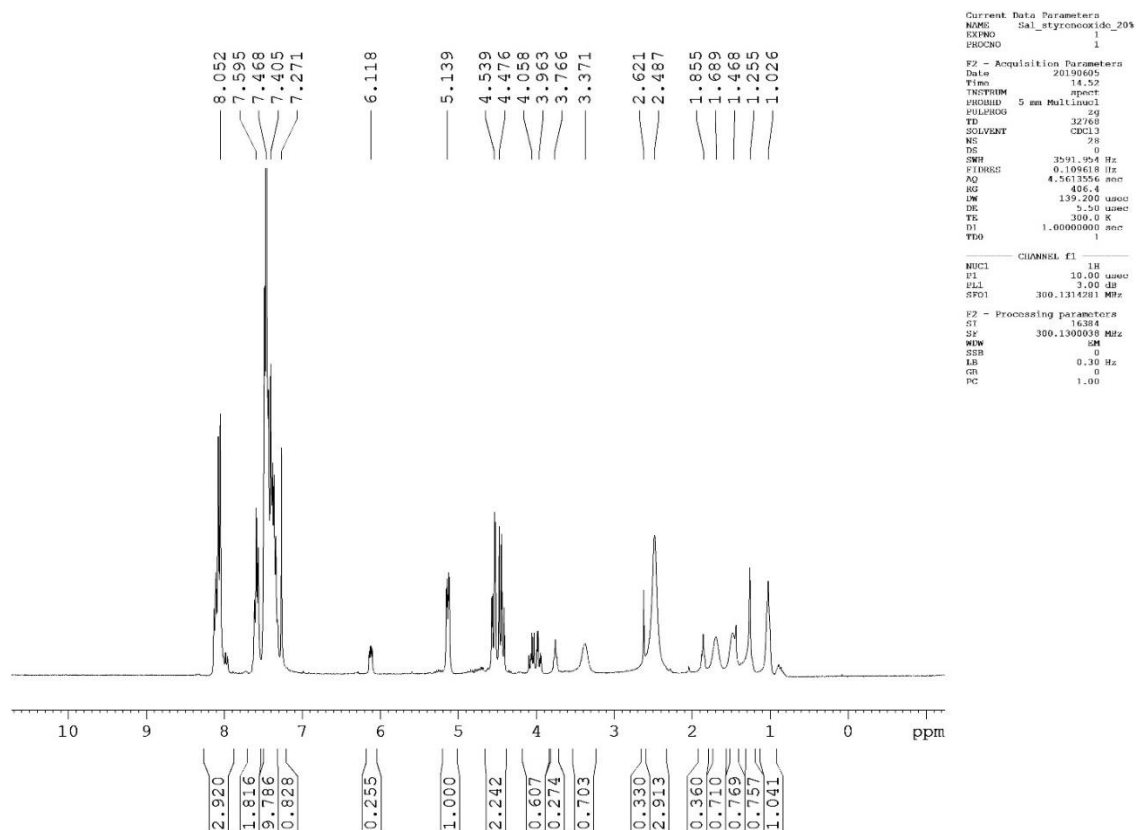


Figure 19. ^1H -NMR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 15% Tetrabutylammonium Bromide in Tetrahydrofuran Solution.

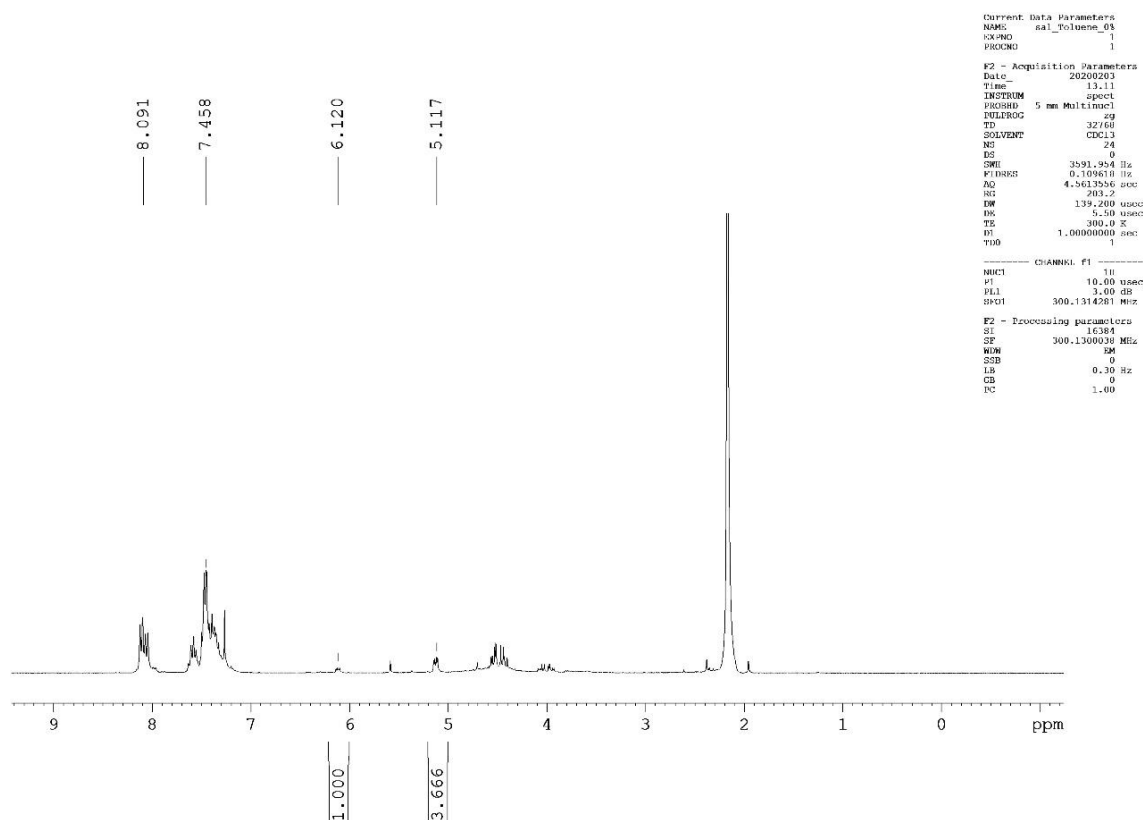


Figure 20. ^1H -NMR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 0% Tetrabutylammonium Bromide in Toluene Solution.

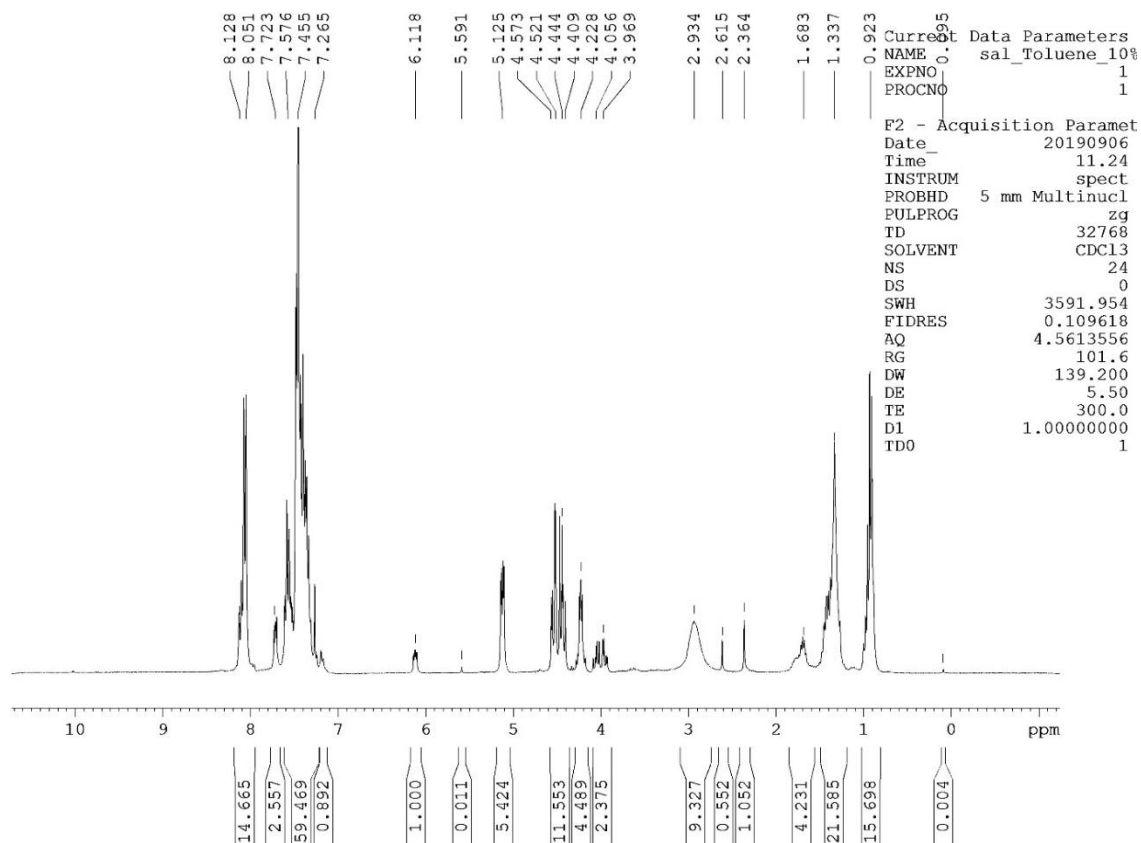


Figure 21. ^1H -NMR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 10% Tetrabutylammonium Bromide in Toluene Solution.

