Master Thesis in Environmental Chemistry

Environmentally Friendly Synthesis of Biobased Plastic from Lignin Derived Building Blocks to Replace Poly(ethylene Terephthalate) (PET)

By

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Abstract

The resources of petroleum are decreasing, and new ways have to be found of producing all the energy and chemicals that today are based on petroleum. An alternative to petroleum is renewable biomass, where lignocellulosic biomass comprises the largest amount. This biomass contains mainly cellulose, hemicellulose and lignin.

One of the products that is usually derived from petroleum is poly(ethylene terephthalate) (PET). This is a common type of plastic, which among other things, is used in food containers and clothing. It is produced from terephthalic acid, which is derived from petroleum, and ethylene glycol, which can be derived either from petroleum or from biomass. An environmental friendly alternative to PET is of great interest.

A biobased alternative to PET has previously been investigated by developing a synthetic route to poly[4-(2-hydroxyethoxy)-3-methoxybenzoic acid] from the potentially biobased vanillic acid in a two-step synthesis via 4-(2-hydroxyethoxy)-3-methoxybenzoic acid. This provides the foundation of this thesis, where the synthetic route will be adopted and adjusted.

The overall results produced the desired monomer after some adjustments to the method. The monomer synthesis provided lower yields than published in the literature. A detailed analysis and elucidation of the product showed a pure product of the desired monomer.

In this thesis, a new method of polymerization is tested. As the stirring needed to be increased, the procedure was executed in a rotary evaporator. This method gave indications of a better degree of polymerization, as well as being easier to handle from a laboratory technical point of view.

By comparing the results of the polymerization to the results found in literature, a higher yield was achieved. The analytical results were somewhat different, as some parameters could not be determined. The values that were found gave a close proximity to the literature values. A close proximity was found to the thermal properties of PET, thus supporting the possibility of replacing this polymer commercially with renewably based chemicals.

Abbreviations

BBO	Bruker Broadband Observe
CAPT	Compensated Attached Proton Test
COSY	Correlation Spectroscopy
DART	Direct Analysis in Real Time
DART-MS	Direct Analysis in Real Time – Mass Spectrometry
DCM	Dichloromethane
DOSY	Diffusion-Ordered Spectroscopy
DSC	Differential Scanning Calorimetry
EtOEt	Diethyl Ether
EtOH	Ethanol
FTIR	Fourier-Transform Infrared (spectroscopy)
GC-FID	Gas Chromatography – Flame Ionization Detector
GC-MS	Gas Chromatography – Mass Spectrometry
GPC	Gel Permeation Chromatography
HMBC	Heteronuclear Multiple-Bond Correlation
HSQC	Heteronuclear Single-Quantum Correlation
IR	Infrared (spectroscopy)
IUPAC	International Union of Pure and Applied Chemistry
MCP	Micro Channel Plate
MeOH	Methanol
MSD	Mass Sensitive Detector
NMR	Nuclear Magnetic Resonance
OMe	Methoxy
PEG600	Polyethylene Glycol, average mass 600 u
PET	Poly(Ethylene Terephthalate)
SEC	Size Exclusion Chromatography
T_g	Glass Transition Temperature
THF	Tetrahydrofurane
TIC	Total Ion Chromatogram
T_m	Temperature of Melting
TOF	Time of Flight
ΔH_m	Enthaply of Melting

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1 Introduction

1.1 Background

In the media, the focus and criticism of the usage of petroleum based fuels in the transport sector has been given a lot of attention. There has been much less attention paid to the fact that a lot of basic chemicals are produced from oil. However, alternative sources like biomass has still been attracting much attention in the research sector.[1-3]

There are discussions regarding how long the oil will last,[4] however as this is a non-renewable product the fact still remains that at some point the oil supply will run out. This could be considered an absolute deadline to have found new sources for everything that today is derived from oil. One of the products usually produced from petroleum is plastic.[5-6] Even though we might still have oil for a long while to come, an argument could still be made to start utilizing biomass as much as possible, as this is a renewable resource as opposed to petroleum.[7]

1.2 Biomass

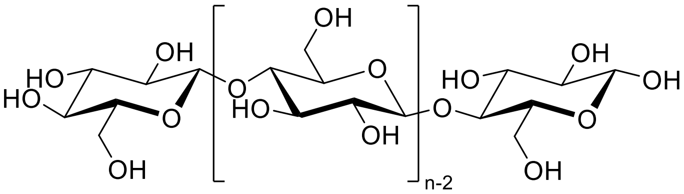
Biomass has several slightly different definitions depending on the source. The International Union of Pure and Applied Chemistry (IUPAC) defines biomass as follows: “Living systems and collection of organic substances produced by living systems that are exploitable as materials, including recent postmortem residues”.[8] Clark, J. et. al. have this explanation to biomass: “Biomass corresponds to any organic matter available on a recurring basis”.[1] In general, these definitions say that biomass is material based on all living organisms living in our era (which is not extinct). Biomass is generally separated into first and second generation, where first generation biomass is edible biomass, such as sugar cane, while second generation is inedible biomass, e.g. timber.[7]

1.2.1 Lignocellulosic Biomass

One type of biomass is based on inedible plants and is thus a second generation resource. This is called lignocellulosic biomass, which consists mainly of cellulose, hemicellulose and lignin, and comprises the largest amount of biomass.[7] The ratio between these biopolymer fractions vary, but lie in the range 40 – 60 % cellulose, 20 – 40 % hemicellulose and 10 – 30 % lignin.[1, 7] These fractions can be separated by a pulping process, which liquefies the lignin part (together with some hemicellulose), or by hydrolysis, which liquefies the cellulose (and some hemicellulose).[7]

1.2.1.1 Cellulose

Cellulose is a linear polymer of β-glucose, as seen in **Figure 1**. There are disagreements as to whether the repeating unit of this is glucose or cellobiose, which is the dimer of glucose. The reason for this disagreement is the 1,4-β-D-glucosidic bond, resulting in every other repeating unit being different from each other. French, A.D. concluded that the repeating unit of cellulose is glucose.[9] Cellulose is used for a number of applications, the largest one being papermaking, which contributes to 95 % of the cellulose production worldwide.[1] Ethanol produced by fermentation from cellulose and hemicellulose is also a major application.[7]



Cellulose

Figure 1: *Structure of cellulose* [9]

1.2.1.2 Hemicellulose

Hemicellulose is a branched copolymer based on several different sugar monomers, consisting of both 5-carbon sugars (pentoses), 6-carbon sugars (hexoses) and 7-carbon sugars (heptoses). Among the most common monomers of hemicellulose are xylose, glucose, mannose and galactose, which are shown in the figure below[7]:

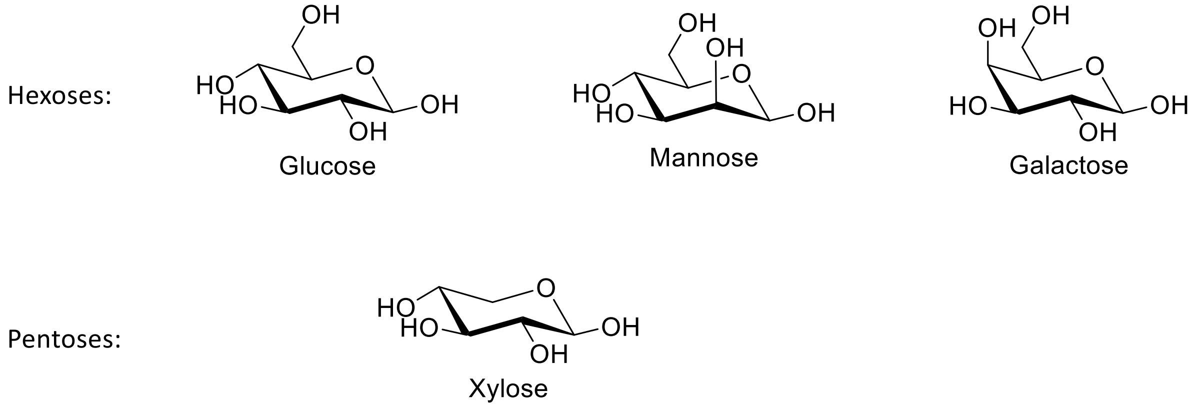
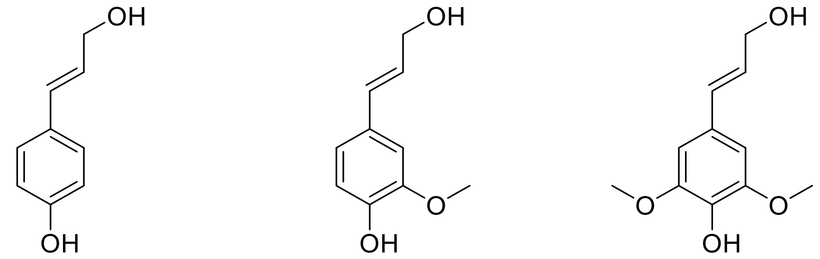


Figure 2: *Common monomers of hemicellulose* [7]

1.2.1.3 Lignin

Lignin, which binds the hemicellulose and the cellulose together in the plant cell wall,[1] is a highly branched copolymer based on three monomeric units, copolymerized without any regular pattern. The three monomeric units are *p*-coumaryl alcohol (H-lignin), coniferyl alcohol (G-lignin, also called guaiacyl alcohol) and sinapyl alcohol (S-lignin, also called syringyl alcohol), as shown in **Figure 3**.[10]



p-coumaryl alcohol (H)

Coniferyl alchohol
Guaiacyl alcohol (G)

Sinapyl alcohol
Syringyl alcohol (S)

Figure 3: *Structures of the three primary monomeric units of lignin*

Together, these three monomers make the lignin copolymer, as will be explained in Chapter 1.3.2, with different kinds of linkages between the monomers (**Figure 4**).

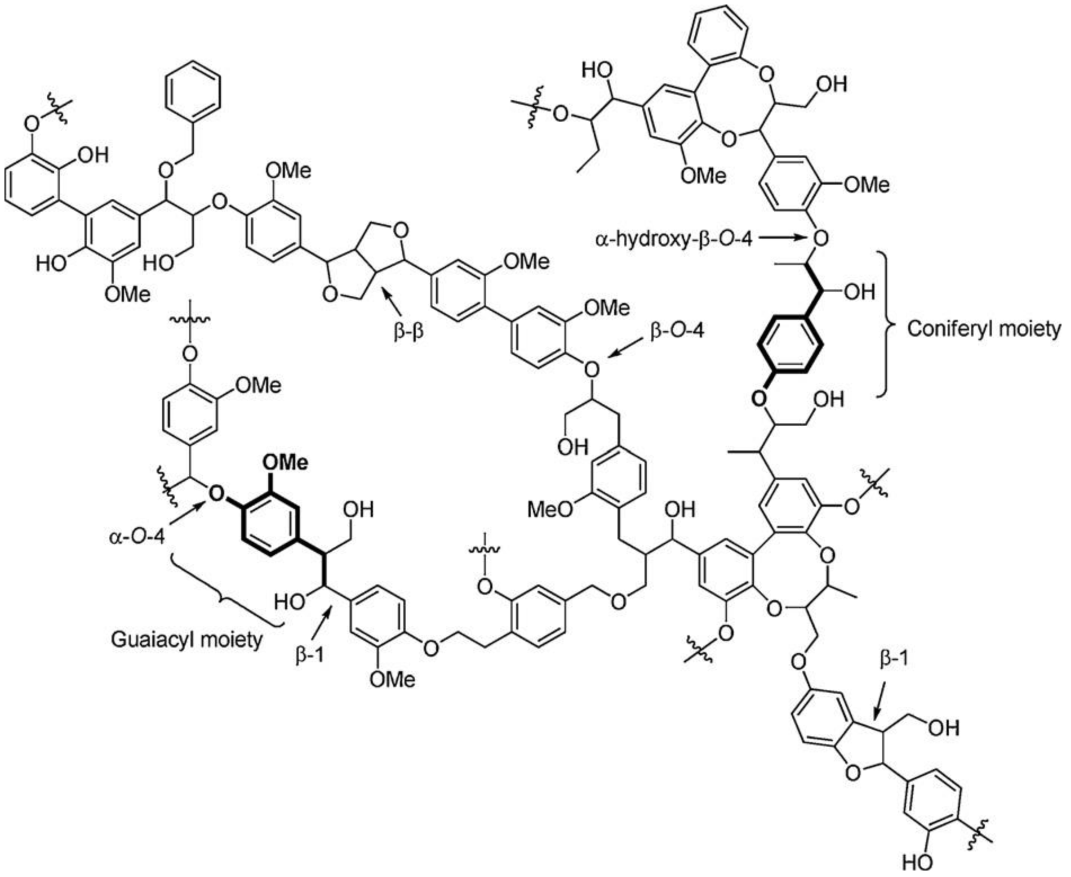


Figure 4: *A possible structure of a lignin structure, courtesy of Holmelid, B.*[11]

The proportion of each of the monomeric units varies between each lignin sample, and is partly based on the origin of the lignin. Azadi, P. et. al. reported the amount of the three monomeric units found in lignin based on softwood, hardwood and grasses shown in the table below[12]:

Table 1: *Conent of the three primary monomeric units of lignin in lignocellulosic biomass[12]:*

Source	Lignin [wt%]	Monomeric unit [%]		
		Coumaryl alcohol	Coniferyl alcohol	Sinapyl alcohol
Softwood	27 – 33	-	90 – 95	5 – 10
Hardwood	18 – 25	-	50	50
Grasses	17 – 24	5	75	25

Lignin is a side product during the pulping process of the paper industry, and also of the bioethanol production, which is increasing rapidly.[13] Most of the lignin waste is burned to generate energy in the production plants,[14] however, as lignin is the only natural polymer with an aromatic backbone,[7] the possibilities of utilizing this as a source of aromatics in a number of synthetic routes seems promising. There is a lot of ongoing research addressing the utilization of lignin for production of both fuels and needed chemicals.[1-2, 15]

1.2.1.4 Utilization of Lignin

Borregaard has been using lignin for production of 4-hydroxy-3-methoxybenzaldehyde (vanillin) for a long time.[16] This is based on timber as feedstock, and uses sulfite pulping, which is a pulping process where the biomass is treated with an acid and further with $\mathrm{HSO_3^-}$ to produce a lignosulfonate.[7] This lignosulfonate is then processed further to obtain vanillin.[16-17] Based on 1000 kg of timber, Borregaard is able to produce 3 kg of vanillin, while the remaining parts become other products,[7] as shown in **Figure 5**.

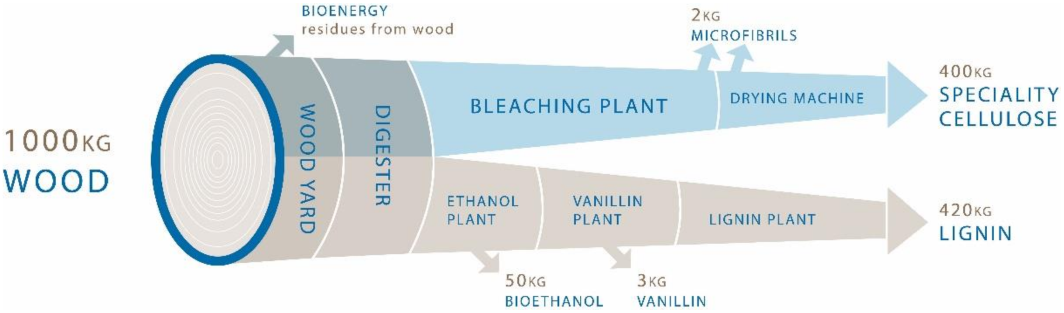


Figure 5: *Products based on 1000 kg of timber by Borregaard. Courtesy and copyright, Borregaard AS[18]*

Alternative uses of lignin include utilization towards biofuels[4, 15] and biobased plastic by several routes and towards several types of polymers. A lot of these routes go via vanillin, referring to the product that is produced at Borregaard.[19] Vanillin is also the building block for several other fine chemicals, such as pharmaceuticals, including papaverine, which is used for the treatment of heart problems, and $_{\text{L}}$-Dopa, which is used as a treatment for Parkinson's Disease, as well as in fragrances and flavors.[20]

One of the routes using lignin to produce a biobased polymer is published by Mialon et. al., who published a method of producing 4-2(-hydroxyethoxy)-3-methoxybenzoic acid from 4-hydroxy-3-methoxybenzoic acid (vanillic acid), in which the vanillic acid is reacted with 2-chloroethanol in a Williamson ether synthesis[21-22] as described in Chapter 1.4. From this product, a polymerization is described in the same article, producing poly[4-(2-hydroxyethoxy)-3-methoxybenzoic acid].[21]

1.3 Plastic and Polymers

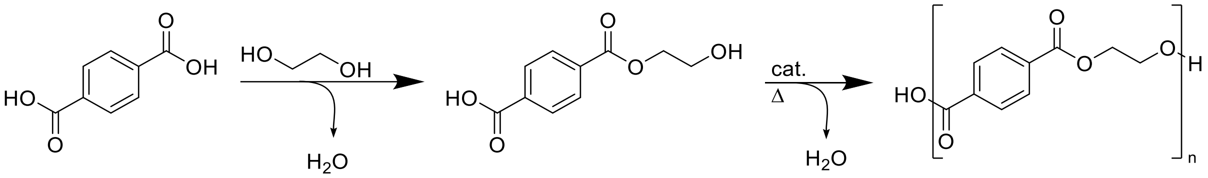
Plastic has a number of uses in our everyday lives, from containing our food and beverages to water pipes and furniture, and is also widely used industrially. The list is long, which makes it necessary to have different properties to the plastic; a food container needs to be strong and usable after being put into a microwave to heat the food, while the safety features of a motorcycle helmet can also be produced from plastic[23]. The plastic film in our kitchens should be elastic and sticky, while plastic bags should carry the weights of our items without stretching. Some of these property changes are small enough that they can be adjusted by additives to the plastic, while others are larger and need the plastic to be produced by a different substance.[24]

IUPAC defines plastic as such: "Generic term used in the case of polymeric material that may contain other substances to improve performance and/or reduce costs.