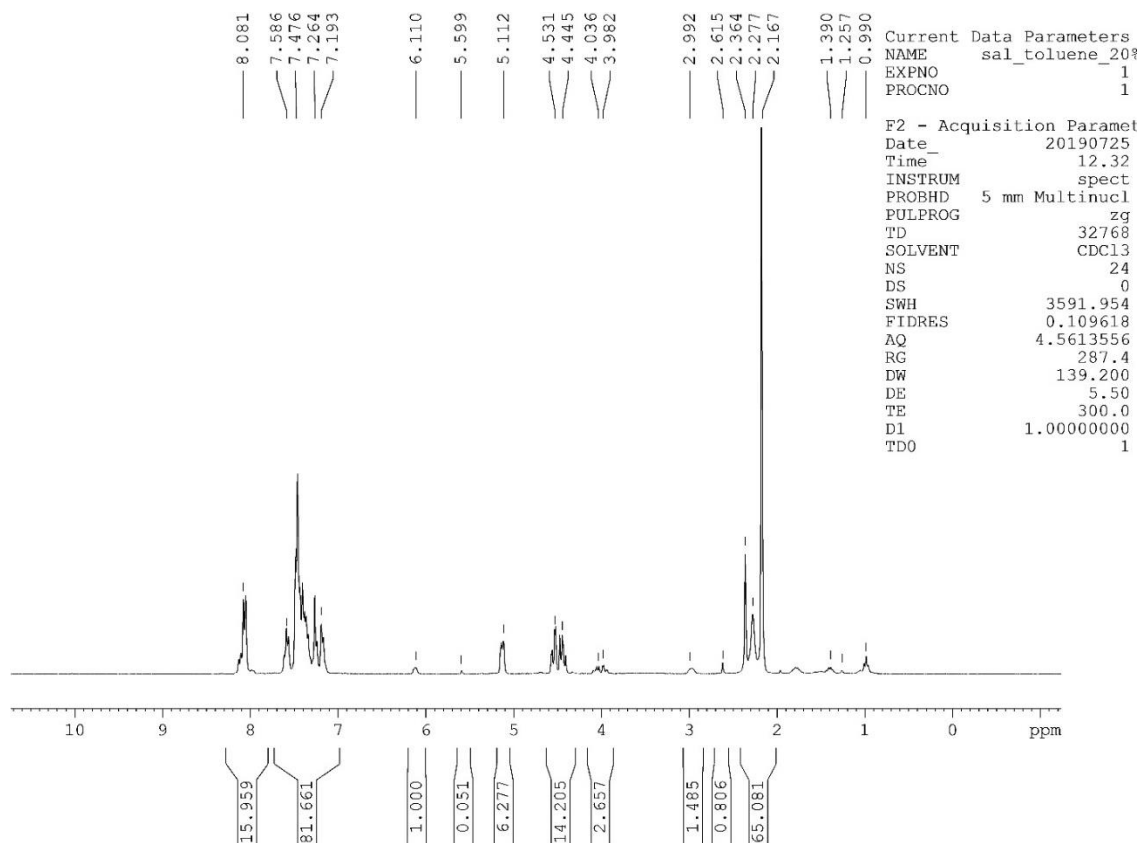


Figure 22. ^1H -NMR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 15% Tetrabutylammonium Bromide in Toluene Solution.

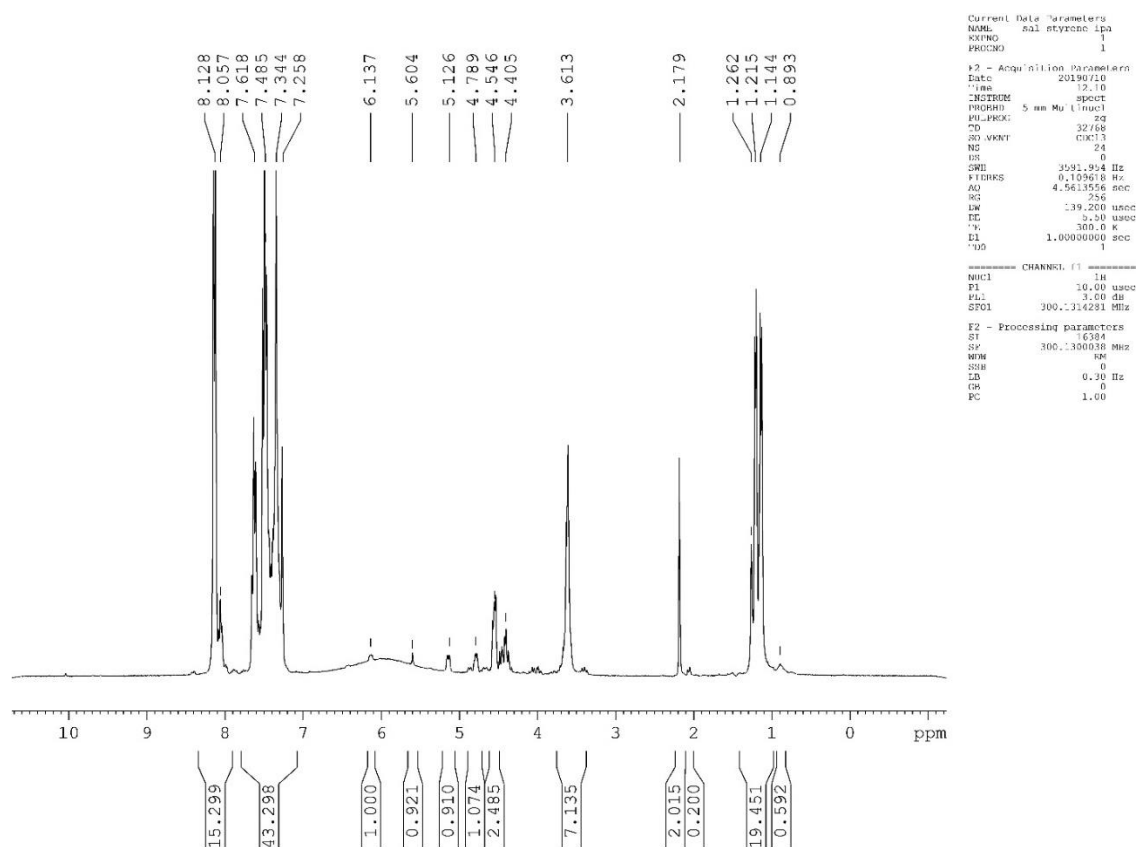


Figure 23. ^1H -NMR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 0% Tetrabutylammonium Bromide in Isopropanol Solution.

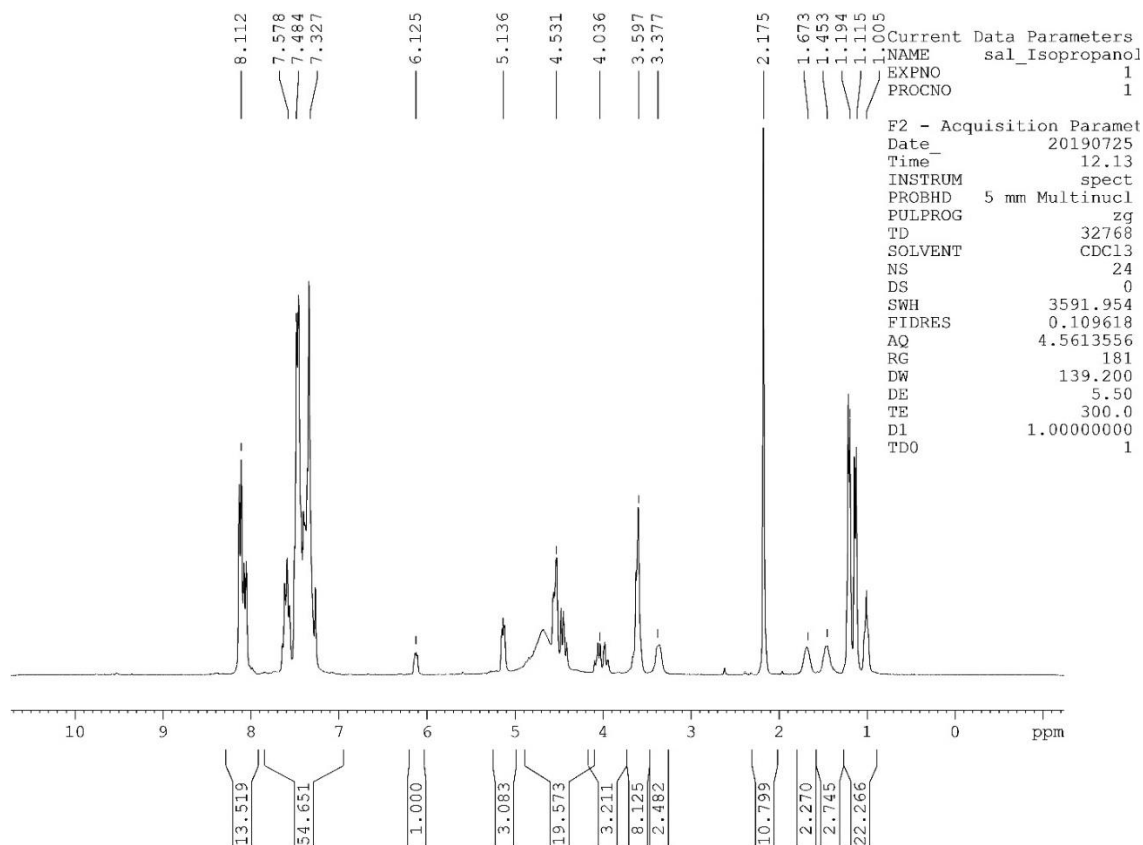


Figure 24. ^1H -NMR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 10% Tetrabutylammonium Bromide in Isopropanol Solution.