Note 1: The use of this term instead of polymer is a source of confusion and thus is not recommended.

Note 2: This term is used in polymer engineering for materials often compounded that can be processed by flow."[8]

This definition says that a plastic is a polymer, often also containing additives to adjust to the desired properties, such as the ones mentioned above. One of the most common types of plastic is poly(ethylene terephthalate) (PET).[25] Among others, this material is used in food containers, drinking bottles, shopping bags and clothing, which is commonly named polyester.[7] This is currently made from ethane-1,2-diol (ethylene glycol) and 1,4-benzenedicarboxylic acid (terephthalic acid), as shown in **Scheme 1**. The reaction can also be done as a one-pot procedure, by adjusting the temperature and pressure during the reaction.[24]



Scheme 1: *Reaction between terephthalic acid and ethylene glycol, producing the monomeric unit of 2-hydroxyethyl terephthalate and further polymerization to PET*

Terephthalic acid is a product derived from the petroleum industry, while ethylene glycol can be made either from oil or from biomass.[5-6] As a result of this PET is, at least partially, derived from petroleum, however some companies focus on using plastic that is partly from biomass. Coca-Cola Company is one example of this as they use what they call "PlantBottle", which is regular PET, in which the ethylene glycol is derived from sugarcane and waste from the sugarcane production process.[26-27] There is also a lot of research done regarding the production of fully biobased plastics.[19, 28-29]

1.3.1 Amount of Plastic Produced Today and a Future Perspective

As plastic is used for a huge variety of areas, the amount used is also large. **Figure 6** shows a steady growth in the production of plastic, which has tripled from 1989 to 2013. Note that the x-axis is not a linear increase of time as it increases quickly from 1950 to 2008, and then by one year for each step further on.

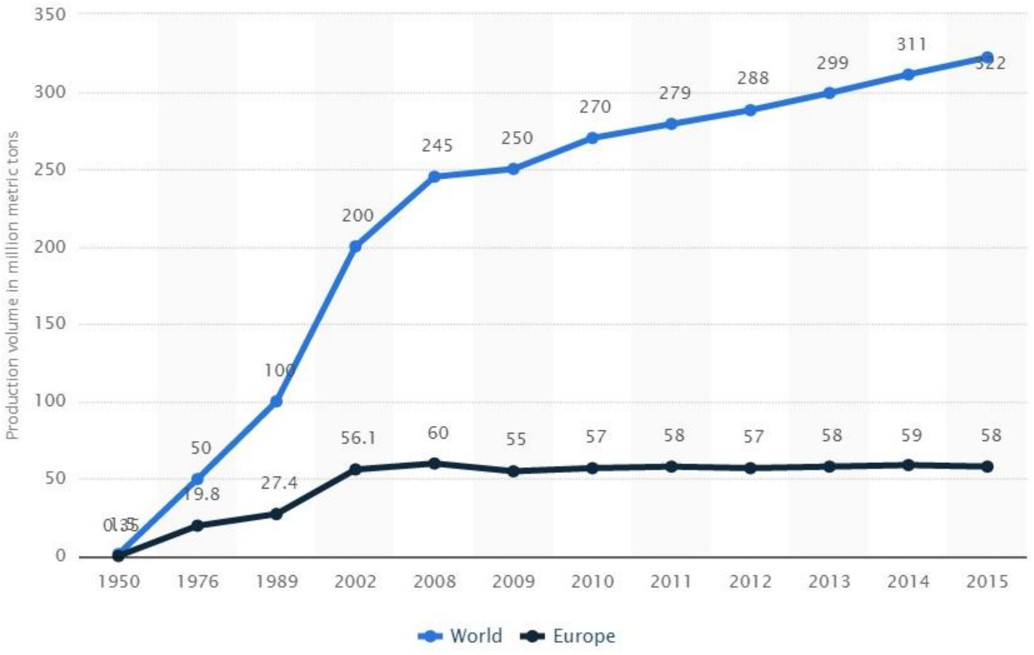


Figure 6: *Global plastic production from 1950 to 2015. Retrieved from Statista* [30]

By comparing the plastic consumption in industrialized countries to developing countries, as seen in **Figure 7**, a large difference is seen. A comparison between Western Europe, the Middle East and Africa shows numbers in two different ranges. Note the world total being quite low, which is due to the influence of the developing countries. It is natural to assume continued growth as more developing countries become industrialized, as is also indicated by the relative growth in e.g. Asia (excluding Japan) from 1980 to 2015. Some reduction in the industrialized countries might be expected as a reduced consumption of plastic is in focus, and as more plastic is being reused, however the expected increase from developing countries is expected to be larger than the reduction from the industrialized countries, and thus the total plastic consumption is expected to increase with time.

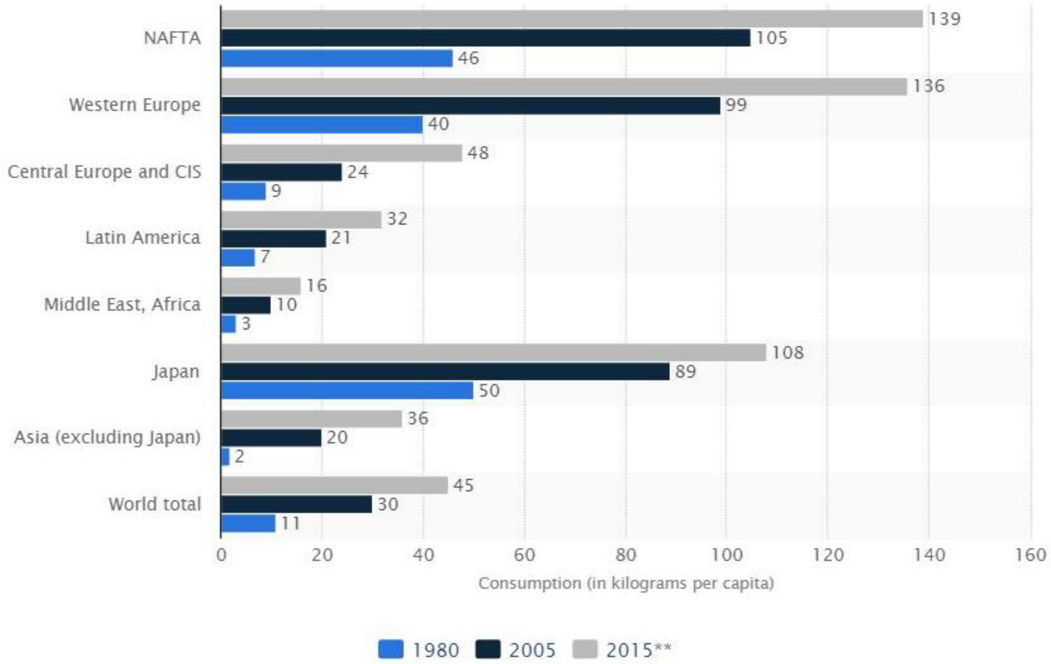
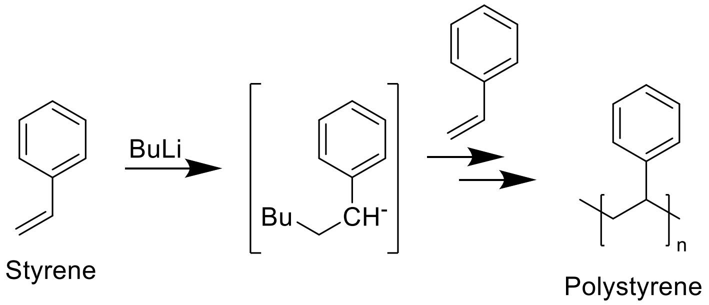


Figure 7: *Global consumtion of plastic materials by region 1980 to 2015. Retrieved from Statista.*[31] *Numbers from 2015 (in grey) are projected numbers.*

1.3.2 Polymers and Polymerization Reactions

A polymerization is a reaction in which one or several monomers react to form a long chain called a polymer. The word “polymer” has a Greek origin and translates to “many members”, referring to the monomer units.[25] By looking at the definition of a monomer, IUPAC refers to monomer molecules, which has this definition: “A molecule which can undergo polymerization, thereby contributing constitutional units to the essential structure of a macromolecule”.[32]

Polymerizations can be divided into two categories of reactions: Step-growth polymerization and chain-growth polymerization.[25] The chain-growth polymers are formed by a chain-reaction polymerization, in which every step of the polymerization adds one more monomer unit to the product. To start this polymerization is a two-step reaction, where the first step initiates the second step, in which a monomer adds to another monomeric unit, which can then react with a third one, and so on.[25, 33] An example of this is given in **Scheme 2**, where ethenylbenzene (styrene) is polymerized into polystyrene. This polymerization is initiated by buthyllithium, which produces the intermediate that can react with another monomer, producing an oligomer which again will become an intermediate that can be reacted with a new monomer, and so on.[33]



Scheme 2: An example of chain-growth polymerization in the production of polystyrene[33]

In the step-growth polymerization on the other hand, any oligomer, polymer or monomer is able to react with each other unit at any time. It is either done by using two monomers with different functional groups, or by using one single monomer with two different functional groups.[25, 33] An example of this is shown in **Scheme 1** in Chapter 1.3, where PET is produced from the monomeric unit, containing both an alcohol and a carboxylic acid. Both PET and the polymers produced in this thesis are straight chained polymers, often called linear polymers, polymerized by step-growth polymerization, and they both have an aromatic and an aliphatic part to the repeating unit.[34]

Some polymers, such as the lignin or hemicellulose mentioned in Chapter 1.2, can be branched due to several locations on the monomer in which the reaction can take place, while others, like the cellulose mentioned in Chapter 1.2 is a linear polymer.[34] Lignin and hemicellulose are also examples of what is called a copolymer. This is a polymer based on several monomers, where the monomers are placed randomly within the polymer.[34]

1.3.3 Analysis and Properties of Polymers

Important features of a polymer include the degree of polymerization (IUPAC: "The number of monomeric units in a macromolecule, an oligomer molecule, a block, or a chain"[32]), which is found by the average molecular weight, $\overline{\mathrm{Mw}}$.[25] It also includes the temperature of melting, T_m, and the glass transition temperature, T_g, which is a temperature in which polymers change their behavior from being hard, below this temperature, to soft and elastomeric (IUPAC: "Polymer that displays rubber-like elasticity"[35]) above this temperature.[24-25]

Some common analytical methods for polymers are Gel Permeation Chromatography (GPC), which is a type of Size Exclusion Chromatography (SEC) and Differential Scanning Calorimetry (DSC).[25] GPC is a chromatographic method that separates the analytes based on physical size, and by this it is possible to find an average molecular weight, $\overline{\mathrm{Mw}}$, of the polymer.[24] DSC finds the thermal properties of the polymer, thus the T_g and the T_m, as well as the enthalpy of melting, ΔH_m.[25] Based on the results of the DSC, it is possible to find an estimate of the average molecular weight by a model based on experiments with known average molecular weights. This is done by Fodor, C. but is at the time still not published.[36]

IR spectroscopy is also used to provide some information regarding the polymer. First, as the polymer increases in size, the end groups of a carboxylic acid and an alcohol decrease in intensity due to the decreasing portion in the polymer structure. The lower the contribution of the carboxylic acid and alcohol is, the higher the grade of polymerization have become. However, no literature has been found regarding the detection level of the end groups compared to the degree of polymerization. As the monomer is a carboxylic acid, but becomes an ester in the polymer, an increase is expected in the wavelength of the carbonyl peak for the polymer.[37-38]
IR might also give some indications regarding the crystallinity of the polymer. Chen, J. et. al. found a change in the placement and width of the carbonyl peak of PET in its amorphous state and its crystalline state where the amorphous state had a wider absorption band at a higher wavelength than for the crystalline state.[39-40]

Given two compounds of identical polarity, but of different molecular weight, the smallest compound is in general easier soluble.[41] A polymer should thus have a poor solubility, decreasing as the degree of polymerization increases.

Diffusion-Ordered Spectroscopy – Nuclear Magnetic Resonance (DOSY–NMR) might be used to find an estimate of the average molecular weight by looking at the diffusion coefficient and inserting this to a standard curve. The standard curve used for this thesis is made by Guo, X., and is based on polystyrene and poly(methyl methacrylate), with standards used from below 10^3 g/mol to above 10^5 g/mol.[42]

1.4 Reactions in this Thesis

Two reactions are central in this thesis. The first one is the preparation of 4-(2-hydroxyethoxy)-3-methoxybenzoic acid from vanillic acid, which follows a Williamson ether synthesis.[22] The second one is the polymerization reaction, in which the hydroxy group of one monomeric molecule reacts with the carboxylic acid of another monomeric molecule to produce an ester. These reactions are described in further detail below.

The two building blocks of these reactions are vanillic acid, which is the carboxylic acid of the vanillin aldehyde, produced by Borregaard from lignin[16-17], and 2-chloroethanol, that can be produced from ethylene glycol,[43] which, as mentioned in Chapter 1.3, can be derived from biomass, as used by Coca-Cola Company.[5, 26]

1.4.1 Williamson Ether Synthesis

A Williamson ether synthesis is a method of producing an ether from an alcohol, where the alcohol first reacts with a base to produce an alkoxide ion, which further reacts with an alkyl halide to produce the desired ether.[22] This reaction is done in the monomer synthesis part of the thesis, and a reaction scheme of these is shown in **Scheme 3**. This happens by the following reaction[22]:

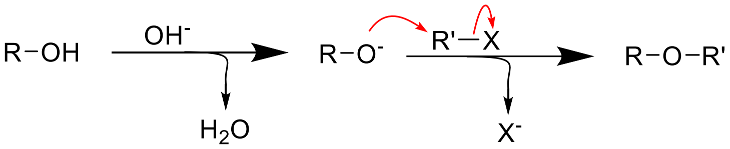


Figure 8: *General mechanism of Williamson ether synthesis as described by McMurry, J.* [22]

1.4.2 Polymerization

The polymerization done in this thesis is a step-growth polymerization, where any monomer, oligomer or polymer can react with any other monomer, oligomer or polymer to increase the degree of polymerization, as explained in Chapter 1.3.2. The hydroxy-group of one monomer, oligomer or polymer reacts with the carboxylic acid of another, and a polyester is formed, as shown in **Scheme 4**. The reaction between an alcohol and a carboxylic acid is commonly done with a Brønsted acid functioning as a catalyst.[33] However, in this polymerization Sb_2O_3 is used as a catalyst. This catalyst is also used in the synthesis of PET.[24] The mechanism for the catalysis in the reaction has not been studied as part of this thesis.

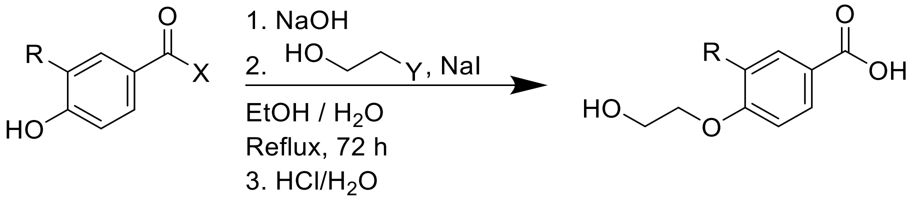
2 Objective

The reaction done by Mialon et. al.[21] described in Chapter 1.2.1.4 provides the foundation of this thesis. The reactions aim at developing a biobased polymer with similar properties to PET. Industrial quality PET has a T_g of 69 °C and a T_m of 280 °C,[24] and the target for the product produced in this thesis is thus to get close to these values.

The thesis adopts and adjusts the methods mentioned above, and addresses topics regarding the efficiency compared to the quality of the product, while keeping the synthesis itself as environmentally friendly as possible. The product of the polymerization is divided into several fractions based on solubility, which are analysed individually to provide the best possible knowledge of the product, and the polymerization is adjusted according to these findings. The main focus areas of this thesis are the following:

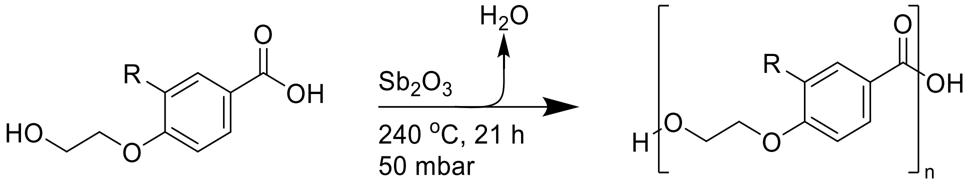
- Adjusting experimental variables as necessary to achieve high synthesis yields of the monomer. Variables that are adjusted include the reaction time, ratio between the reagents, solvent ratio and starting materials.
- Adjusting variables in the polymerization as necessary to increase the degree of polymerization. Variables that are adjusted include the temperature, scale and method of the polymerization itself, which primarily changes the efficiency of the stirring.
- Keeping a biobased route of both synthetic routes.
- Performing thorough analysis of the products from both reactions, using NMR, MS, IR and melting point analysis for the monomers and IR, DSC and NMR for the polymers.
- Performing thorough elucidation of the monomer, using ^{1}H-, ^{13}C-, COSY-, HSQC- and HMBC-NMR, and comparing the result with previous analyses.

3 Reaction Schemes



***Scheme 3**: Synthesis of 4-(2-hydroxyethoxy)-3-methoxybenzoic acid (R = OMe) or 4-(2-hydroxyethoxy)-benzoic acid (R = H) using 2-chloroethanol (Y = Cl) or 2-bromoethanol (Y = Br)* [a] *from vanillic acid (R = OMe, X = OH), 4-hydroxybenzoic acid (R = H, X = OH) or methyl 4-hydroxybenzoate (R = H, X = OMe)*

[a] NaI is not used when Y = Br



***Scheme 4:** Polymerization of poly[4-(2-hydroxyethoxy)-3-methoxybenzoic acid] (R = OMe) or poly[4-(2-hydroxyethoxy)-benzoic acid] (R = H) from 4-(2-hydroxyethoxy)-3-methoxybenzoic acid (R = OMe) or 4-(2-hydroxyethoxy)-benzoic acid (R = H)*

4 Experimental

The experimental part is divided into three sections: Step one and two of the synthesis (monomer synthesis and polymerization), and specifications of the analytical instruments that are used. All chemicals used during the experiments was bought from Sigma Aldrich and used without further purification unless otherwise specified.

4.1 Monomer Synthesis

This chapter will describe the experimental part of the final method, and any changes will be specified below. A flowchart of the general procedure is shown in **Figure 9**.

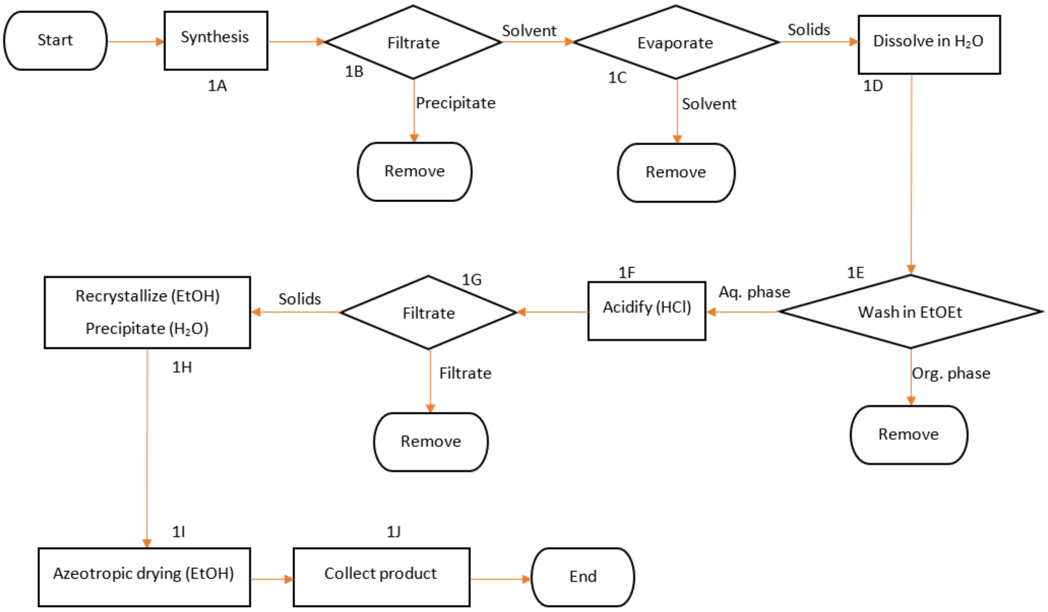


Figure 9: *Flowchart of monomer synthesis including workup*

NaOH (4 eq.) and NaI (0.25 eq) were added to water (40 mL) in a round bottomed flask. Vanillic acid (0.089 mol) was added portion wise to this solution. The reactor was covered with aluminum foil, and a nitrogen atmosphere was applied. A solution of 2-chloroethanol (1.5 eq.) in ethanol (50 mL) was added slowly (20 min. addition time) before the reaction mixture was heated and refluxed for 72 hours. The reaction mixture was cooled to room temperature and filtrated by vacuum filtration before the solvent was removed by rotary evaporator (30 mbar, 50 °C). The remaining solids were dissolved in water (approx. 250 mL) and washed with diethyl ether (3 x 200 mL). The aqueous phase was acidified with HCl (3 M) until precipitation (pH ≈ 4), and filtered by vacuum filtration. The dried solids were recrystallized by dissolving in absolute ethanol (approx. 100 mL) and precipitating with water (approx.

500 mL), and filtered using vacuum filtration. An azeotropic drying was done by dissolving the product in absolute ethanol which was then removed with remaining water in a rotary evaporator (40 mbar, 50 °C) to obtain the purified product.

4.1.1 Starting with Vanillic Acid, Preliminary Runs

The quantitative description of experiments 1 and 2 is given in **Table 2**. Products of experiments 1 and 2 were analysed by melting point analysis, IR, ^{1}H-NMR and ^{13}C-NMR.

Table 2: *Quantitative description of experiments 1 and 2:*

Expt #	Chemical	m [g]	V [mL]	n [mol]	Yield [%]
1	Vanillic acid	79.97	-	0.48	-
	NaOH	80.78	-	2.0	-
	NaI	14.90	-	0.10	-
	Water	-	100	-	-
	2-chloroethanol	50.04	-	0.62	-
	Ethanol	-	200	-	-
	4-(2-hydroxyethoxy)-3-methoxybenzoic acid	1.517	-	0.0071	1.5
2	Vanillic acid	12.12	-	0.072	-
	NaOH	12.80	-	0.32	-
	NaI	2.275	-	0.015	-
	Water	-	15	-	-
	2-chloroethanol	8.160	-	0.10	-
	Ethanol	-	30	-	-
	4-(2-hydroxyethoxy)-3-methoxybenzoic acid	0.575	-	0.0027	3.8

4.1.1.1 Variations from the Procedure

Experiments 1 and 2 used vanillic acid as a starting material. The work was done as described by Mialon et. al.[21]. Compared to the procedure given in Chapter 4.1, the reflux in these experiments was set to 24 hours instead of the given 72 hours. The solution of 2-chloroethanol in ethanol was added to the reaction mixture after heating the reaction mixture to reflux. No filtration was done to remove the salts that had precipitated during the reaction (process 1B in **Figure 9**). The final drying of these products was done by air drying instead of azeotropic drying.

The relative amounts of the chemicals were different from the ones described above as there were a lot more of the solids compared to the solvents, and the ratio between water and ethanol was 1:2 instead of 4:5 which is used in the final runs. In addition, the amount of 2-chloroethanol was 1.25 eq. instead of 1.5 eq.

4.1.2 Starting with 4-hydroxybenzoic Acid

The quantitative description of experiments 3 and 4 is given in **Table 3**.

During experiment 4, samples were taken for TLC. In addition, the filtrate after the acidification (the filtrate from process 1G in **Figure 9**) was evaporated and analysed by ^{1}H-NMR. This sample is referred to as Sample 4.10. The crude product (see **Figure 9**, solids after process 1G) was analysed by ^{1}H-NMR, Compensated Attached Proton Test (CAPT)-NMR, Correlation Spectroscopy (COSY)-NMR, Heteronuclear Single-Quantum Correlation (HSQC)-NMR and Heteronuclear Multiple-Bond Correlation (HMBC)-NMR. The products of both experiments were analysed by melting point analysis, IR, ^{1}H-NMR and ^{13}C-NMR. The product of experiment 3 were also analysed by Gas Chromatography – Flame Ionization Detector (GC-FID). The product of experiment 4 was analysed by Gas Chromatography – Mass Spectrometry (GC-MS) and Direct Analysis in Real Time – Mass Spectrometry (DART-MS).

Table 3: *Quantitative description of experiments 3 and 4:*

Expt #	Chemical	m [g]	V [mL]	n [mol]	Yield [%]
3	4-hydroxybenzoic acid	12.23	-	0.089	-
	NaOH	14.23	-	0.36	-
	NaI	3.273	-	0.022	-
	Water	-	30	-	-
	2-chloroethanol	9.008	7.5	0.11	-
	Ethanol	-	40	-	-
	4-(2-hydroxyethoxy)-benzoic acid	2.878	-	0.014	15.3
4	4-hydroxybenzoic acid	12.36	-	0.090	-
	NaOH	14.40	-	0.36	-
	NaI	3.443	-	0.023	-
	Water	-	30	-	-
	2-chloroethanol	9.008	7.5	0.11	-
	Ethanol	-	40	-	-
	4-(2-hydroxyethoxy)-benzoic acid	1.694	-	0.0093	10.4

4.1.2.1 Variations from the Procedure

Experiments 3 and 4 were done as described in Chapter 4.1, using 4-hydroxybenzoic acid as a starting material. The amount of 2-chloroethanol was set to 1.25 eq. instead of 1.5 eq. as described above.

4.1.3 Starting with Methyl 4-hydroxybenzoate

The quantitative description of experiments 5 and 6 is given in **Table 4**. The products of both experiments were analysed by melting point analysis, IR, ^{1}H-NMR, ^{13}C-NMR and DART-MS.

***Table 4:** Quantitative description of experiments 5 and 6:*

Expt #	Chemical	m [g]	V [mL]	n [mol]	Yield [%]
5	Methyl 4-hydroxybenzoate	13.68	-	0.090	-
	NaOH	14.40	-	0.36	-
	NaI	5.204	-	0.035	-
	Water	-	40	-	-
	2-chloroethanol	10.81	9.0	0.13	-
	Ethanol	-	45	-	-
	4-(2-hydroxyethoxy)-benzoic acid	8.138	-	0.045	49.7
6	Methyl 4-hydroxybenzoate	5.677	-	0.037	-
	NaOH	6.039	-	0.15	-
	Water	-	13	-	-
	2-bromoethanol	7.052	4.0	0.056	-
	Ethanol	-	15	-	-
	4-(2-hydroxyethoxy)-benzoic acid	2.600	-	0.014	38.2

4.1.3.1 Variations from the Procedure

Experiments 5 and 6 were done as described in Chapter 4.1, using methyl 4-hydroxybenzoate as a starting material. In experiment 6, 2-bromoethanol was used instead of the combination of 2-chloroethanol and NaI.

4.1.4 Starting with Vanillic Acid, Final Run

The quantitative description of experiment 10 is given in **Table 5**. Experiment 10 was done as described in Chapter 4.1, using vanillic acid as a starting material. The product of this experiment was analysed by melting point analysis, IR, ^{1}H-NMR, ^{13}C-NMR, COSY-NMR, HSQC-NMR, HMBC-NMR and DART-MS.

***Table 5:** Quantitative description of experiment 10:*

Expt #	Chemical	m [g]	V [mL]	n [mol]	Yield [%]
10	Vanillic acid	15.04	-	0.089	-
	NaOH	14.30	-	0.36	-
	NaI	3.464	-	0.023	-
	Water	-	40	-	-
	2-chloroethanol	10.81	9.0	0.13	-
	Ethanol	-	50	-	-
	4-(2-hydroxyethoxy)-3-methoxybenzoic acid	9.620	-	0.045	50.7

4.2 Polymerization

This chapter describes two procedures of step two of the synthesis, the polymerization. Which method used for each experiment will be specified below. A flowchart of the processes is shown in **Figure 10**. For both methods, all filtrations are done by vacuum filtration, first on a Büchner funnel, then vacuum filtrating again on a glass filter paper with a pore size of 1.2 µm.

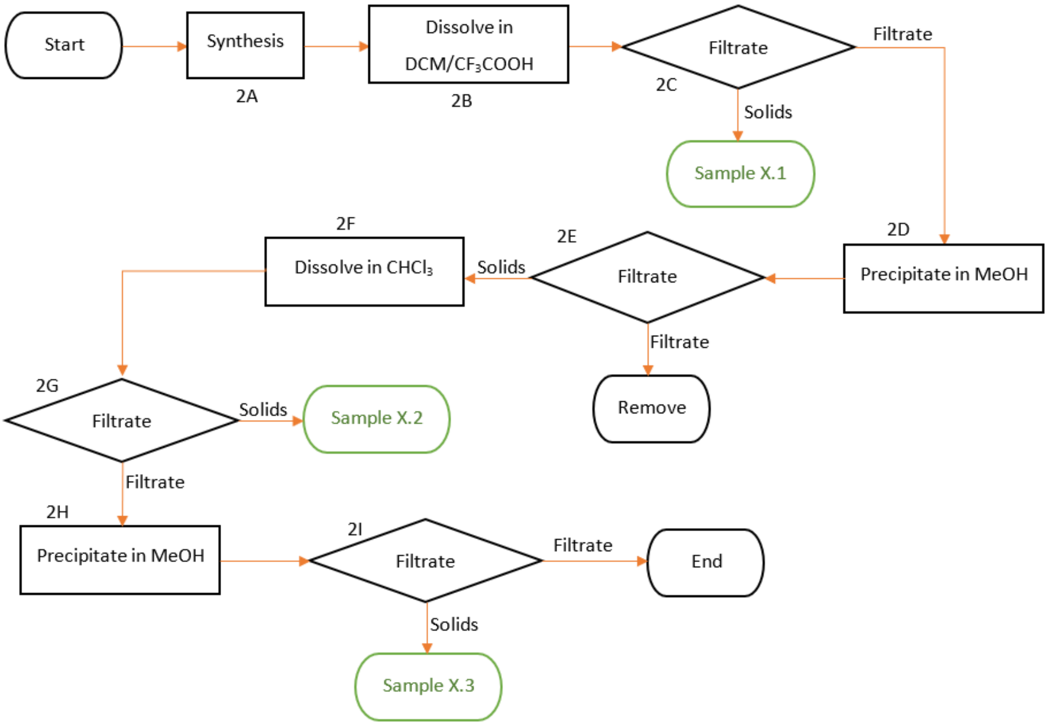


Figure 10: *Flowchart of polymerizations, including workup*

4.2.1 Method 1

4-(2-hydroxyethoxy)-3-methoxybenzoic acid (0.012 mol), Sb_2O_3 (0.03 eq.) and tetrahydrofurane (THF) (5 mL) were added to a 250 mL round bottomed flask and the mixture was stirred until homogenization. The solvent was removed by nitrogen and heat, and the reaction mixture was heated under a nitrogen atmosphere until melting (210 °C) under continuous stirring. This temperature was kept for 1 hour before the pressure was carefully reduced to 100 mbar and the temperature was increased to 240 °C. The pressure was further reduced to 50 mbar and the reaction was left overnight (21 hours). After cooling to room temperature, the product was dissolved in CF_3COOH/dichloromethane (DCM) (1/1, V/V) (approx. 100 mL used). The mixture was filtered and the solids were saved as sample X.1 (in which X is the experiment number) (product, not dissolved in DCM/CF_3COOH). The remaining mixture was precipitated in methanol and filtered, and the precipitates were dissolved in $CHCl_3$. The mixture was filtered and the precipitates were saved as sample X.2 (product, dissolved in CF_3COOH/DCM, not dissolved in $CHCl_3$). The remaining mixture was precipitated in methanol and filtered, where the precipitates were saved as sample X.3 (product, dissolved in $CHCl_3$, precipitated in MeOH).