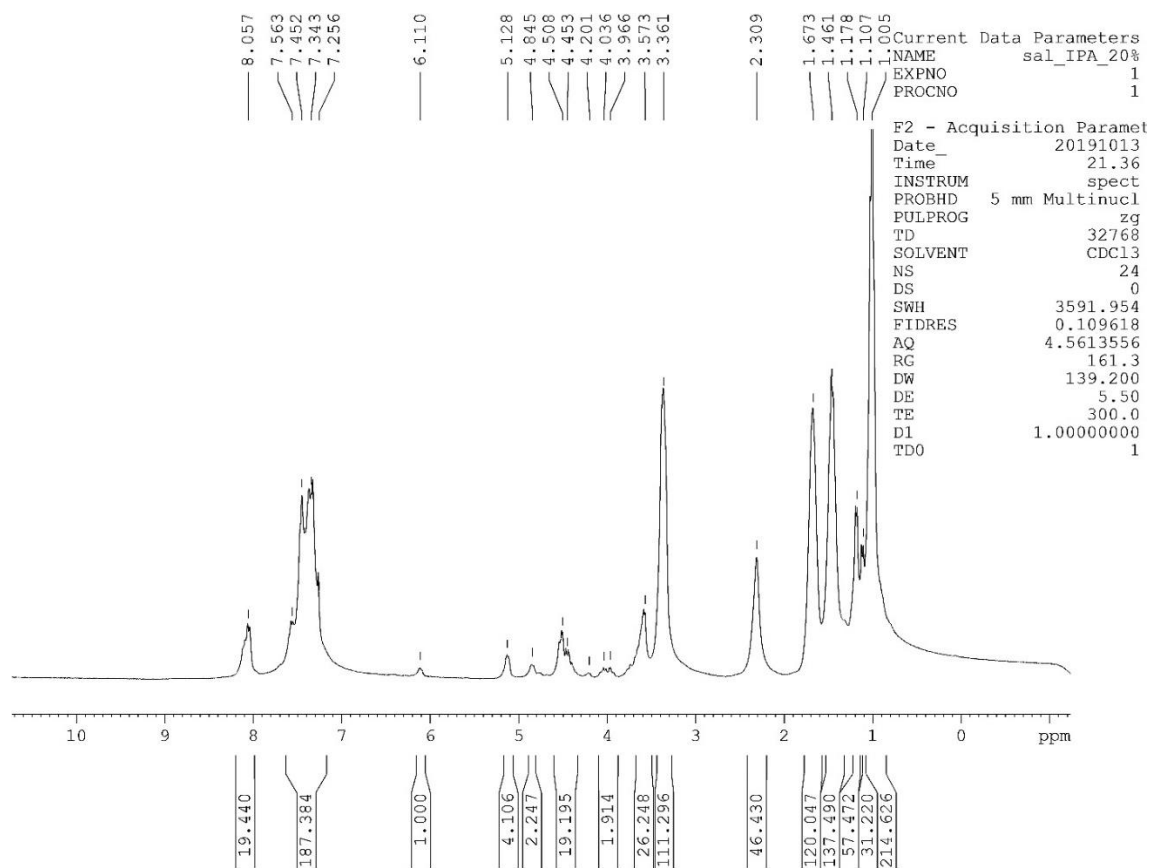


Figure 25. ^1H -NMR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 15% Tetrabutylammonium Bromide in Isopropanol Solution.

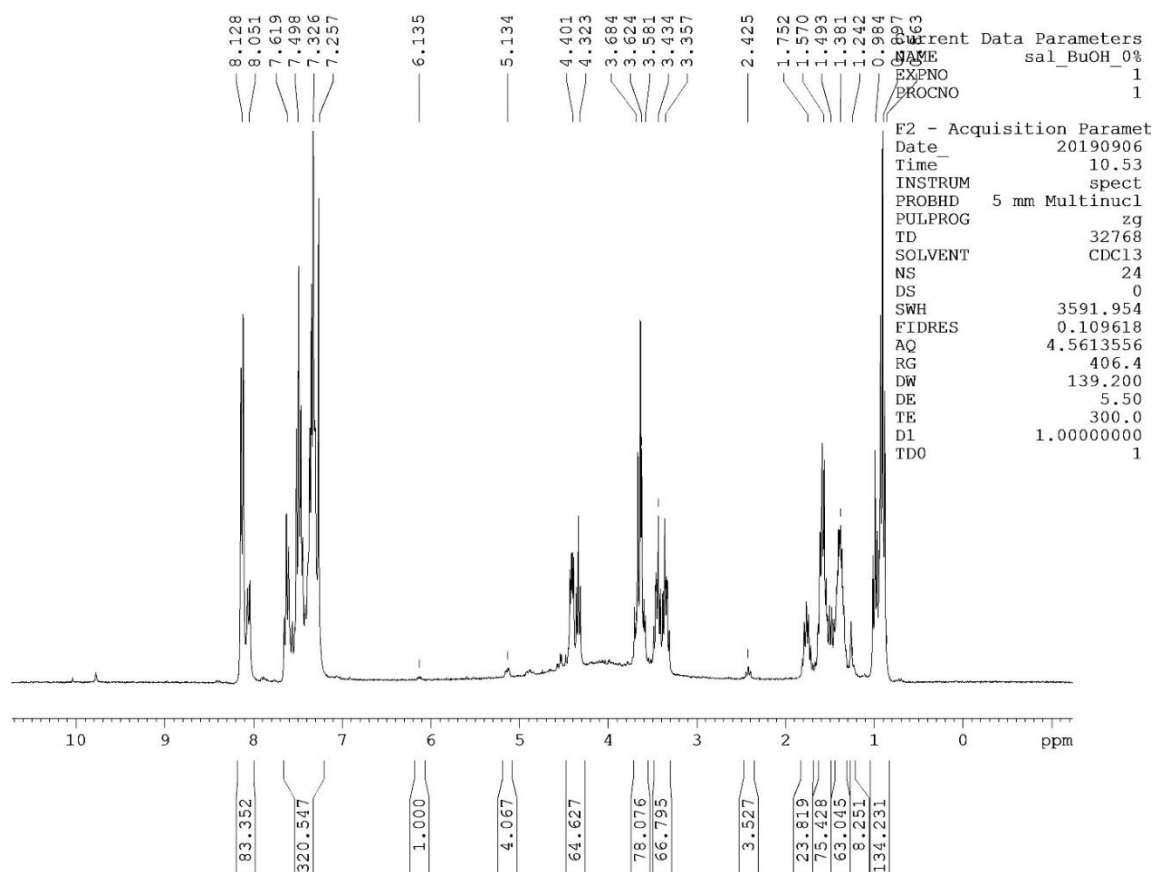


Figure 26. ^1H -NMR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 0% Tetrabutylammonium Bromide in 1-Butanol Solution.

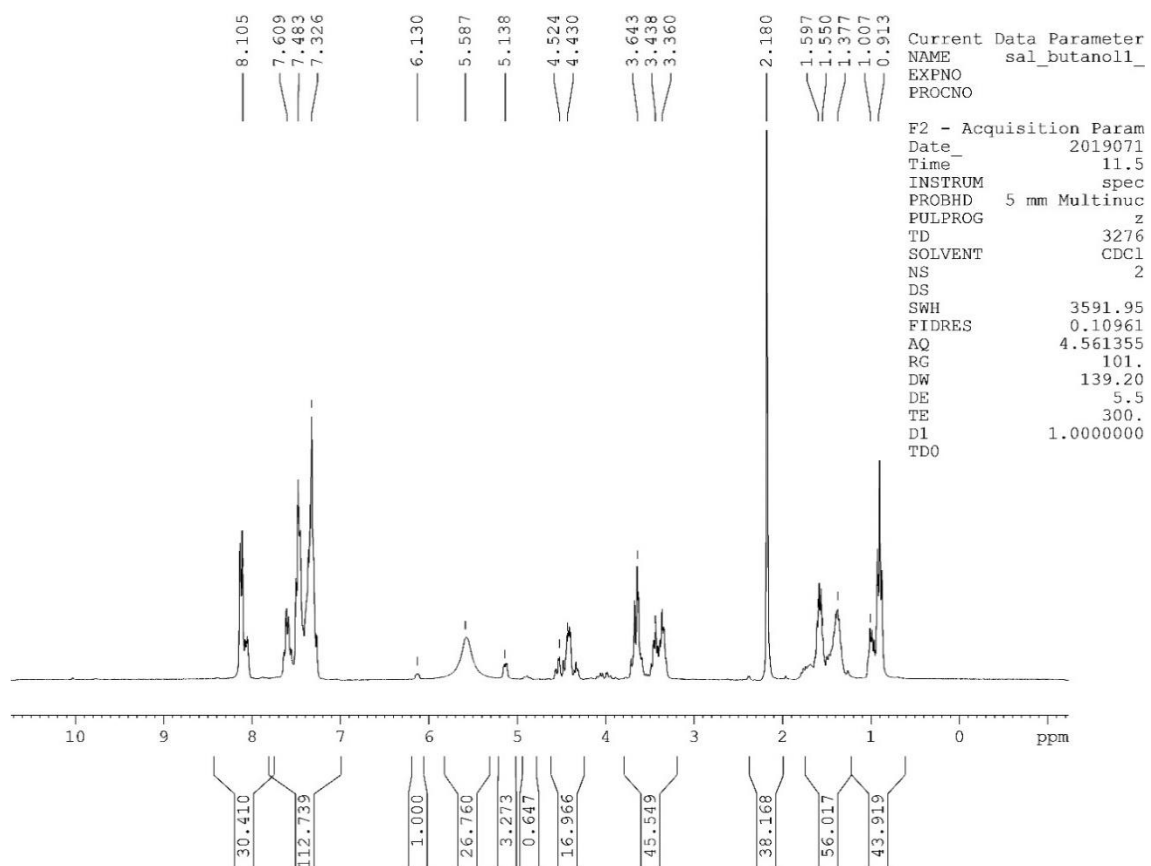


Figure 27. ^1H -NMR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 10% Tetrabutylammonium Bromide in 1-Butanol Solution.