4.2.2 Method 2

4-(2-hydroxyethoxy)-3-methoxybenzoic acid (0.012 mol), Sb_2O_3 (0.03 eq.) and THF (5 mL) were added to a 250 mL round bottomed flask which was then connected to a rotary evaporator. The setup was flushed with nitrogen through the pressure outlet valve, and the mixture was stirred by a combination of a magnetic stirrer and the rotation of the rotary evaporator to obtain homogenization. The solvent was evaporated by temperature and a slightly reduced pressure. The mixture was heated until melting (210 ^{o}C), while vigorous stirring was done, still by means of the rotary evaporator in combination with the magnetic stirrer. When the reaction mixture had melted, the temperature was kept for 1 hour before the pressure was carefully reduced to 100 mbar and the temperature was increased to 240 ^{o}C. The pressure was further reduced to 50 mbar and the reaction was left overnight (21 hours). The workup was done as described in Chapter 4.2.1.

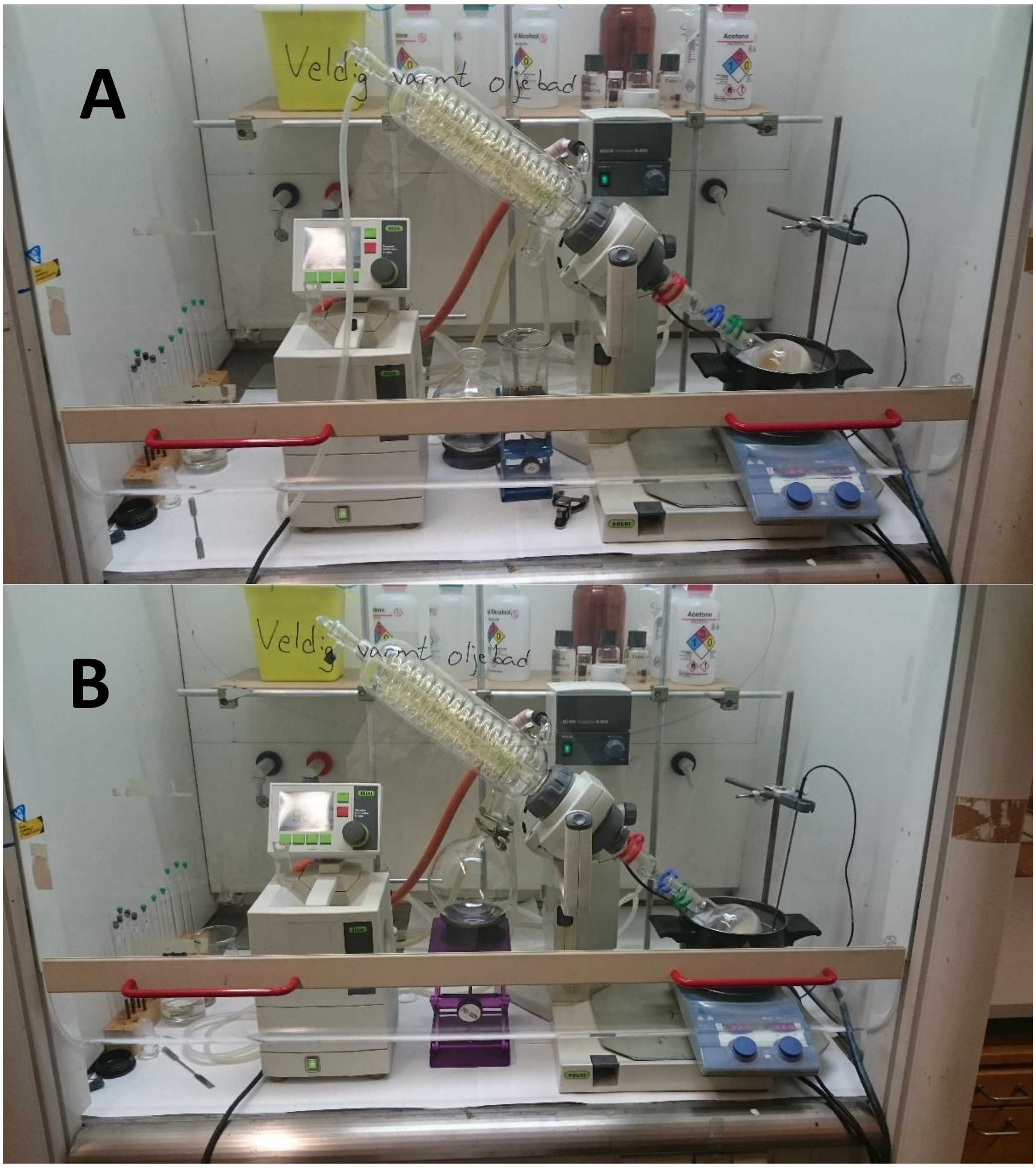


Figure 11: ***A****: The system being flushed with nitrogen through the vacuum outlet valve prior to the reaction in the rotary evaporator.* ***B****: The reaction taking place in the rotary evaporator*

4.2.3 Starting with 4-(2-hydroxyethoxy)-benzoic Acid

The quantitative description of experiments 7 – 9 is given in **Table 6**. The products of all experiments were analysed by IR, DSC and GPC. For experiment 7, ^{1}H-NMR was done as well. For experiment 9, solid-phase NMR (^{13}C-NMR) and elemental analysis were done. The carbonyl-peak of all IR-spectra were compared.

Table 6: *Quantitative description of experiments 7, 8 and 9:*

Expt #	Chemical	m [g]	n [mmol]	Yield [%]
7	4-(2-hydroxyethoxy)-benzoic acid	0.477	2.6	-
	Sb_2O_3	0.0227	0.078	-
	Poly[4-(2-hydroxyethoxy)-benzoic acid)	0.307	-	71.4
8	4-(2-hydroxyethoxy)-benzoic acid	0.513	2.8	-
	Sb_2O_3	0.0230	0.079	-
	Poly[4-(2-hydroxyethoxy)-benzoic acid)	0.355	-	76.7
9	4-(2-hydroxyethoxy)-benzoic acid	2.52	14	-
	Sb_2O_3	0.145	0.50	-
	Poly[4-(2-hydroxyethoxy)-benzoic acid)	2.23	-	98.1

4.2.3.1 Variations from the Procedure

Experiments 7, 8 and 9 were using 4-(2-hydroxyethoxy)-benzoic acid, taken from the product of experiment 5 using the first method described above. The reaction mixtures were melted at an oil bath temperature of 185 °C. Experiment 7 was done at a polymerization temperature of 215 °C instead of 240 °C, and the reaction time was 18 hours instead of 21 hours. Experiments 7 and 8 were done in a 25 mL round bottomed flask. No filtrations were done to retrieve samples X.1.

4.2.4 Starting with 4-(2-hydroxyethoxy)-3-methoxybenzoic Acid

The quantitative description of experiments 11 – 14 is given in **Table 7**. The products of all experiments were analysed by IR and DSC. Samples 12.3 was not analysed due to low amounts. Samples 13.3 and 14.1 were not analysed by DSC. The carbonyl-peaks of all IR-spectra were compared. Samples 11.1 – 11.3 were analysed by DART-MS.

Table 7: *Quantitative description of experiments 11 – 14:*

Expt #	Chemical	m [g]	n [mmol]	Yield [%]
11	4-(2-hydroxyethoxy)-3-methoxybenzoic acid	2.53	12	-
	Sb_2O_3	0.111	0.38	-
	Poly[4-(2-hydroxyethoxy)-3-methoxybenzoic acid)	2.22	-	96.0
12	4-(2-hydroxyethoxy)-3-methoxybenzoic acid	2.57	12	-
	Sb_2O_3	0.124	0.43	-
	Poly[4-(2-hydroxyethoxy)-3-methoxybenzoic acid)	2.29	-	97.7
13	4-(2-hydroxyethoxy)-3-methoxybenzoic acid	2.61	12	-
	Sb_2O_3	0.111	0.38	-
	Poly[4-(2-hydroxyethoxy)-3-methoxybenzoic acid)	2.51	-	105
14	4-(2-hydroxyethoxy)-3-methoxybenzoic acid	1.53	7.2	-
	Sb_2O_3	0.0652	0.22	-
	Poly[4-(2-hydroxyethoxy)-3-methoxybenzoic acid)	1.36	-	97.0

4.2.4.1 Variations from the Procedure

Experiments 11 – 14 were using 4-(2-hydroxyethoxy)-3-methoxybenzoic acid from experiment 10 as a starting material. Experiment 11 was done as described in the first method above, while experiments 12 – 14 were done as described in the second method. Experiment 14 is equal to experiments 12 and 13, but in a smaller scale (1.5 g of monomer compared to 2.5 g used in the previous experiments).
Samples 13.3 and 14.1 were analysed on glass filter paper and filter paper, respectively. IR was also taken of glass filter paper and filter paper, and these were subtracted from the original spectra of samples 13.3 and 14.1. The original spectra, together with the spectra of the filter papers are included in appendix E.

4.3 Analytical Specifications

4.3.1 NMR

The instrument used for taking NMR was a 500 MHz Bruker Biospin AV500WB superconductive magnet with a Bruker Broadband Observe (BBO) probehead. Wilmad 528 5 mm NMR-tubes were used. To obtain the spectra, a standard analysis was taken with IconNMR. The spectra were recorded at 298 K. For ^{13}C-NMR, the spectral width is 238.7687 ppm with center at 99.996 ppm. For ^{1}H-NMR, the spectral width is 20.6557 ppm with center at 6.175 ppm.
The software used was TopSpin 3.5 pl7. In this software, calibrations for ^{1}H-NMR was done by the acetone d_6-peak, set to 2.05 ppm. At ^{13}C-NMR the CH_3-peak from acetone d_6 was set to 29.92 ppm. These values are found at Cambridge Isotope Laboratories, Inc.[44]. Baseline corrections have been done for accurate integrals.

The solid phase experiment was performed using a Bruker AVIII magnet operating at 500 MHz for protons. The ^{13}C CP-MAS spectrum was recorded at 298 K and a MAS spinning rate of 14 kHz., crosspolarization time of 4350 ms and a number of free induction decays of 23000.[45] No axis calibrations were done for this analysis. The analysis was performed by Willy Nerdal and Olav-Audun Bjørkelund at UiB.

The molecular weight was estimated using Diffusion Ordered NMR Spectroscopy (DOSY) using a Bruker 500M Hz WB instrument equipped with a commercial probe head (diffBB). A diffusion coefficient was measured, and based on the power law curve in the published article by Guo. X et. al.[42] the molecular weight was estimated.[46] This analysis, collecting data and processing included, was performed by John Georg Seland.

4.3.2 IR

The instrument used for recording IR spectra was a Nicolet Protege 460 FTIR with a wavelength area from 4000 to 650 cm^{-1}, using a cell for DTR (solids). The spectra were taken with 32 scans and a resolution of 4000.

The software used was OMNIC 9. In this software, all peaks from CO_2 have been removed from the spectra by replacing these with a flat line.

4.3.3 DART-MS

A DART-100 ion source from IonSense Inc. (Model number DART 100, Saugus, MA, USA) was interfaced to an AccuTOF^{TM} JMS T100LC mass spectrometer from JEOL USA, Inc. (Peabody, MA, USA) that uses an orthogonal accelerated time of flight single state reflectron mass analyser and a dual micro channel plate (MCP) detector. A detailed description of the instrumental settings / conditions is as follows; The DART ion source was operated with a temperature of 220 °C and a gas flow of 2.0 L/min. The distance between the DART source exit and the cone inlet was 12 mm. The DART discharge needle voltage was set to +3000 V and a perforated electrode voltage (electrode 1) of +150 V was applied. The grid voltage was set to 250 V. The AccuTOF^{TM} mass spectrometer operated in the negative mode at a resolving power of approximately 6000 FWHM. The atmospheric pressure interface conditions were as follows; Orifice 1 = -19 V, orifice 2 = -4 V and ring lens = -11 V. The temperature of orifice 1 was kept at 120 °C. The voltage of the ion guide (peak to peak voltage) was varied between 1200 and 2500 V in order to apply transmission of ions of different *m/z* ratios. Detector voltage = 2350 V, acquisition range; 100 – 1000 *m/z*. The spectra acquisition settings applied were as follows; spectral recording interval = 0.5 s, wait time = 0.03 ns and data sampling interval = 0.5 ns. The samples were analysed as solids and introduced to the DART gas stream by a glass capillary. Internal mass calibrations were performed using a 10 ppm solution of PEG600 (polyethylene glycol average mass 600 u) in methanol recorded in the same acquisition as the chemical sample. The total ion chromatogram (TIC) was acquired for approximately 0.5 min and the data were processed by creating extracted ion chromatograms with an *m/z* interval of ±0.1 u. The mass spectrums were calibrated using the mass spectrum of PEG600 acquired during the same set of experiments.[47] All analyses were done by Bjarte Holmelid at University of Bergen.

4.3.4 Melting Point Analysis

Melting point analyses were done on a Stuart Scientific melting point apparatus SMP3 with a visual registration of melting. The heating slope were set to 1.0 °C/min and all analyses were done twice, where the average temperatures were used.

4.3.5 DSC

The instrument used for taking DSC was a Netzsch 204-F1. All analyses were done at and by Norner. Conditions: heating 30 to 230 °C / 240 °C, cooling to -30 °C, heating to 250 °C / 240 °C. Rate of heating and cooling: 20 °C/min. Test reports are found in appendix D, where further details are described.

4.3.6 GPC

The molecular weights (Mn number and Mw weight average molecular weights) and the dispersity (D) of the samples were determined by GPC using a Viscotek GPCmax, GPC column oven VE2585 and two analytical columns (PLgel 5 µm MIXED-C, 300 mm) from Agilent Technologies with a separation range from 200 to $2*10^6$ g/mol thermostatted to 35 °C in $CHCl_3$ containing 6 v/v% HexaFluorIsoPropanol (HFIP) with a flow rate of 1.0 mL/min by using a Schambeck RI2012, a refractive index detector. The molecular weight determination of the oligomer and polymer samples were based on narrow dispersity polystyrene (PSt) standards (Agilent and Polymer Laboratories) in the range of 645 to $3.0*10^6$ g/mol. For the sample preparation the purified dry samples (12 mg) were dissolved in HFIP (180 µL) and after complete dissolving dilluted with $CHCl_3$ (2.82 mL). The samples were filtered through a PTFE syringe filters (Minisart SRP 15, Sartorius stedim biotech, PTFE-membrane filter; pore size: 0.45 µm, filter diameter: 15 mm) and analysed by GPC. The collected spectra were analysed with the use of OmniSEC (v5.0) (Malvern).[36] All preparations and analyses were done by Csaba Fodor, University of Groningen.

4.3.7 GC-FID

Samples from experiment 3 were analysed by GC-FID using an Thermo Finnigan Trace GC equipped with an autosampler and a FID-detector. For each sample 1 µL were injected in splitless mode to an Agilent Technologies HP-5ms column of 30 m length, ID of 250 µm and thickness of 0.25 µm. The flow of the Helium carrier gas was 1.5 mL/min, using a constant pressure of 100 kPa. The injector temperature was set to 250 °C and the detector temperature was 330 °C. The following GC temperature program was used:

Table 8: *GC temperature program used for GC-FID:*

Starting temperature [°C]	Final temperature [°C]	Heating rate [°C/min]	Hold time [min]
30	30	-	5
30	250	10	5

4.3.8 GC-MS

Samples from experiment 4 were analysed by GC-MS using an Agilent Technologies 7890A GC-system equipped with an autosampler and an Agilent Technologies 5977A MSD (Mass Sensitive Detector). For each sample 1 µL was injected in a splitless mode to an Agilent Technologies HP-5ms column of 30 m length, ID of 250 µm and thickness of 0.25 µm. The flow of the Helium carrier gas was 1 mL/min. The injector temperature was set to 280 °C and the detector temperature was 250 °C. The following GC temperature program was used:

Table 9: *GC temperature program used for GC-MS:*

Starting temperature [°C]	Final temperature [°C]	Heating rate [°C/min]	Hold time [min]
40	40	-	5
40	280	6	-
280	300	40	5

The MS had a solvent delay of 4.60 min and operated from *m/z* 45.00 to 400.00 with a positive mode. The ion source temperature was 254 °C.

4.3.9 Elemental Analysis

The instrument used for elemental analysis was a Vario EL IIT, Elemental Analysis (micro analysis instrument) from Elementar, production year 2005. "Elemental Analyser for simultaneous C-, H-, N-, and S-analysis". The instrument is calibrated for C, H, N analysis, but not for Sulphur analysis.[48] All analyses were taken by Inger Johanne Fjellanger at UiB.

5 Results

This chapter will describe the results of the experiments given in Chapter 4, first for the monomer synthesis, and then to the polymerization. Further on, there will be a comparison of the results to the ones published by Mialon et. al.[21], and lastly the environmental friendliness of the process will be discussed.

5.1 Monomer Synthesis

Table 10 shows the reaction conditions of all monomer syntheses, together with the yield and the appearance of the product. As seen, the first two reactions had poor yield, which were improved somewhat in experiments 3 and 4. Experiments 5 and 6 were similar, but the difference between these was the 2-chloroethanol and NaI used in experiment 5, while 2-bromoethanol without the catalyst is used in experiment 6 for comparison of the yields. This gained a better yield by using 2-chloroethanol and NaI. Experiment 10 resulted in a yield of 51 %.

Table 10: *General results from monomer synthesis based on vanillic acid (R = OMe, X = OH), 4-hydroxybenzoic acid (R = H, X = OH) and methyl 4-hydroxybenzoate (R = H, X = OMe), using 2-chloroethanol (Y = Cl) or 2-bromoethanol (Y = Br):*

Expt.	Starting materials [a]			Reaction conditions			Product		
	R	X	Y	n(reactant) [mol]	Addition time (reagent) [min]	Reaction time [h]	Appearance	n(product) [mol]	Yield [%]
1	OMe	OH	Cl	0.48	n.d.	24	Off-white powder	0.00715	1.5
2	OMe	OH	Cl	0.072	n.d.	24	Off-white powder	0.00271	3.8
3	H	OH	Cl	0.089	n.d.	72	White powder	0.0136	15.3
4 [b]	H	OH	Cl	0.090	20	72	White powder	0.00930	10.4
5	H	OMe	Cl	0.090	10	72	White powder	0.0447	49.7
6	H	OMe	Br	0.037	5	72	White powder	0.0143	38.2
10	OMe	OH	Cl	0.089	20	72	White powder	0.0453	50.7

[a] See **Scheme 3**. [b] The crude product of experiment 4 showed two different colors. These were separated manually, and the following purification were done on both fractions. Both ended in a white powder.

5.1.1 Starting with Vanillic Acid, Preliminary Runs

As found in **Table 10**, experiment 1 and experiment 2, both of which started with vanillic acid and using 2-chloroethanol, yielded 1.5 % and 3.8 % respectively.

The table below shows the result of the melting point analysis of experiments 1 and 2, compared to the literature values of the monomer and the desired product. Both products started melting at a temperature in-between the two literature values, indicating an impure starting compound or a different compound altogether. The product of experiment 2 had a slightly large range of melting, also indicating an impure product. The product of experiment 1 continued melting at several stages. At 350 °C, the sample was still not completely melted, but the analysis was ended. Later analyses show that the polymer from the desired product has a melting point of around 212 – 215 °C (Chapter 5.2). These parts of the product are thus unresolved as to structure elucidation, however as no filtration was done when the reaction was finished this might be residues of salts that formed during the reaction. Due to the large range of melting, the heating rate was not set to 1 °C/min all the way to 350 °C as described in Chapter 4.3.4, but was increased stepwise.

Table 11: *Melting point analysis of experiments 1 and 2:*

	Melting start [°C]	**Melting end [°C]**
Literature value, vanillic acid [49]	208	210
Literature value, 4-(2-hydroxyethoxy)-3-methoxybenzoic acid [50]	199	200
Product expt. 1	202.6	> 350
Product expt. 2	201.4	204.0

The IR spectra (**Figure 12**) of the products from these experiments are very similar to the vanillic acid, indicating that the reaction has not taken place to the desired product. Based on later results with better indications (Chapter 5.1.4), the spectra are not as desired.

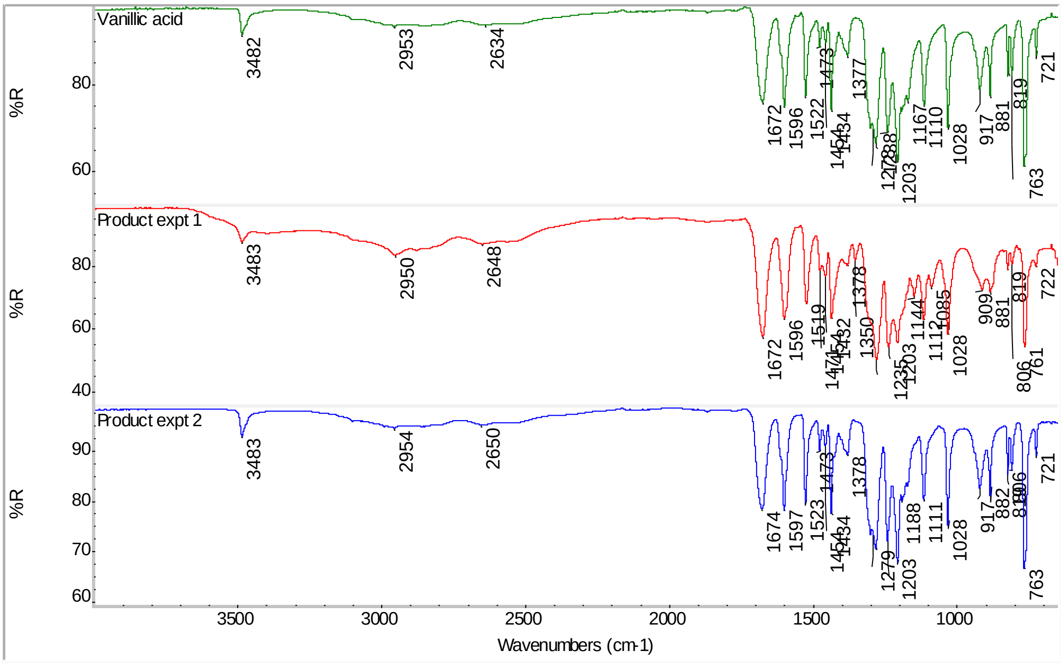


Figure 12: *IR of products of experiment 1 (red) and 2 (blue) compared to vanillic acid (green)*

Both the product of experiment 1 and 2 were only partly dissolved in acetone d_6, and the NMR spectra (**Figure 13** and **Table 12**) are thus only showing a part of the product. The remaining part could not be analysed by NMR. In the figure the products of experiment 1 (red) and 2 (blue) are seen compared to vanillic acid (green). All the peaks are very similar to the ones from vanillic acid, except for the one at 2.83 ppm from experiment 1. This is present in all the spectra, but the intensity is different. This peak shows both the proton of the hydroxy-group and of water. As the sample did not completely dissolve in the deuterated solvent, the concentration is thereby quite low, and a certain amount of water will be shown as a large peak by comparison. This is however also true of the analysis of experiment 2, as this were neither completely dissolved in acetone d_6, so the relative amount of water should be indicated by the spectra.

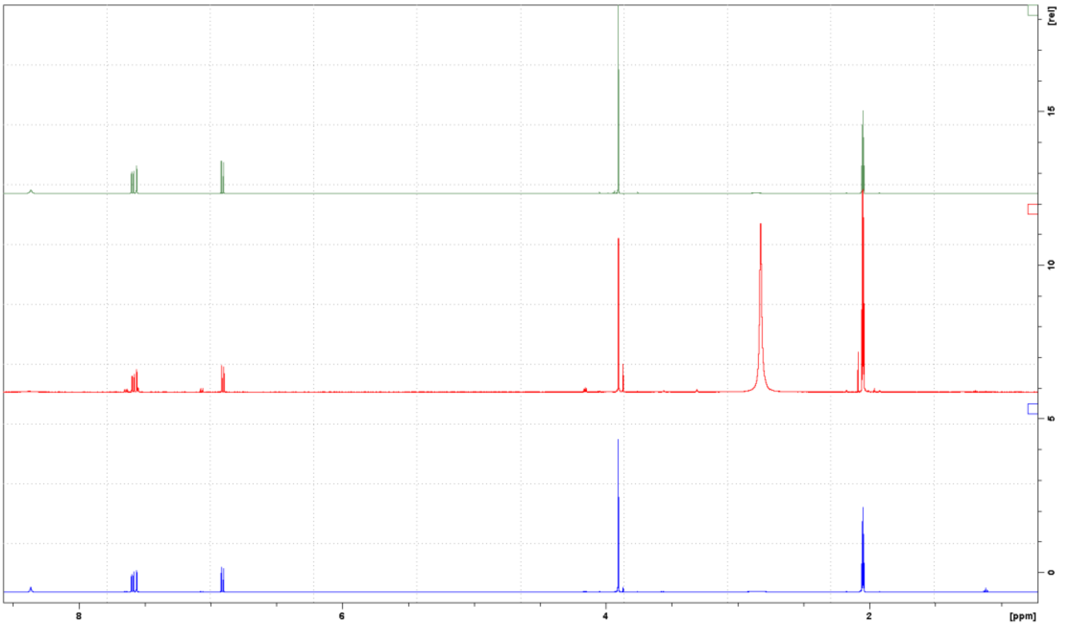


Figure 13: ^{1}H-NMR of products of experiment 1 (red) and 2 (blue) compared to vanillic acid (green)

Table 12: *Analysis table of spectra shown in* ***Figure 13****:*

Compound	Peak	Shift [ppm]	Multiplicity	J [Hz]	Integration a)	Assigned
Vanillic acid	-	2.05	p	2.2	-	Acetone d$_6$
	A	2.90	br s	-	1	-OH
	B	3.91	s	-	3	-CH$_3$
	C	6.91	d	8.3	1	Ar-H
	D	7.56	d	1.9	1	Ar-H
	E	7.59	dd	8.2, 1.9	1	Ar-H
	F	8.86 b)	br s	-	2 (1)	-COOH
Product expt. 1	-	2.05	p	2.2	-	Acetone d$_6$
	A	2.83	br s	-	39 (1)	-OH (H$_2$O)
	B	3.90	s	-	3	-CH$_3$
	C	6.91	d	8.2	1	Ar-H
	D	7.56	d	1.9	1	Ar-H
	E	7.59	dd	8.2, 2.0	1	Ar-H
	F	10.87 b)	br s	-	2 (1)	-COOH
Product expt. 2	-	2.05	p	2.2	-	Acetone d$_6$
	A	2.85	br s	-	1	-OH
	B	3.91	s	-	3	-CH$_3$
	C	6.91	d	8.3	1	Ar-H
	D	7,56	d	1.9	1	Ar-H
	E	7.59	dd	8.3, 2.0	1	Ar-H
	F	10.86 b)	br s	-	1	-COOH

a) Numbers in parentheses are what the integrals are supposed to be. b) Not shown in **Figure 13** due to low visibility.

The ^{13}C-NMR spectra of the product of experiments 1 and 2, compared to the carbon spectrum of vanillic acid, is shown in **Figure 14** and described in **Table 13**. As the products only partly dissolved in the solvent, this shows only parts of the product, as for the ^{1}H-NMR. The spectra of the dissolved material are very like the one of vanillic acid, indicating that the reaction has not taken place.

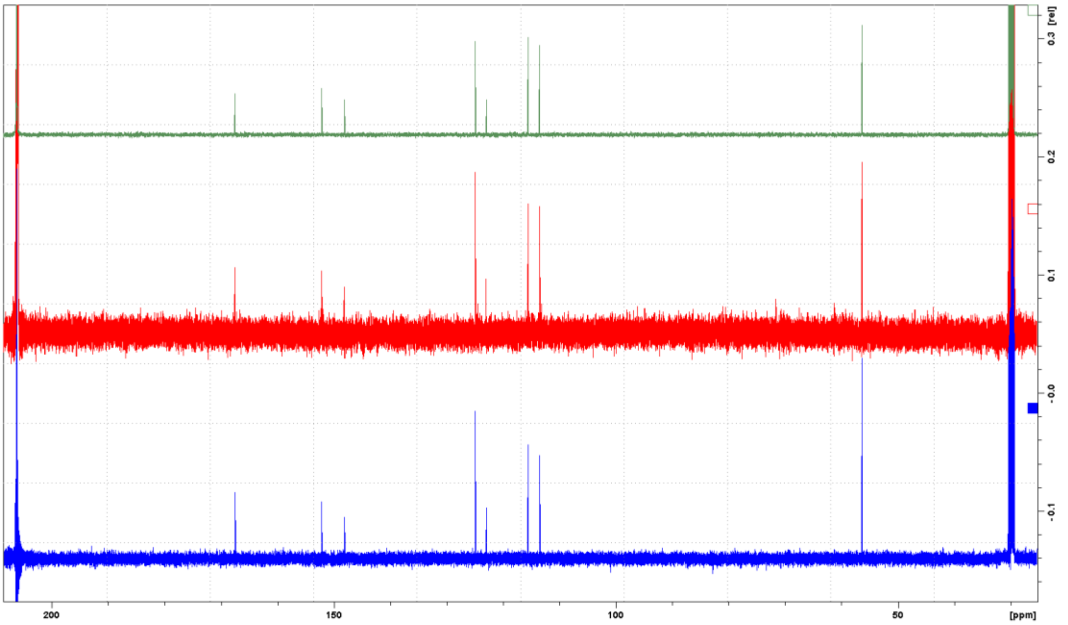


Figure 14: *^{13}C-NMR of products of experiment 1 (red) and 2 (blue) compared to vanillic acid (green)*

Table 13: *Analysis table of spectra shown in* ***Figure 14****:*

Peak	Shift, vanillic acid [ppm]	Shift, product expt. 1 [ppm]	Shift, product expt 2 [ppm]	Assigned
-	29.92	29.92	29.92	Acetone d_6
1	56.4	56.4	56.4	CH_3
2	113.5	113.6	113.5	Ar-H
3	115.6	115.6	115.6	Ar-H
4	123.0	123.0	122.9	Ar
5	124.9	124.9	124.9	Ar-H
6	148.1	148.2	148.1	Ar
7	152.1	152.1	152.1	Ar
8	167.6	167.5	167.5	-COOH
-	206.2	206.2	206.2	Acetone d_6

5.1.2 Starting with 4-hydroxybenzoic Acid

During the reflux of experiment 3, the solvent had evaporated due to an inefficient reflux cooling. This was not noticed until the reaction was finished as the setup is covered in aluminum foil to prevent light. Thus, the actual time of reaction is unknown for experiment 3.

Table 10 shows the yields of experiments 3 and 4 to be 15.3 % and 10.4 % respectively. The crude product of experiment 4 had two different colors, which were separated before the purification. The samples were a beige powder, and brown lumps. The purified products are referred to as sample 4.8,

which is the purified brown lumps, and sample 4.9, which is the purified beige powder. Sample 4.8 yielded 6.3 % of the product, while the product of sample 4.9 yielded 4.1 %.
Samples were taken from the reaction during experiment 4, for TLC analysis, but no suitable eluent composition was found that would separate the product from the starting material.

The melting points of the products from experiments 3 and 4 are given in the table below, together with the literature values of the starting material, 4-hydroxybenzoic acid, and the desired product, 4-(2-hydroxyethoxy)-benzoic acid. The melting point of the product from experiment 3 is well below either of these, indicating possibly another product than the desired ether. As for sample 4.8, this is somewhat below the literature value, indicating some impurities. Sample 4.9 has the start of melting at about the same temperature as sample 4.8, however it shows indications of several compounds in the sample as the melting started and stopped before continuing at a higher temperature. Thus, the point where the first part stopped melting, and the point where the second part started melting was not found. The temperature in which the sample was completely melted could give indications of the starting material in the sample. It's low compared to the starting material, but as there is several compounds, the melting temperature would lower due to the impurities.

Table 14: *Melting point analysis of experiments 3 and 4:*

	Melting start [°C]	**Melting end [°C]**
Literature value, 4-hydroxybenzoic acid [51]	213	217
Literature value, 4-(2-hydroxyethoxy)-benzoic acid [a) 52]	179	180
Product expt. 3	147.8	148.8
Sample 4.8	169.3	174.3
Sample 4.9	169.9	n.d.
	n.d.	195.0

[a)] SciFinder reported the literature value of 4-(2-hydroxyethoxy)-benzoic acid to be 179 – 180 °C from 3 sources, but a fourth source reported this to be 152 °C.[52] Due to the majority reporting 179 – 180 °C, this is the value that is used for comparison.

The IR of the product from experiment 3, together with the two products from experiment 4 and the starting material is shown in the figure below. The -OH-stretch of the carboxylic acid has shifted from 3383 cm^{-1} for the 4-hydroxybenzoic acid to 3287 cm^{-1} for the product. Both for the product of experiment 3, and for sample 4.9, both of these are visible to some degree. All the spectra of the products show a peak at 2953 cm^{-1} (not indicated for sample 4.9 in **Figure 15**, but a small peak is visible) indicating the aliphatic CH$_2$–stretches of the attached ether. The carbonyl stretch is quite equal for all spectra, but a difference is also seen for the two aromatic peaks. An IR with a closer look to these peaks is given in appendix E. For the starting material, these are given at 1607 and 1594 cm^{-1}, while for sample 4.8, they are seen at 1605 and 1580 cm^{-1}. The product of experiment 3 shows all three of these peaks, and sample 4.9 shows a righthand tailing effect of the peak at 1593 cm^{-1}, both of which indicates a mixture between the starting material and the desired product.