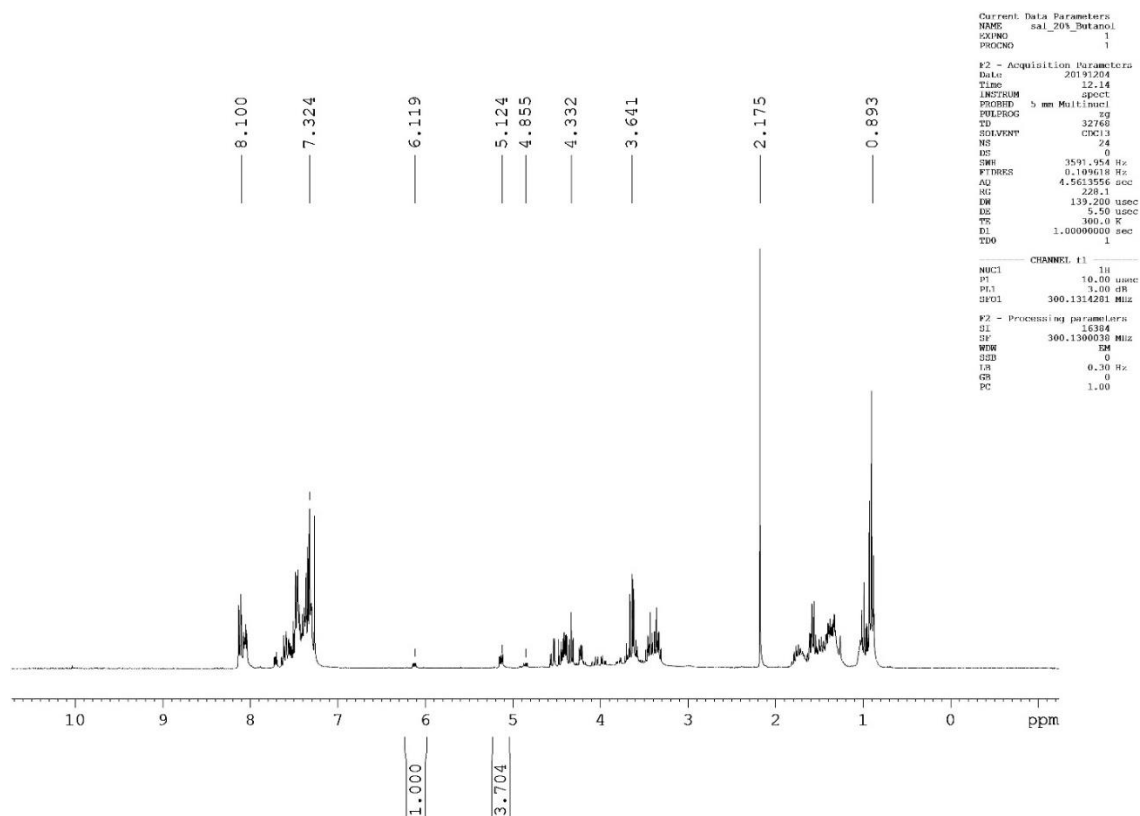


Figure 28. ^1H -NMR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 15% Tetrabutylammonium Bromide in 1-Butanol Solution.

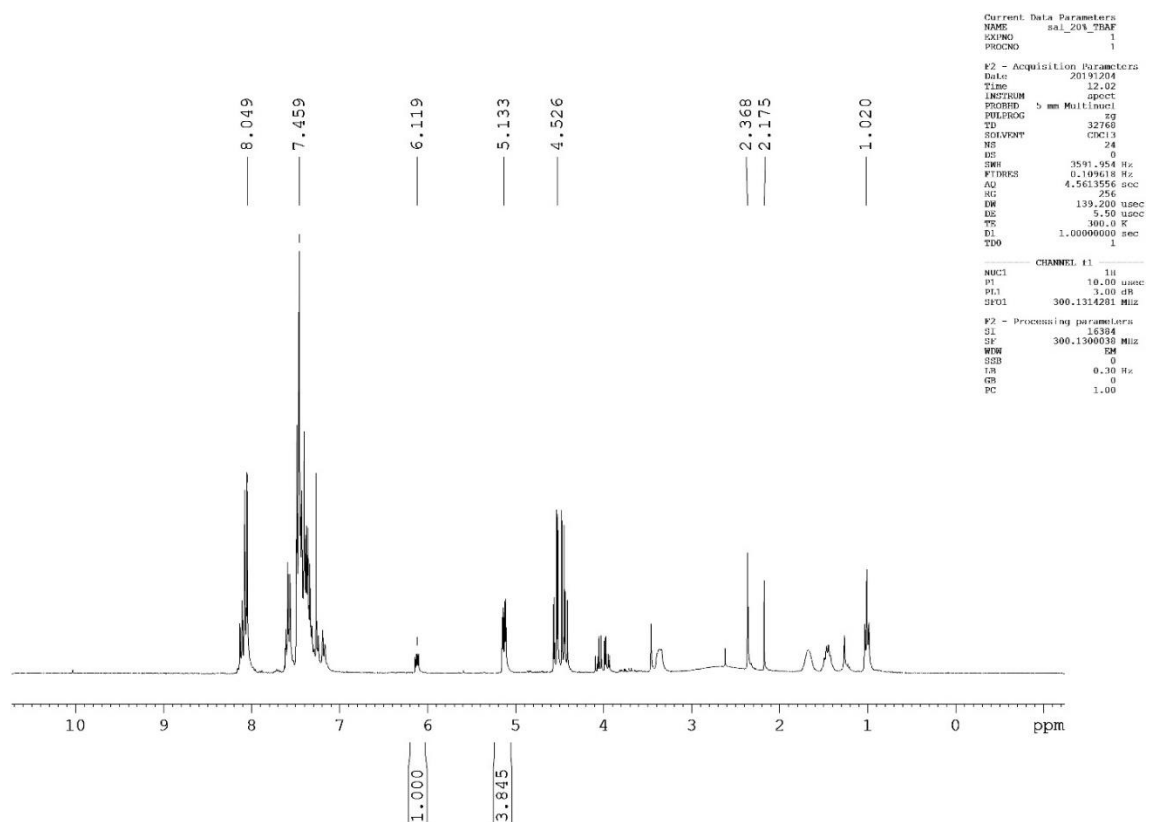


Figure 29. ^1H -NMR Spectra of Addition of Benzoic Acid to Styrene Oxide using 15% Tetrabutylammonium Fluoride in Toluene Solution.

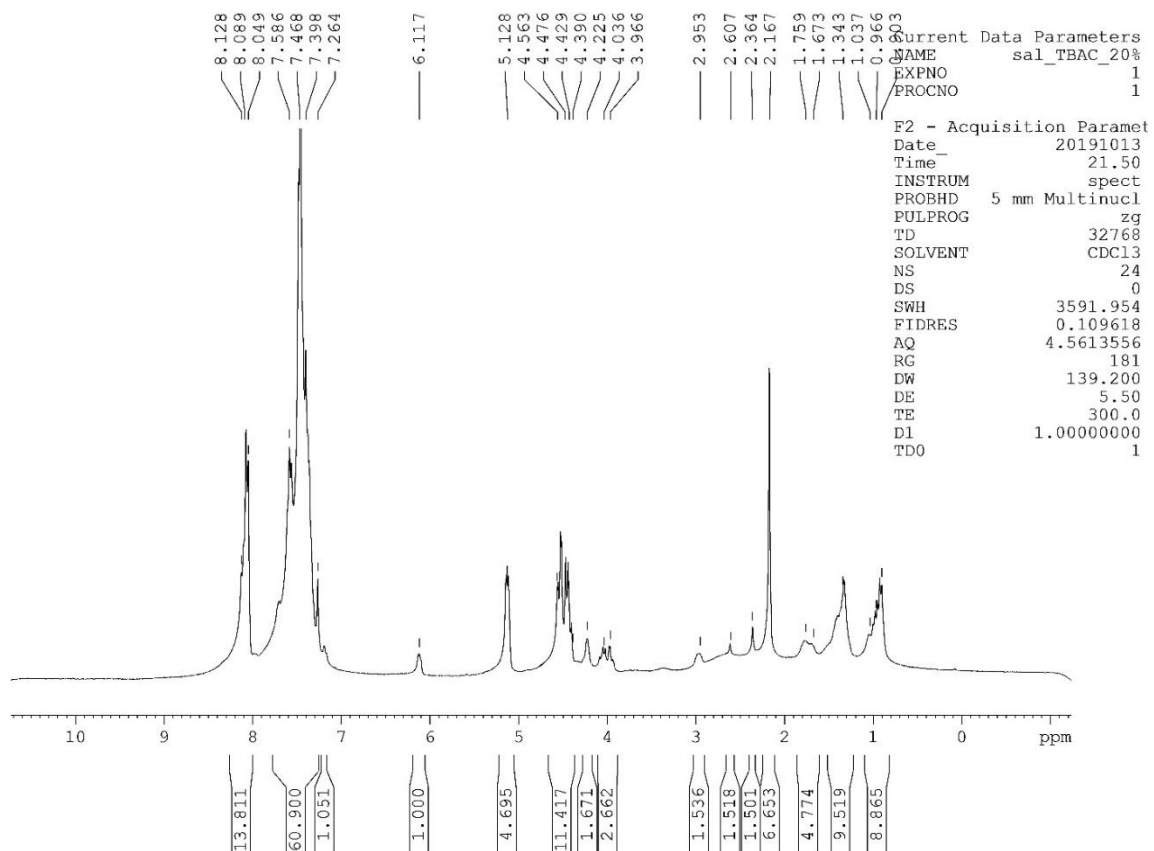


Figure 30. ^1H -NMR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 15% Tetrabutylammonium Chloride in Toluene Solution.

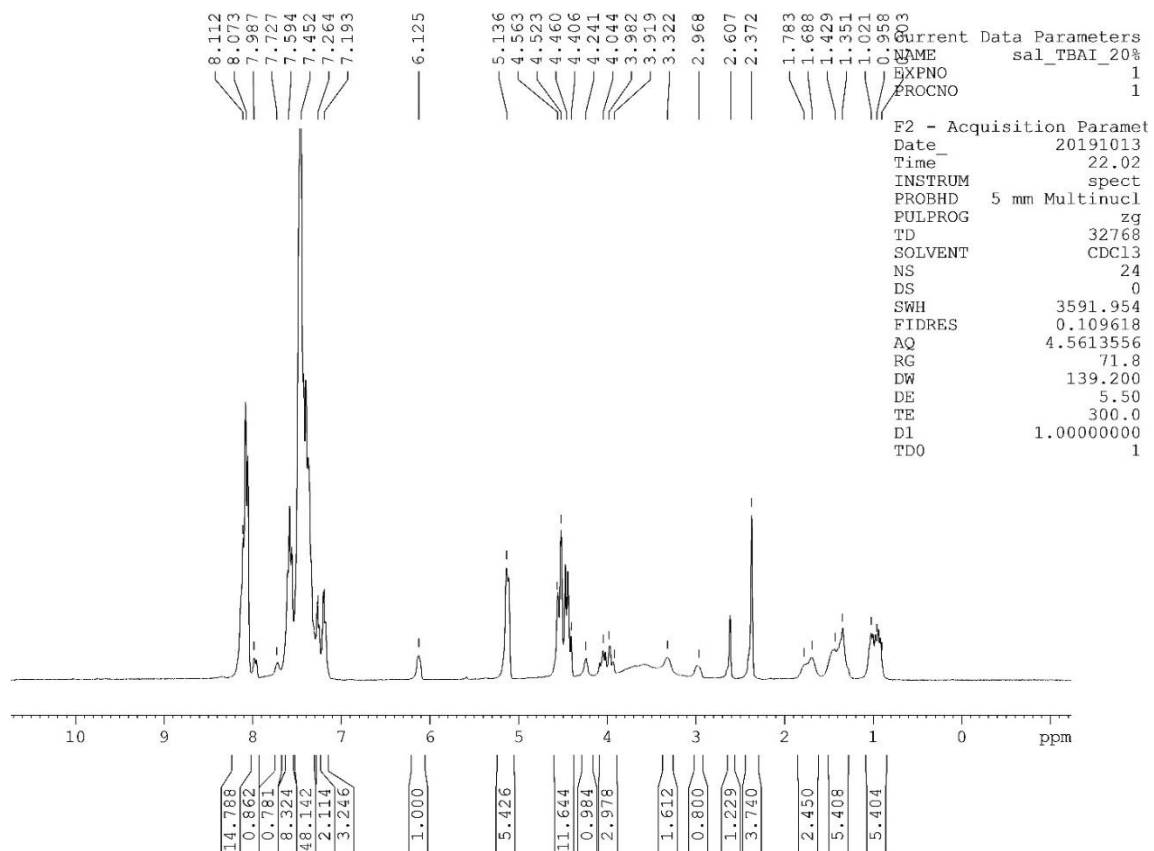


Figure 31. ^1H -NMR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 15% Tetrabutylammonium Iodide in Toluene Solution.

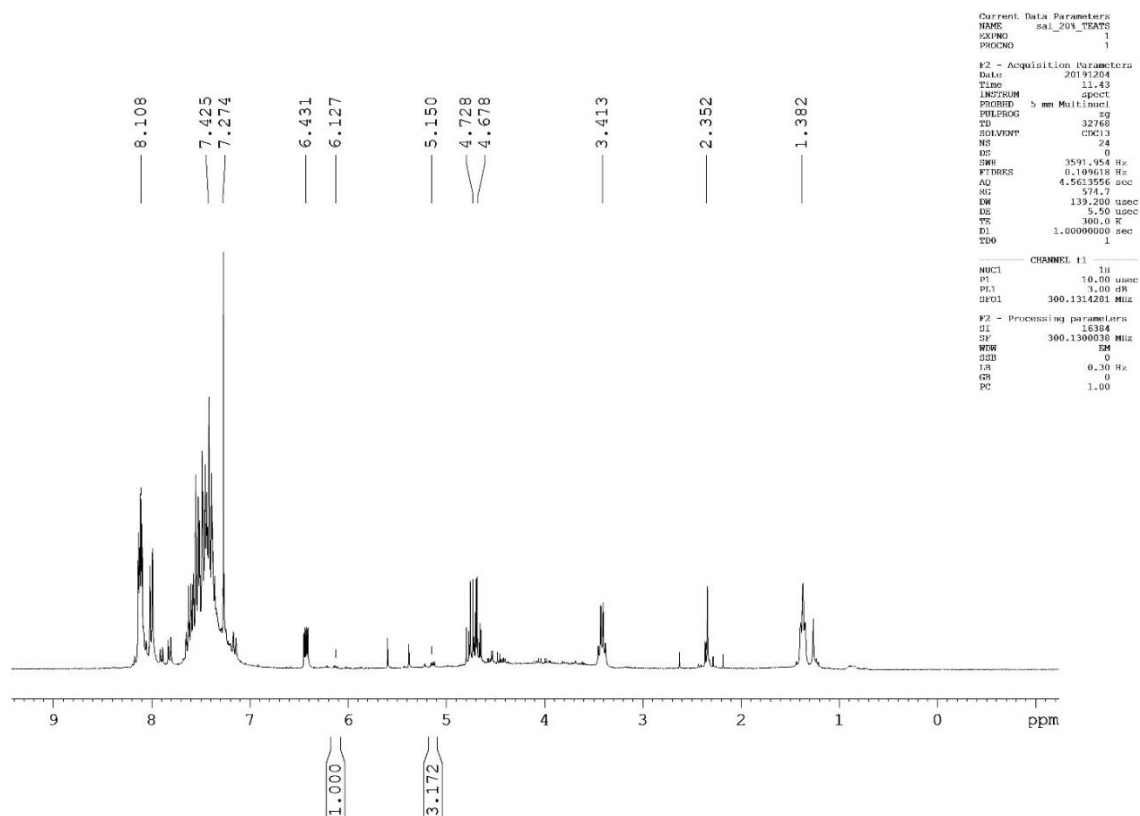


Figure 32. ^1H -NMR Spectrum of Addition of Benzoic Acid to Styrene Oxide using 15% Tetraethylammonium p-Toluenesulfonate in Toluene Solution.

PART III. FT-IR Spectra of Flame Retardants

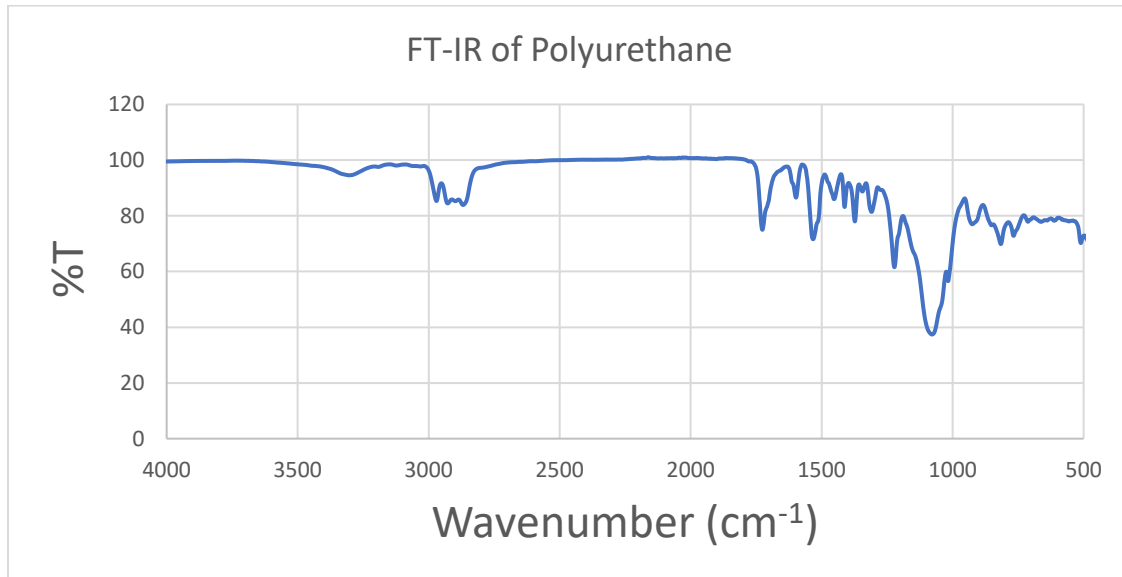


Figure 33. FT-IR Spectrum of Polyurethane.