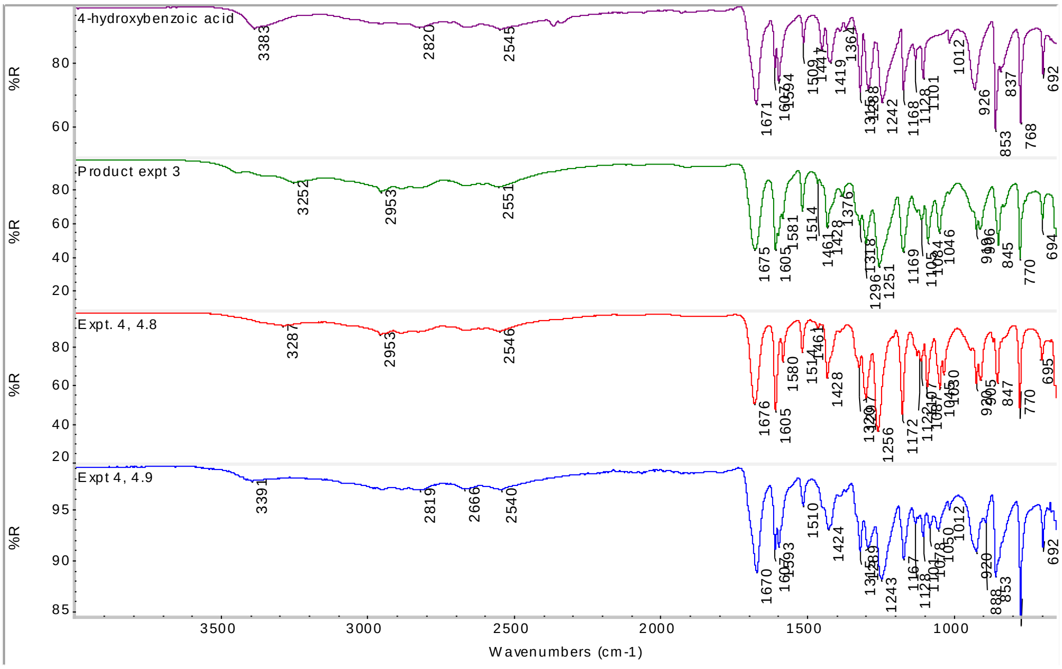


Figure 15: *IR of products of experiment 3 (green) and 4 (sample 4.8 in red, sample 4.9 in blue), compared to 4-hydroxybenzoic acid (purple)*

The ^{1}H-NMR of the products from experiments 3 and 4 are shown in **Figure 16**, described in **Table 15**. The product from experiment 3 shows double sets of the aromatic peaks, indicating a mixture of the starting material (attached in appendix F) and the product of the reaction. The integrals of these indicate about 55 mol% of the product and 45 mol% of the starting material in this product. Sample 4.8 only shows the desired peaks, while sample 4.9 shows only traces of the desired peaks, with mostly the starting material shown. The integrals of the aromatic peaks indicate about 70 mol% of the starting material, and about 30 mol% of the desired product. All three spectra have two triplets at 3.90 and 4.16 ppm that shows the attached group.

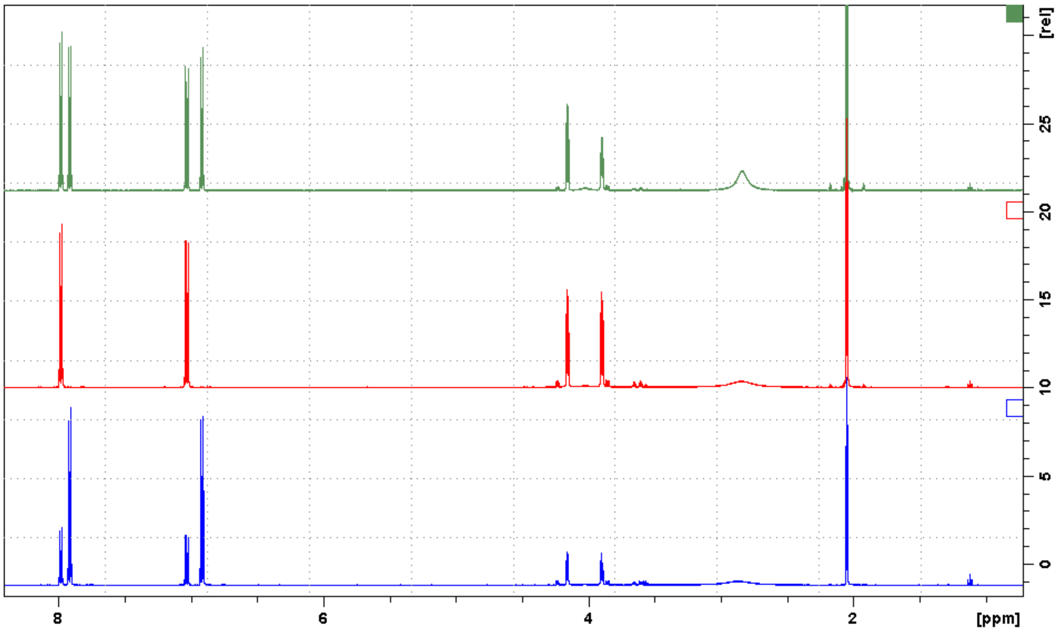


Figure 16: *^{1}H-NMR of products from experiment 3 (green) and 4 (sample 4.8 in red, sample 4.9 in blue)*

***Table 15:** Analysis table of spectra shown in **Figure 16**:*

Compound	Peak	Shift [ppm]	Multiplicity	J [Hz]	Integration [a]	Assigned
Product expt. 3	-	2.05	p	2.2	-	Acetone d_6
	A	2.84	br s	-	6.6 (1)	-OH (H_2O)
	B	3.90	t	5.0	2	-CH_2(-OH)
	C	4.16	t	5.1	2	(-O)-CH_2-
	1 [b]	6.90 – 9.93	m	-	1.7 (2)	2 x Ar-H
	D	7.01 – 7.05	m	-	2	2 x Ar-H
	2 [b]	7.90 – 7.93	m	-	1.7 (2)	2 x Ar-H
	E	7.97 – 8.00	m	-	2	2 x Ar-H
	3 [b, c]	9.12	br s	-	1	-OH
	F [c]	10.82	br s	-	1	-COOH
Sample 4.8	-	2.05	p	2.2	-	Acetone d_6
	A	2.85	br s	-	3 (1)	-OH (H_2O)
	B	3.90	t	5.0	2	-CH_2(-OH)
	C	4.16	t	5.1	2	(-O)-CH_2
	D	7.02 – 7.04	m	-	2	2 x Ar-H
	E	7.97 – 8.00	m	-	2	2 x Ar-H
	F [c]	10.88	br s	-	1	-COOH
Sample 4.9	-	2.05	p	2.2	-	Acetone d_6
	A	2.87	br s	-	7 (1)	-OH (H_2O)
	B	3.90	t	5.0	2	-CH_2(-OH)
	C	4.16	t	5.1	2	(-O)-CH_2
	1 [b]	6.90 – 6.93	m	-	5 (2)	2 x Ar-H
	D	7.02 – 7.04	m	-	2	2 x Ar-H
	2 [b]	7.90 – 7.93	m	-	5 (2)	2 x Ar-H
	E	7.97 – 8.00	m	-	2	2 x Ar-H
	F [c]	10.03	br s	-	7 (1)	-COOH

[a] Numbers in parentheses are what these integrals are supposed to be. [b] Residue from start material.
[c] Not shown in **Figure 16** due to low visibility.

The ^{13}C-NMR spectra that are shown in **Figure 17** and described in **Table 16** give the same indications that were found from the ^{1}H-NMR regarding the purities of the samples. The product from experiment 3 shows peaks both of the product and of the starting material, the peaks from the product being slightly higher than those of the starting material. Sample 4.8 shows only the desired peaks of the product, while sample 4.9 have more of the starting material than of the desired product. ^{13}C-NMR of the starting material is attached in appendix F for reference.

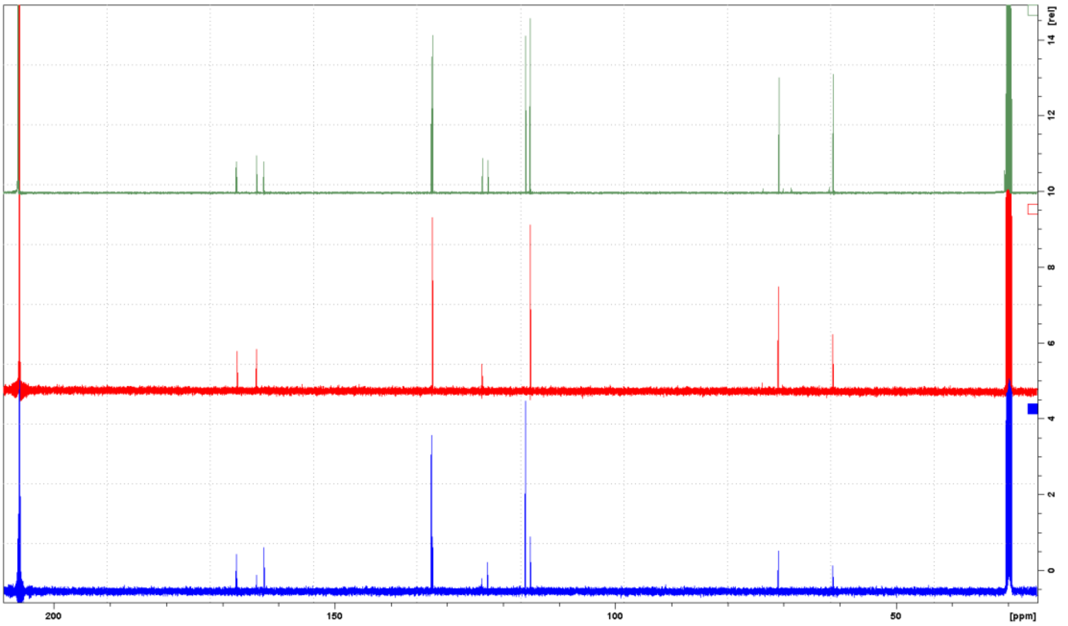


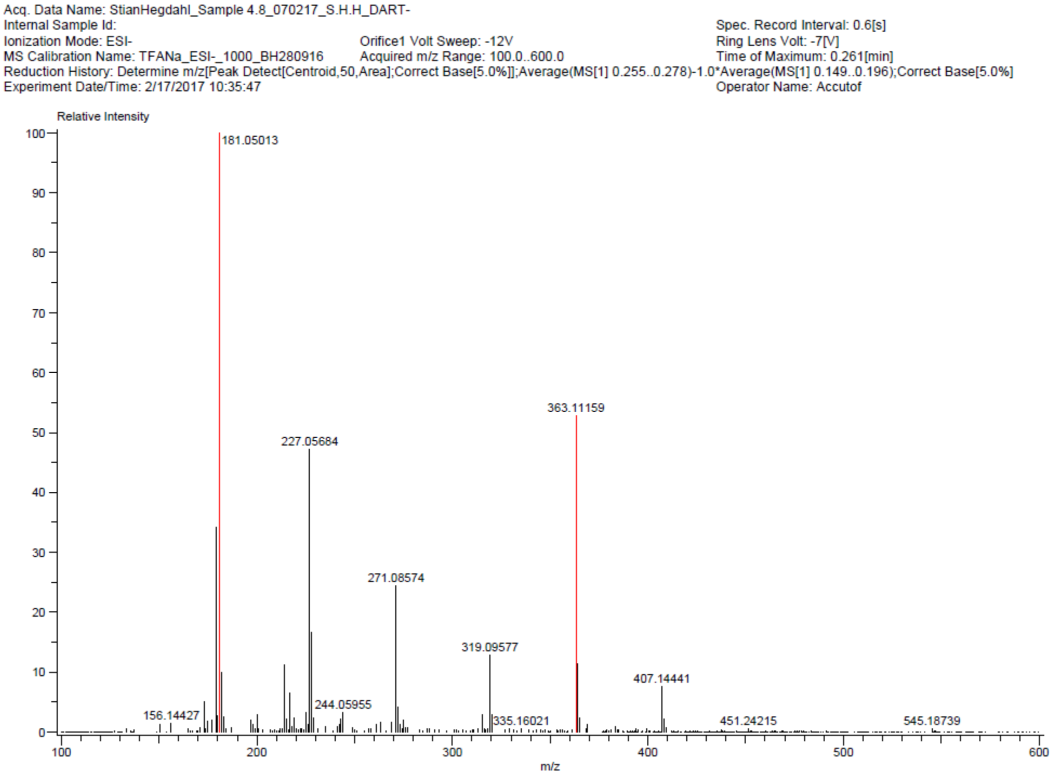
Figure 17: *^{13}C-NMR of products from experiment 3 (green) and 4 (sample 4.8 in red, sample 4.9 in blue)*

Table 16: *Analysis table of spectra shown in* ***Figure 17****:*

Peak	Shift, product expt. 3 [ppm]	Shift, sample 4.8 [ppm]	Shift, sample 4.9 [ppm]	Assigned
-	29.92	29.92	29.92	Acetone d_6
1	61.1	61.3	61.3	-CH$_2$-OH
2	70.9	71.0	71.0	-O-CH$_2$-
3	115.1	115.2	115.2	2 x Ar-H
- a)	116.0	-	116.1	2 x Ar-H
- a)	122.7	-	122.8	Ar
4	123.7	123.8	123.8	Ar
5	132.6	132.6	132.6	2 x Ar-H
- a)	132.8	-	132.8	2 x Ar-H
- a)	162.6	-	162.6	Ar
6	164.0	164.0	164.0	Ar
7	167.5	167.4	167.4	-COOH
- a)	167.6	-	167.5	-COOH
-	206.4	206.2	206.2	Acetone d_6

a) Residue from starting material

The DART-MS, shown in **Figure 18** and **Table 17**, show the expected $[M-1]^-$ and $[2M-1]^-$ within acceptable ranges of the calculated masses. When comparing the extra peaks in the figure to the peaks given in later experiments (Chapter 5.1.3), and as DART-MS only do some simple cleaves of the compound, and no rearrangements, these are found to be impurities to the sample. These are however small enough not to be detected by NMR, as seen by the ^{1}H-NMR and the ^{13}C-NMR above.



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Acq. Data Name: StianHegdahl_Sample 4.8_070217_S.H.H_DART-
Internal Sample Id:                                                            Spec. Record Interval: 0.6[s]
Ionization Mode: ESI-                          Orifice1 Volt Sweep: -12V       Ring Lens Volt: -7[V]
MS Calibration Name: TFANa_ESI-_1000_BH280916  Acquired m/z Range: 100.0..600.0  Time of Maximum: 0.261[min]
Reduction History: Determine m/z[Peak Detect[Centroid,50,Area];Correct Base[5.0%]];Average(MS[1] 0.255..0.278)-1.0*Average(MS[1] 0.149..0.196);Correct Base[5.0%]
Experiment Date/Time: 2/17/2017 10:35:47                                       Operator Name: Accutof
```

Figure 18: *DART-MS of product of sample 4.8*

Table 17: *Description of DART-MS found in* ***Figure 18****:*

Expt.	Found mass	Calculated mass	Mass difference [mmu]	Possible formula
6	181.05013	181.05008	0.05	$C_9H_9O_4$
	363.11159	363.10799	3.6	$C_{18}H_{19}O_8$

Neither GC-FID from experiment 3, nor GC-MS from experiment 4 gave any results of interest. All analyses are found in appendix G and H.

5.1.2.1 Elucidation of Crude Product

An elucidation of the crude product was done to confirm that the reaction had taken place at the hydroxy-group instead of the carboxylic acid. This would produce an ester instead of the desired ether, and the regular analyses from compounds would be quite similar. The structures in question are given in **Figure 19**:

4-(2-hydroxyethoxy)-benzoic acid   2-hydroxyethyl 4-hydroxybenzoate

Figure 19: *Structure of the two possibilities of product*

The elucidation of the crude product that were to become sample 4.8 after purification gave the following results:

Figure 20 shows the ^{1}H-NMR spectrum of the crude product from experiment 4, described in **Table 18**. Two triplets indicating the attached group is found at 3.89 and 4.13 ppm, and two multiplets indicating the four aromatic hydrogens, again indicating a symmetric structure are found. All of these are given a chemical environment A – D that is connected to the ^{13}C-NMR shown in **Figure 21**, using the HSQC-NMR shown in **Figure 22**. This relation is shown in **Table 19**.

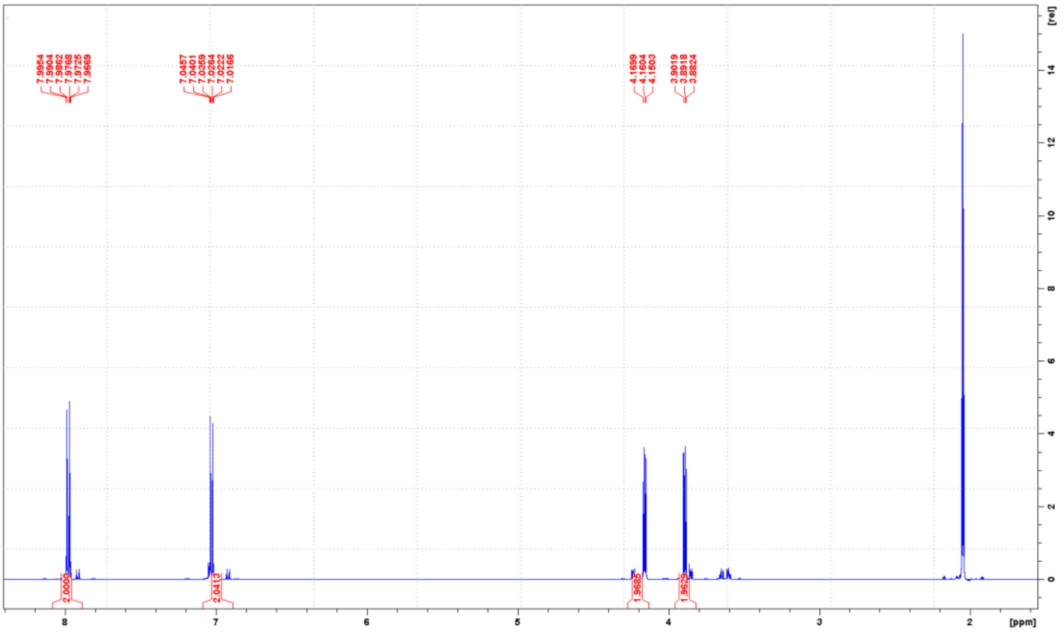


Figure 20: *^{1}H-NMR of crude product of experiment 4*

Table 18: *Analysis table of spectrum shown in* ***Figure 20****:*

Compound	Peak	Shift [ppm]	Multiplicity	J [Hz]	Integration	Assigned
	-	2.05	p	2.2	-	Acetone d_6
Crude product expt. 4	A	3.89	t	5.1	2	-$\underline{CH_2}$(-OH)
	B	4.16	t	5.1	2	(-O)-$\underline{CH_2}$
	C	7.02 – 7.05	m	-	2	2 x Ar-H
	D	7.97 – 8.00	m	-	2	2 x Ar-H

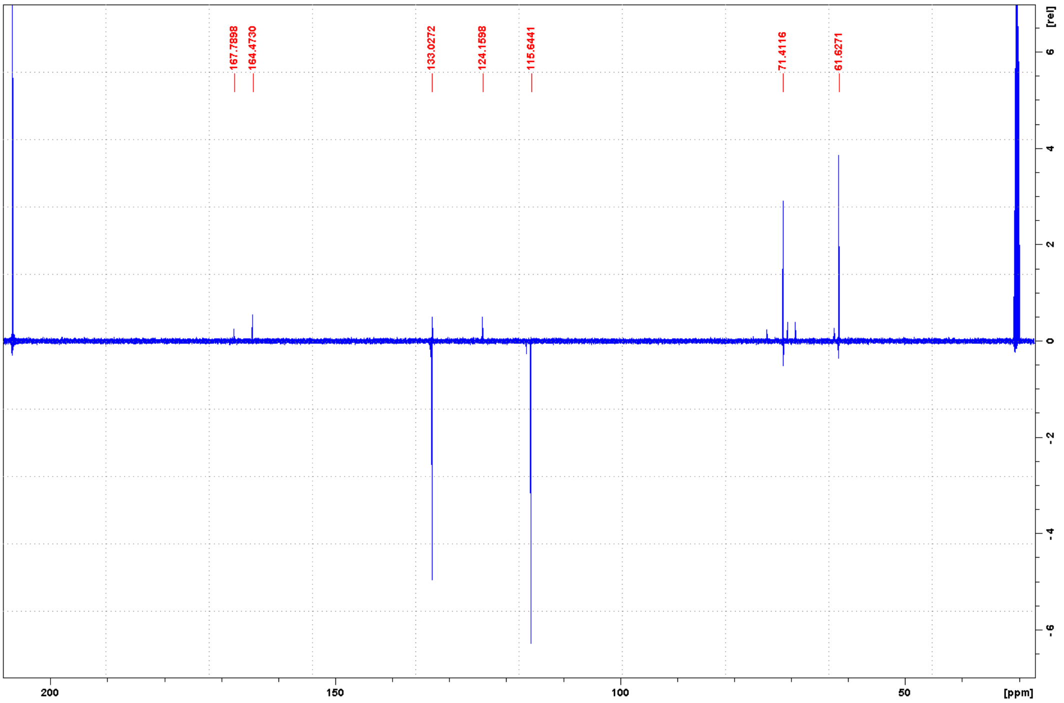


Figure 21: *CAPT-NMR of crude product from experiment 4*

The COSY-NMR given in appendix F supports the statement of which peaks being the aromatic ring and which peaks being the attached aliphatic part. It also shows that there are no ^{3}J-connections between these chemical environments.

Table 20 describes the cross peaks found in the HMBC-NMR in **Figure 22** and what can be understood by these. Carbon peak A and B only have cross peaks to each other, which confirms the previous statement that these are the attached group of the molecule. The carbon peak at 164.5 ppm has cross peaks to both aromatic environments, H_C and H_D. Due to the bond distance of these, this carbon have to be a carbon of the aromatic ring as the carbon from the carbonyl would only have a cross peak to the closest environment of the aromatic ring (a cross peak to the furthest Ar-H-environment would be a ^{4}J and thus a very weak cross peak, if visible at all). The cross peak from the carbon peak at 164.5 ppm to H_B shows that the carbon in question is connected to the attached aliphatic group. Due to the bond distance, this has to be attached to the hydroxy-group, as an attachment to the carboxylic acid would make a ^{4}J between these and thus again probably not a visible cross peak. This gives indications that the carbon at 164.5 ppm is the carbon where the hydroxy-group was, and that this is also where the reaction has taken place, producing the desired ether. This is supported by the carbon at 167.8 ppm, which has a cross peak to H_D, which is the case of the carbonyl group. If the reaction would provide the ester, this would have a ^{3}J to the closest aliphatic CH_2 and thus have a strong cross peak. The peaks are thus found to be as shown in **Figure 23**:

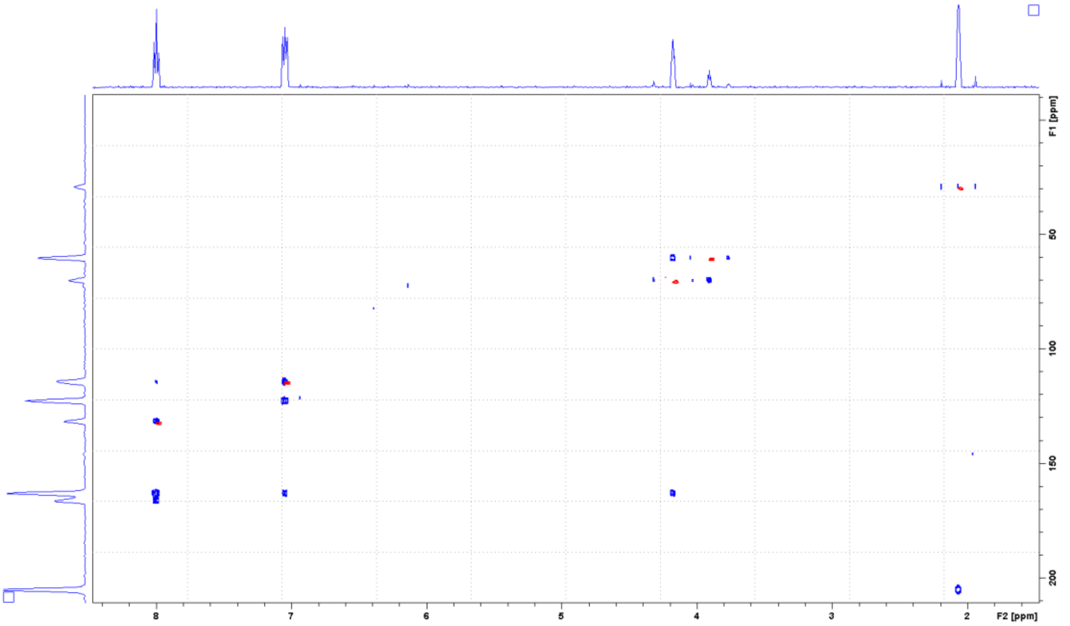


Figure 22: *HSQC-NMR (red) and HMBC-NMR (blue) of crude product from experiment 4*

Table 19: *Relation between ^{1}H-NMR (**Figure 20**) and ^{13}C-NMR (**Figure 21**) based on HSQC-NMR (**Figure 22**):*

Peak	**^{1}H-NMR**				**^{13}C-NMR**
	Shift [ppm]	**Multiplicity**	**J [Hz]**	**Integration**	**Shift [ppm]**
A	3.89	t	5.1	2	61.2
B	4.16	t	5.1	2	71.0
C	7.02 – 7.05	m	-	2	115.2
D	7.97 – 8.00	m	-	2	132.6

Table 20: *Cross peaks found in **Figure 22**:*

Carbon peak	**Cross peak**	**Bond distance [a)]**	**Deduction**
A	H_A H_B	^1J ^2J	Confirms environments A and B to be located closely
B	H_A H_B	^2J ^1J	Confirms environments A and B to be located closely
C	H_C H_D	^1J ^2J	Confirms environments C and D to be located closely
124.2	H_C	^3J	Aromatic carbon where the carboxylic acid is located
D	H_D	^1J	Confirms relation found in **Table 19**
164.5	H_B H_C H_D	^3J ^2J ^3J	Aromatic carbon where the 2-hydroxyethoxygroup is located. Shows that environment B is closer to the aromatic part than environment A, thus confirming the relative locations of A and B
167.8	H_D	^3J	Carbonyl

[a)] Based on how strong the cross peaks are relative to each other.

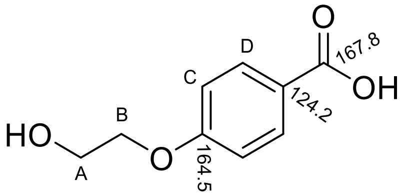
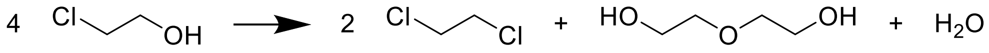


Figure 23: *4-(2-hydroxyethyxy)-benzoic acid, with chemical environments indicated*

5.1.2.2 Analysis of Filtrate

The purpose of the ^{1}H-NMR analysis of sample 4.10 found in **Figure 24** with the following description in **Table 21** is to find side reactions that are occurring during the reaction. These show ethylene glycol oligomers by two multiplets from 3.50 to 3.67 ppm, which together with the 1,2-dichloroethane found as a singlet at 3.87 ppm, might be produced by a reaction of 2-chloroethanol reacting with other 2-chloroethanol molecules. Both of the side products found have been confirmed by comparing the side products to pure samples from Sigma-Aldrich. The ^{1}H-NMR of the pure products are found in appendix F. A scheme of the reaction described above is shown in **Scheme 5**:



Scheme 5: *Side reaction producing 1,2-dichloroethanol and ethylene glycol*

As a result of this finding, the relative amount of 2-chloroethanol was increased to 1.5 eq.

Other than these side reactions, the chemicals found by the analysis are ethanol, some of the desired product, and the starting material.

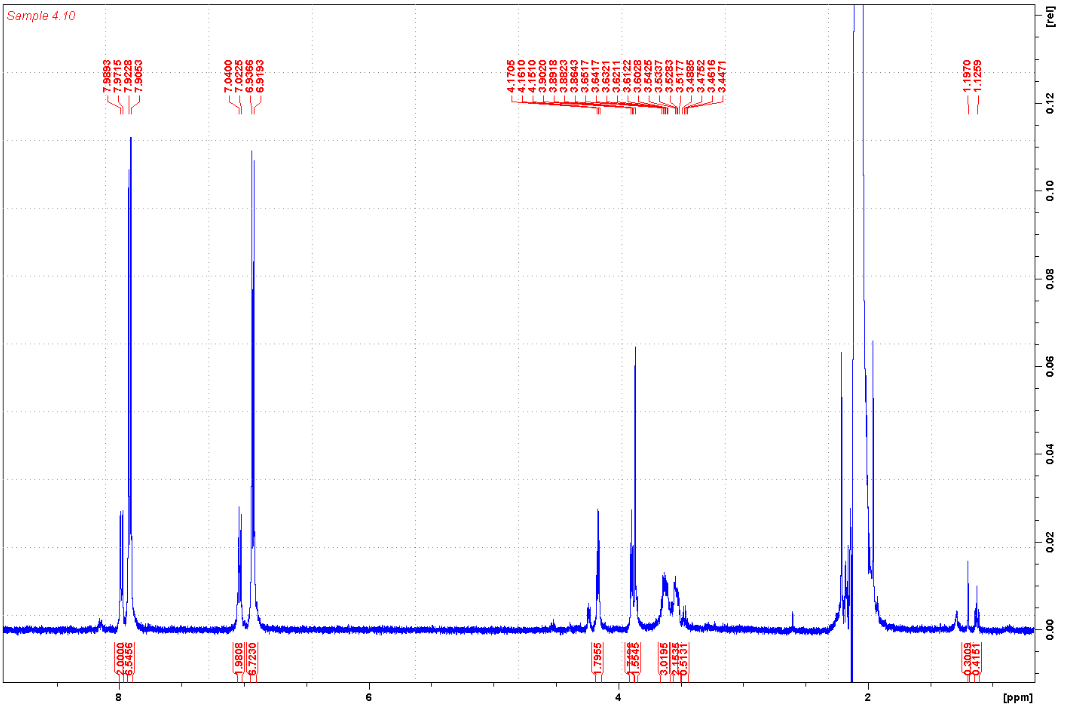


Figure 24: *NMR of evaporated filtrate after acidification, sample 4.10*

***Table 21:** Analysis table of spectrum shown in **Figure 24**:*

Compound	Peak	Shift [ppm]	Multiplicity	J [Hz]	Integration [a]	Assigned
Sample 4.10	1 [b]	1.13	t	6.9	0.4	CH_3
	2	1.20	s	-	0.3	n.d.
	3 [b]	3.47	q	6.8	0.5	CH_2
	4 [c]	3.50 – 3.56	m	-	2.2	n.d. x CH_2
	5 [c]	3.59 – 3.67	m	-	3.0	n.d. x CH_2
	6 [d]	3.87	s	-	1.6	2 x CH_2
	7 [e]	3.89	t	5.1	1.7 (2)	CH_2
	8 [e]	4.16	t	5.0	1.8 (2)	CH_2
	9 [f]	6.89 – 6.95	m	-	6.7	2 x Ar-H
	10 [e]	7.02 – 7.06	m	-	2	2 x Ar-H
	11 [f]	7.90 – 7.93	m	-	6.5	2 x Ar-H
	12 [e]	7.97 – 8.00	m	.	2	2 x Ar-H

[a] Numbers in parentheses are what these integrals are supposed to be. [b] Ethanol residue. [c] Ethylene glycol oligomers. [d] 1,2-dichloroethane. [e] The desired product. [f] Remaining start compound, 4-hydroxybenzoic acid.

5.1.3 Starting with Methyl 4-hydroxybenzoate