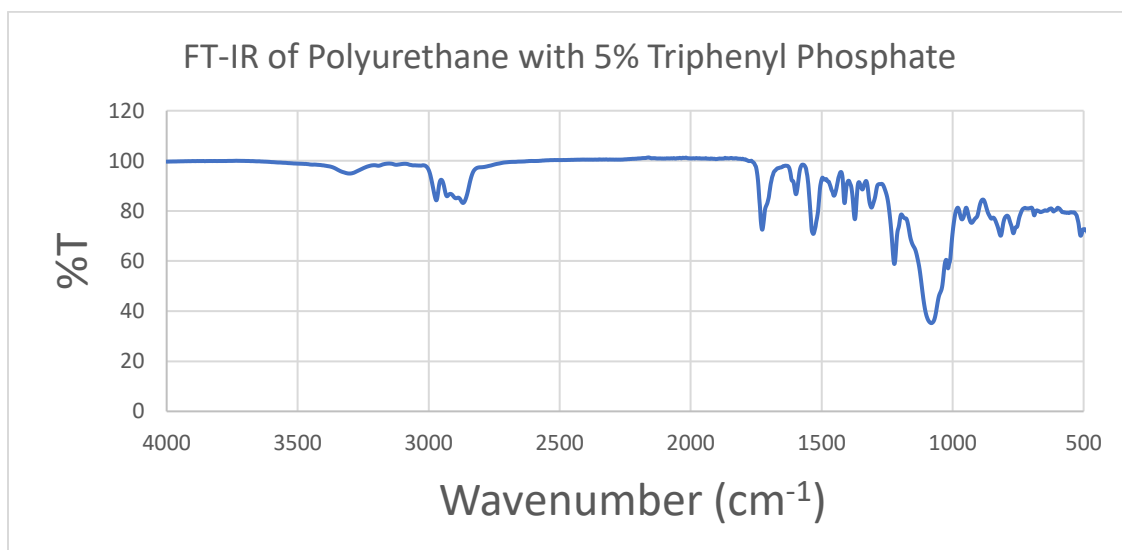


Figure 34. FT-IR Spectrum of 5% Triphenyl Phosphate mixed with Polyol and Isocyanate.

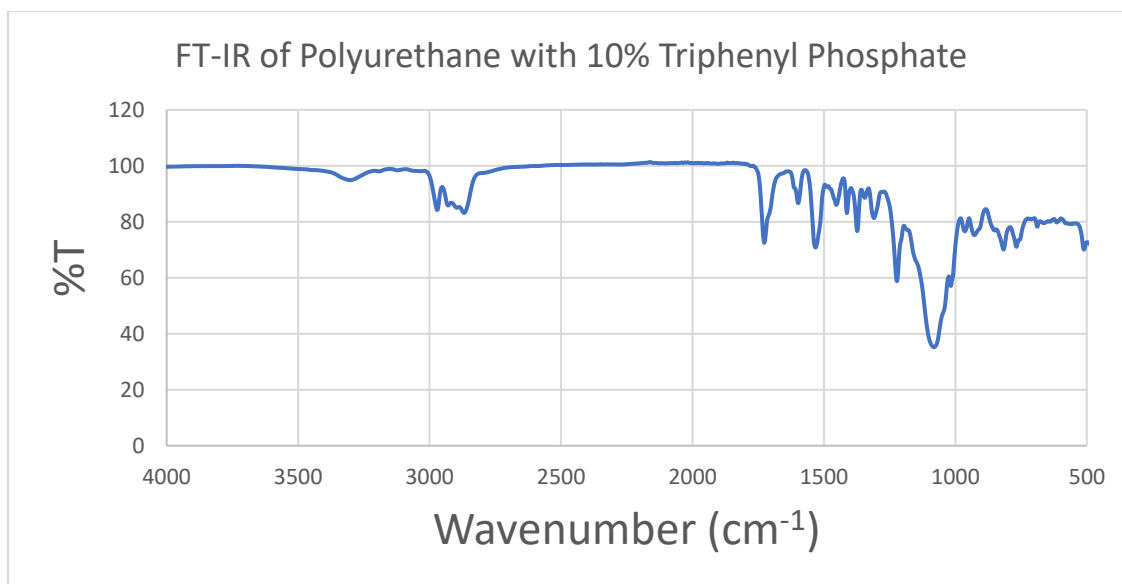


Figure 35. FT-IR Spectrum of 10% Triphenyl Phosphate mixed with Polyol and Isocyanate.

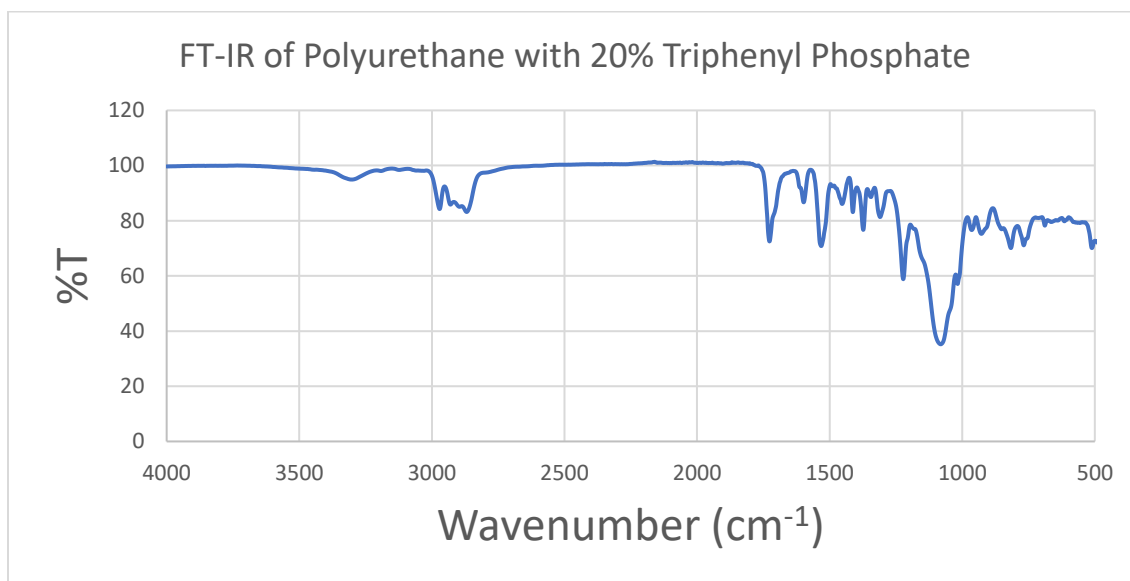


Figure 36. FT-IR Spectrum of 20% Triphenyl Phosphate mixed with Polyol and Isocyanate.

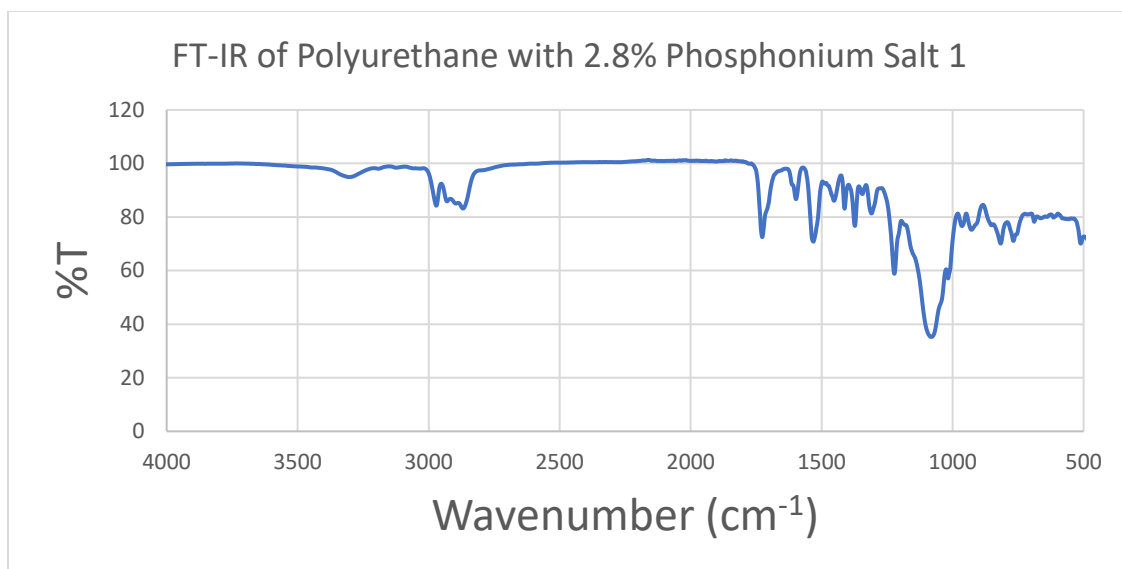


Figure 37. FT-IR Spectrum of 2.8% Phosphonium Salt 1 mixed with Polyol and Isocyanate.

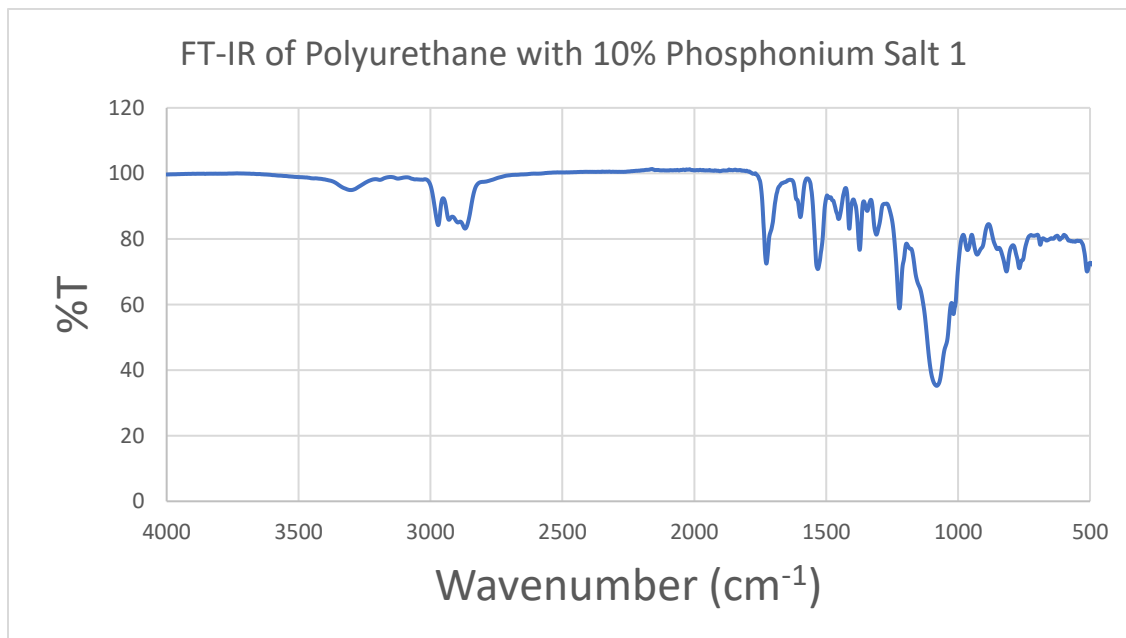


Figure 38. FT-IR Spectrum of 10% Phosphonium Salt 1 mixed with Polyol and

Isocyanate.

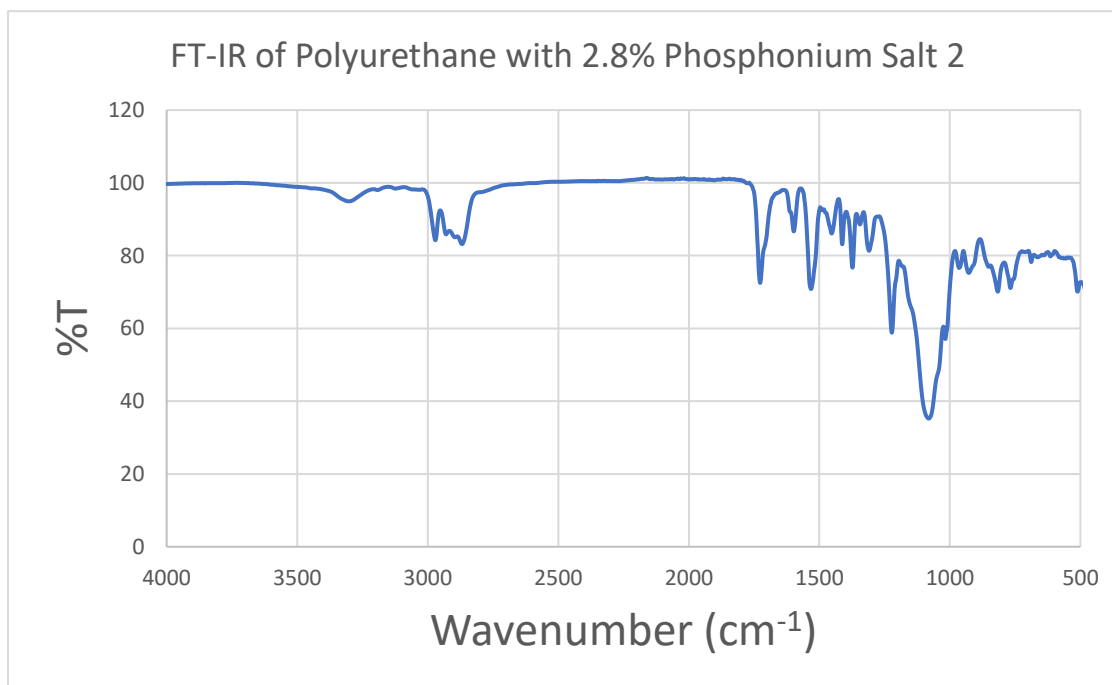


Figure 39. FT-IR Spectrum 2.8% Phosphonium Salt 2 mixed with Polyol and Isocyanate.

Part IV. Flame Retardants TGA

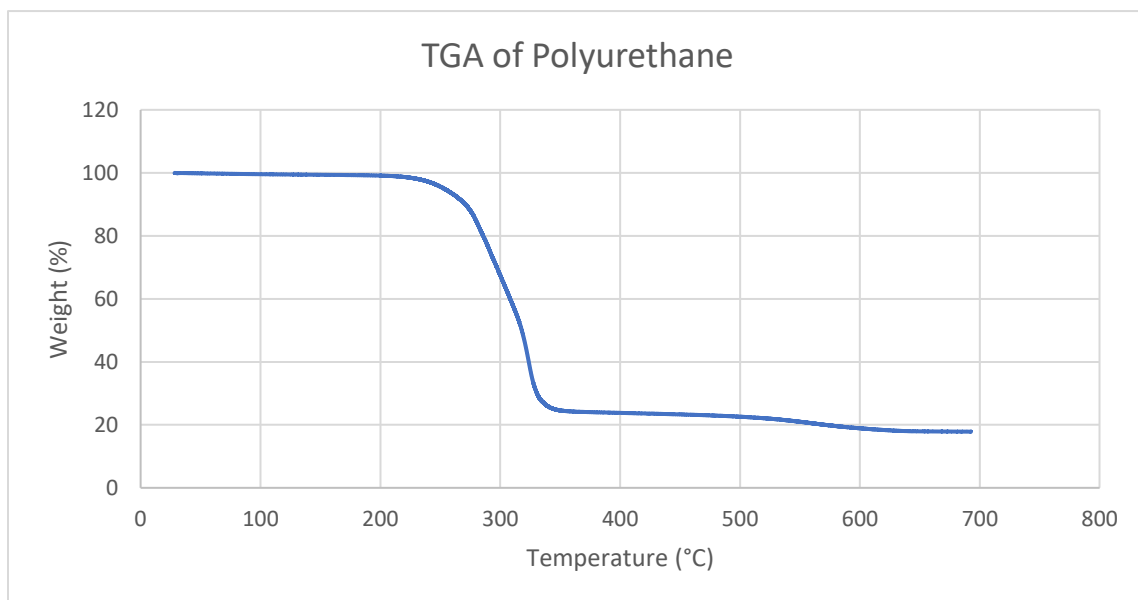


Figure 40. TGA Spectrum of 0% Triphenyl Phosphate mixed with Polyol and Isocyanate.

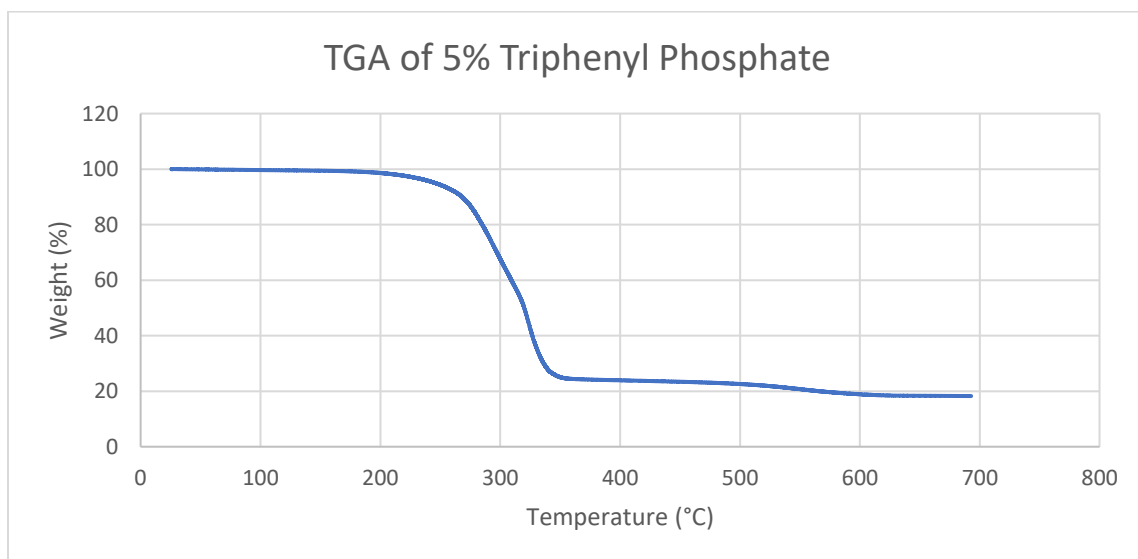


Figure 41. TGA Spectrum of 5% Triphenyl Phosphate mixed with Polyol and Isocyanate.

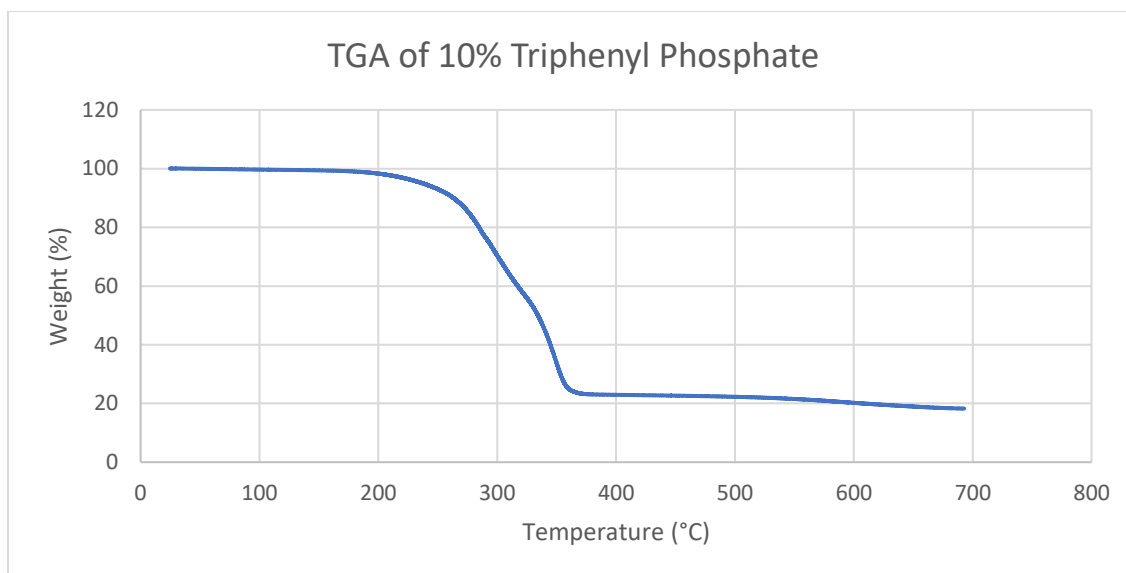


Figure 42. TGA Spectrum of 10% Triphenyl Phosphate mixed with Polyol and Isocyanate.

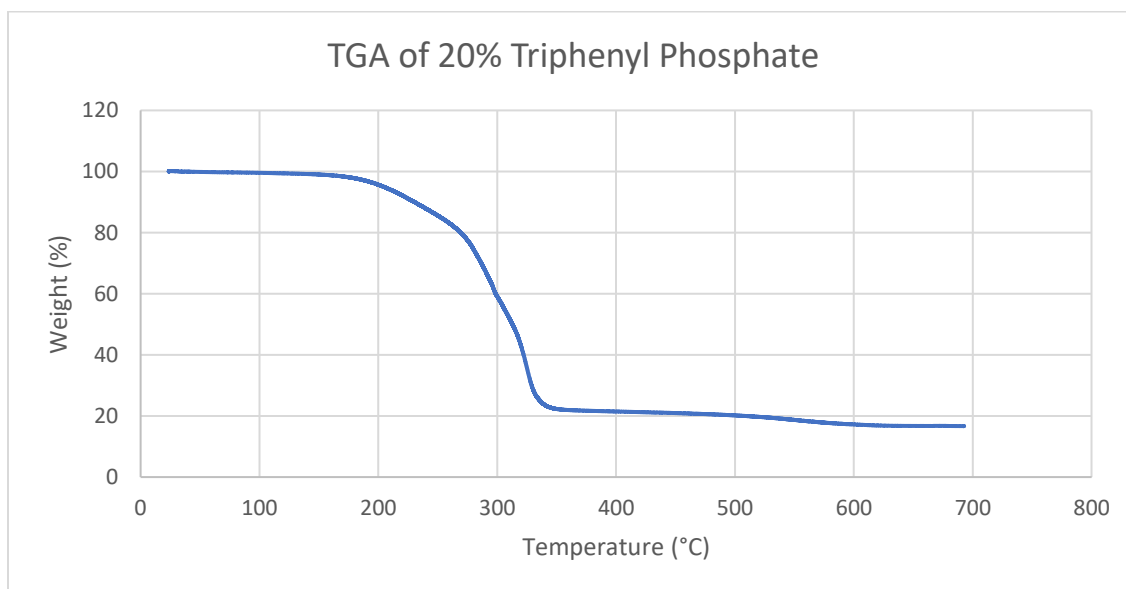


Figure 43. TGA Spectrum of 20% Triphenyl Phosphate mixed with Polyol and Isocyanate.

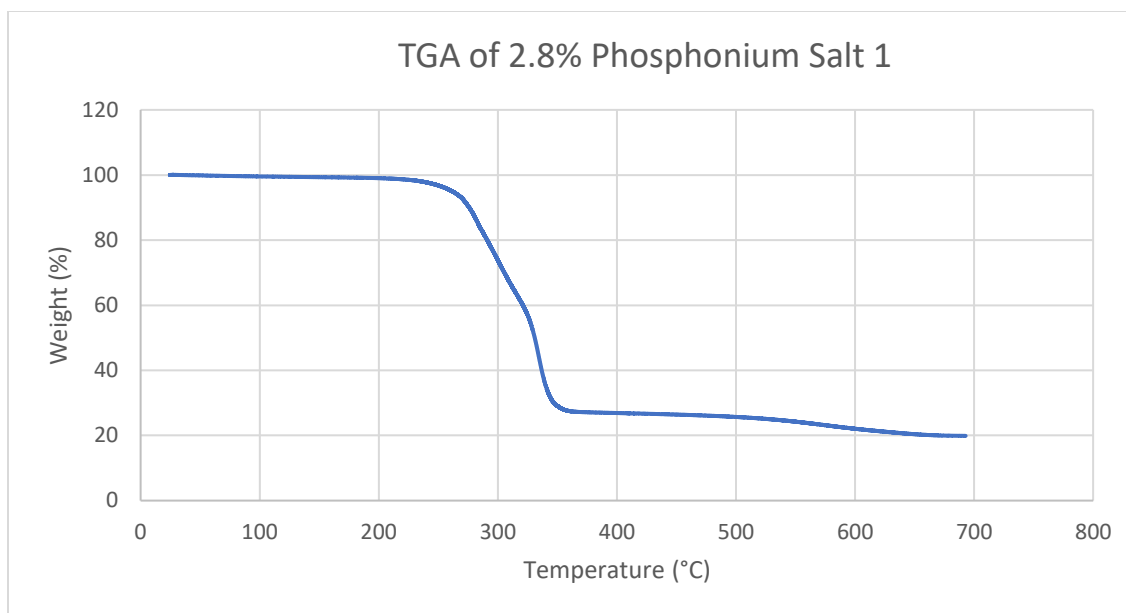


Figure 44. TGA Spectrum of 2.8% Phosphonium Salt 1 mixed with Polyol and Isocyanate.

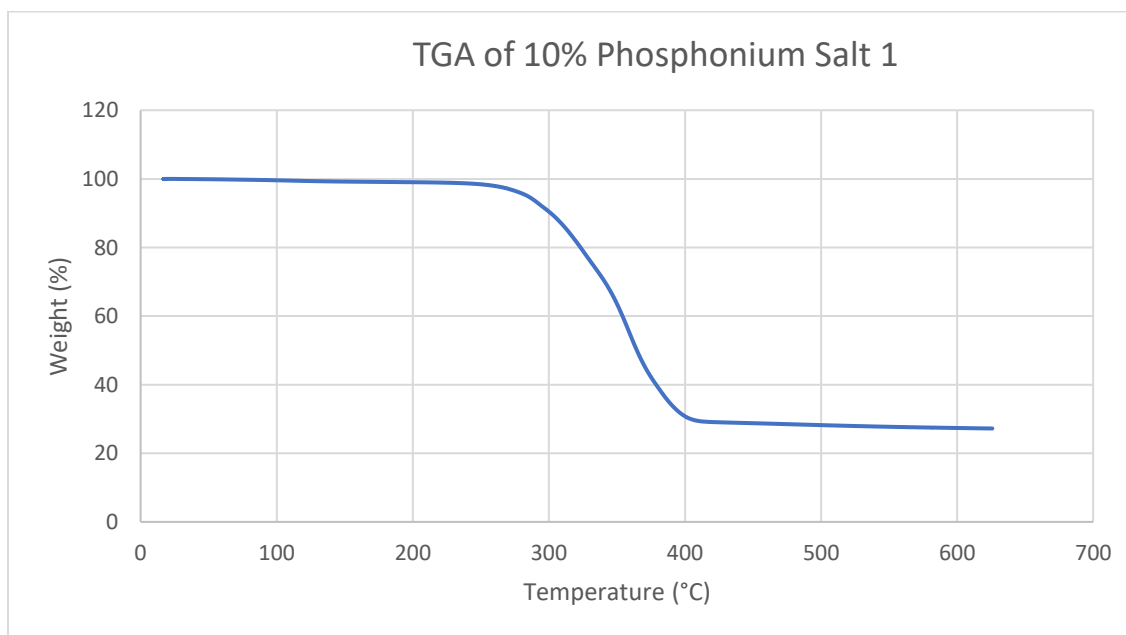


Figure 45. TGA Spectrum of 10% Phosphonium Salt 1 mixed with Polyol and Isocyanate.

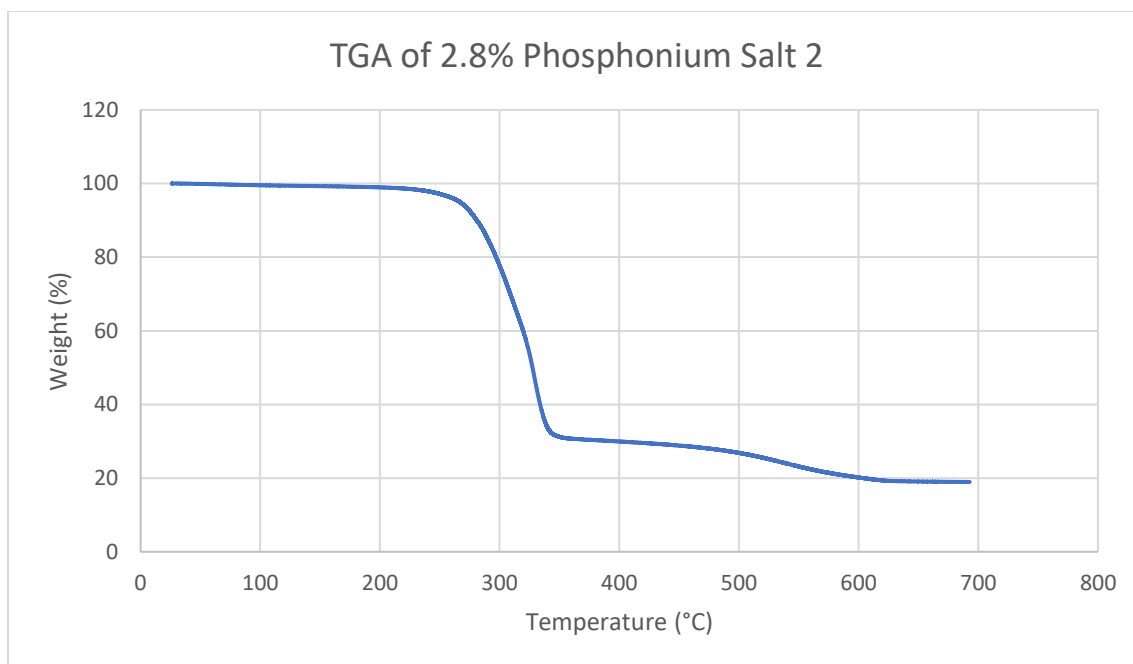


Figure 46. TGA Spectrum of 2.8% Phosphonium Salt 2 mixed with Polyol and Isocyanate.