Experiments 5 and 6 were done similarly, with the difference being 2-chloroethanol and NaI used in experiment 5, while 2-bromoethanol and no catalyst was used in experiment 6. As found in **Table 10**, the experiments yielded 49.7 % and 38.2 %, respectively.

The melting points of experiments 5 and 6 are shown in the table above, together with the literature values of the starting material and the desired product. In addition, the melting point of 4-hydroxybenzoic acid is included as any starting material left would still be reacted with the base and further with the acid to produce the carboxylic acid. As the desired product is the same as in Chapter 5.1.2, the literature value of this is uncertain, as explained below **Table 14**. The melting point of both experiment 5 and 6 are somewhat below the literature value of the desired product, indicating some minor impurities to the samples. The range of melting is however quite short, indicating the opposite.

Table 22: *Melting point analysis of experiments 5 and 6:*

	Melting start [°C]	**Melting end [°C]**
Literature value, methyl 4-hydroxybenzoate [49]	125	128
Literature value, 4-hydroxybenzoic acid [51]	213	217
Literature value, 4-(2-hydroxyethoxy)-benzoic acid [a)] [52]	179	180
Product expt. 5	173.6	174.4
Product expt. 6	173.9	174.5

[a)] See **Table 14**

The IR spectra of the products from these experiments, shown in appendix E, are very close to the IR spectrum of sample 4.8, found in **Figure 16**. A newly acquired peak of the -OH-stretch of a carboxylic acid is seen, and the aliphatic CH_2-stretches are seen at 2956 and 2954 cm^{-1}, respectively. No change is to be seen in the peak of the carbonyl regarding the wavelength from the starting material (also given in appendix E), however a change is seen at the aromatic peaks. The first one has no change in wavelength, however the second one has shifted from 1586 cm^{-1} of the starting material, to 1580 cm^{-1} of the product. In addition, the ration between these two peaks have shifted. In total the IR spectra of the products indicate the desired product, similar to sample 4.8.

As for the ^{1}H-NMR, shown in **Figure 25** and described in **Table 23**, this shows a very pure product, no extra peaks seen except for the peak of the hydroxy-group being slightly larger than expected, possibly due to some water left in the product. If this water is present as water of crystallization, the slightly low melting point shown in **Table 22** could be explained as well.

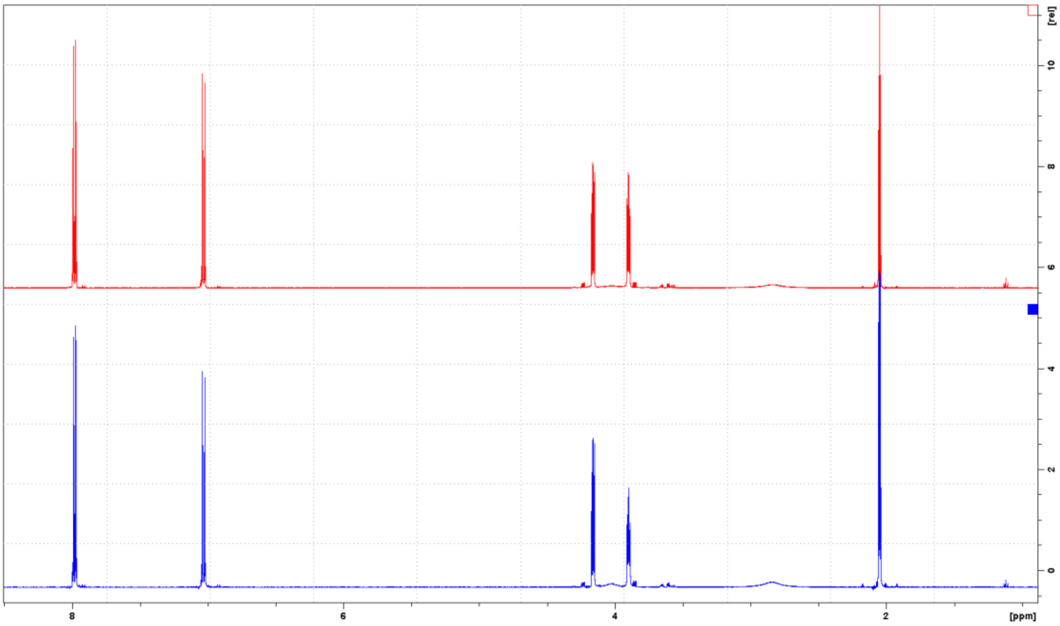


Figure 25: ^{1}H-NMR of products of experiments 5 (red) and 6 (blue)

Table 23: *Analysis table of spectra shown in* ***Figure 25****:*

Compound	Peak	Shift [ppm]	Multiplicity	J [Hz]	Integration [a)]	Assigned
Product expt. 5	-	2.05	p	2.2	-	Acetone d_6
	A	2.84	br s	-	1.2 (1)	-OH (H_2O)
	B	3.90	t	5.0	2	-$\underline{CH_2}$(-OH)
	C	4,16	t	5.2	2	(-O)-$\underline{CH_2}$
	D	7.02 – 7.05	m	-	2	2 x Ar-H
	E	7.97 – 8.00	m	-	2	2 x Ar-H
	F	10.89 [b)]	br s	-	1	-COOH
Product expt. 6	-	2.05	p	2.2	-	Acetone d_6
	A	2.85	br s	-	1.5 (1)	-OH (H_2O)
	B	3.90	t	5.0	2	-$\underline{CH_2}$(-OH)
	C	4.16	t	5.1	2	(-O)-$\underline{CH_2}$
	D	7.02 – 7.04	m	-	2	2 x Ar-H
	E	7.97 – 8.00	m	-	2	2 x Ar-H
	F	10.91 [b)]	br s	-	1	-COOH

[a)] Numbers in parentheses are what these integrals are supposed to be. [b)] Not shown in figure due to low visibility

The ^{13}C-NMR spectra from experiments 5 and 6, shown in **Figure 26** and described in **Table 24** show both of the products to be very pure as no extra peaks are to be found. Two peaks are seen at 61.3 and 71.0 ppm, indicating the attached group. Further, the two peaks at 115.2 and 132.6 ppm shows the four (due to a symmetric compound) unsubstituted aromatic carbons. The peaks at 123.8 ppm show the carbon where the carboxylic acid is located, as found in Chapter 5.1.2.1. The peaks at 164.0

ppm are the carbon where the ether is attached, and the peaks at 167.4 ppm show the carbonyl of the carboxylic acid.

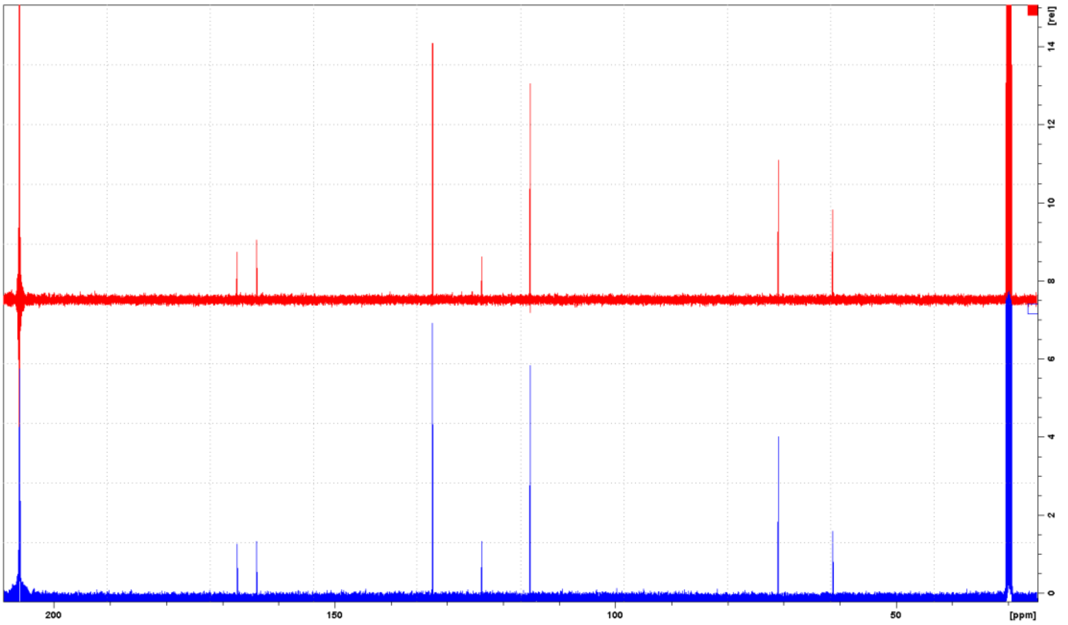
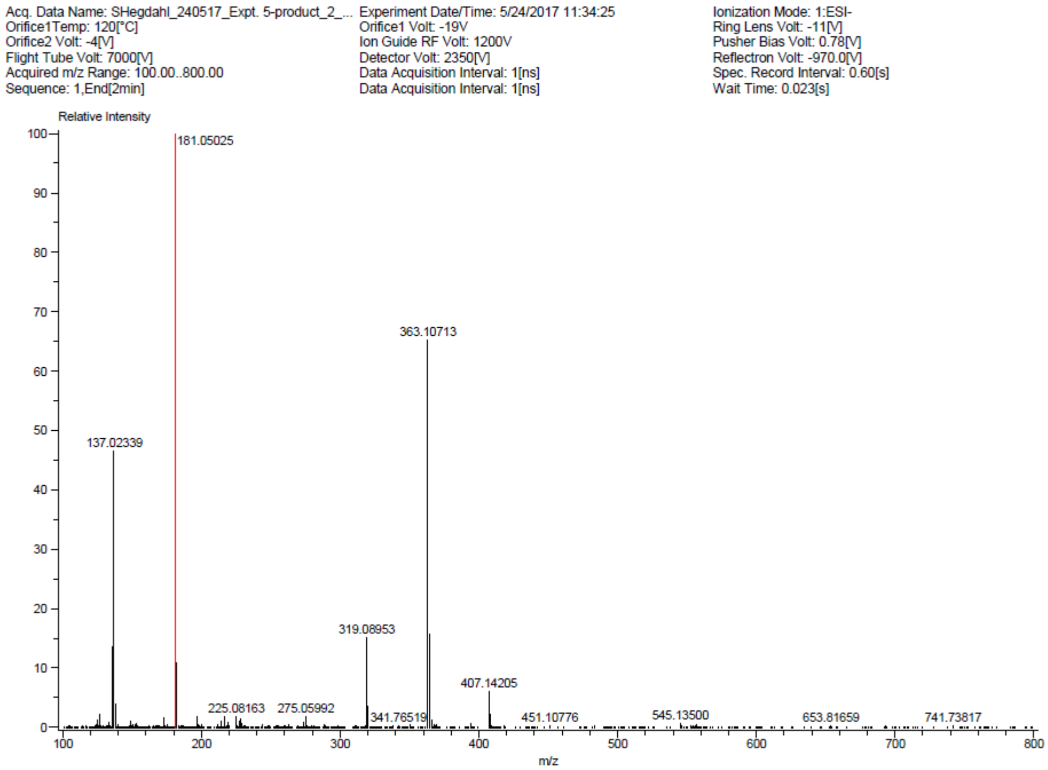


Figure 26: *^{13}C-NMR of products of experiments 5 (red) and 6 (blue)*

Table 24: *Analysis table of spectra shown in* ***Figure 26****:*

Peak	Shift, product expt. 5 [ppm]	Shift, product expt. 6 [ppm]	Assigned
-	29.92	29.92	Acetone d_6
1	61.3	61.3	$-CH_2-OH$
2	71.0	71.0	$-O-CH_2-$
3	115.2	115.2	2 x Ar-H
4	123.8	123.8	Ar
5	132.6	132.6	2 x Ar-H
6	164.0	164.0	Ar
7	167.4	167.4	-COOH
-	206.2	206.2	Acetone d_6

The DART-MS from experiments 5 (**Figure 27**) and 6 (**Figure 28**), both of which are described in **Table 25** show the expected $[M-1]^-$ and $[2M-1]^-$ well within reasonable margins of error. In addition, peaks are seen at $[M-45]^-$ and $[2M-45]^-$, which are the product after cleaving the carboxylic acid (in the case of $[2M-45]^-$, this cleavage has been done on one of the monomeric units only). These peaks also indicate that the reaction has taken place at the hydroxy-group instead of the carboxylic acid, as found in Chapter 5.1.2.1, as a loss from the ester otherwise produced would give a larger loss than $[M-45]^-$.



Acq. Data Name: SHegdahl_240517_Expt. 5-product_2_...
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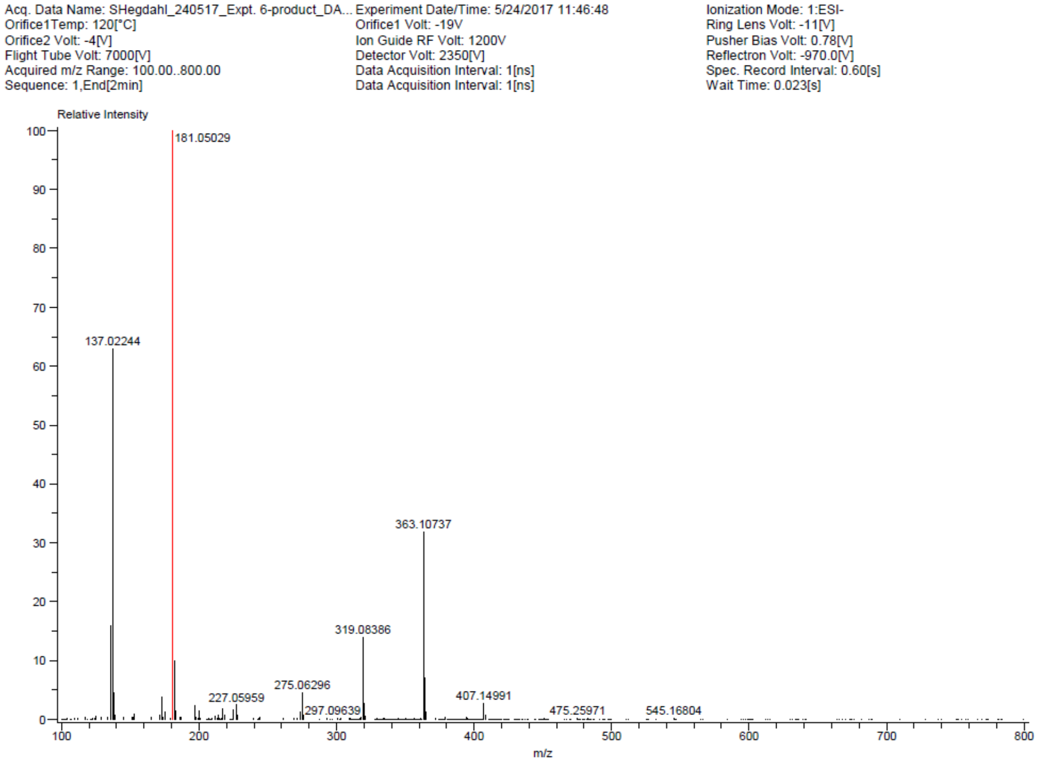
Orifice2 Volt: -4[V]
Flight Tube Volt: 7000[V]
Acquired m/z Range: 100.00..800.00
Sequence: 1,End[2min]

Experiment Date/Time: 5/24/2017 11:34:25
Orifice1 Volt: -19V
Ion Guide RF Volt: 1200V
Detector Volt: 2350[V]
Data Acquisition Interval: 1[ns]
Data Acquisition Interval: 1[ns]

Ionization Mode: 1:ESI-
Ring Lens Volt: -11[V]
Pusher Bias Volt: 0.78[V]
Reflectron Volt: -970.0[V]
Spec. Record Interval: 0.60[s]
Wait Time: 0.023[s]

Figure 27: *DART-MS of product of experiment 5*



Acq. Data Name: SHegdahl_240517_Expt. 6-product_DA...
Orifice1Temp: 120[°C]
Orifice2 Volt: -4[V]
Flight Tube Volt: 7000[V]
Acquired m/z Range: 100.00..800.00
Sequence: 1,End[2min]

Experiment Date/Time: 5/24/2017 11:46:48
Orifice1 Volt: -19V
Ion Guide RF Volt: 1200V
Detector Volt: 2350[V]
Data Acquisition Interval: 1[ns]
Data Acquisition Interval: 1[ns]

Ionization Mode: 1:ESI-
Ring Lens Volt: -11[V]
Pusher Bias Volt: 0.78[V]
Reflectron Volt: -970.0[V]
Spec. Record Interval: 0.60[s]
Wait Time: 0.023[s]

Figure 28: *DART-MS of product of experiment 6*

Table 25: *Description of DART-MS found in* ***Figure 27*** *and* ***Figure 28****:*

Expt.	Found mass	Calculated mass	Mass difference [mmu]	Possible formula
5	181.05025	181.05008	0.16	$C_9H_9O_4$
	363.10713	363.10799	0.86	$C_{18}H_{19}O_8$
6	181.05029	181.05008	0.21	$C_9H_9O_4$
	363.10737	363.10799	0.62	$C_{18}H_{19}O_8$

5.1.4 Starting with Vanillic Acid, Final Run

As found in **Table 10**, experiment 10 yielded 50.7 %.

The melting point of the product from experiment 10, showed in **Table 26**, proved to be quite close to the literature value, indicating a quite pure product. This is supported by the range of melting being quite short.

Table 26: *Melting point analysis of experiment 10:*

	Melting start [°C]	Melting end [°C]
Literature value, vanillic acid [49]	208	210
Literature value, 4-(2-hydroxyethoxy)-3-methoxybenzoic acid [50]	199	200
Product expt. 10	196.4	197.2

The IR spectrum of the product from experiment 10 is shown in **Figure 29**. A peak of the -OH-stretch from a carboxylic acid is seen at 3337 cm^{-1}, as well as a wide peak of the hydroxy-group, ranging from about 2300 to 3100 cm^{-1}. The aliphatic added group, together with the CH_3 of the methoxy group, is visible as a peak at 2919 cm^{-1}. The carbonyl is found as a tall peak at 1670 cm^{-1}, which gives an indication that the reaction took place at the hydroxy-group of the starting material to produce the desired ether. If this reaction were to take place at the carboxylic acid, the carbonyl group would shift towards higher wavenumbers as this would now be an ester. The aromatic C=C bonds are found as peaks at 1599 and 1588 cm^{-1}.

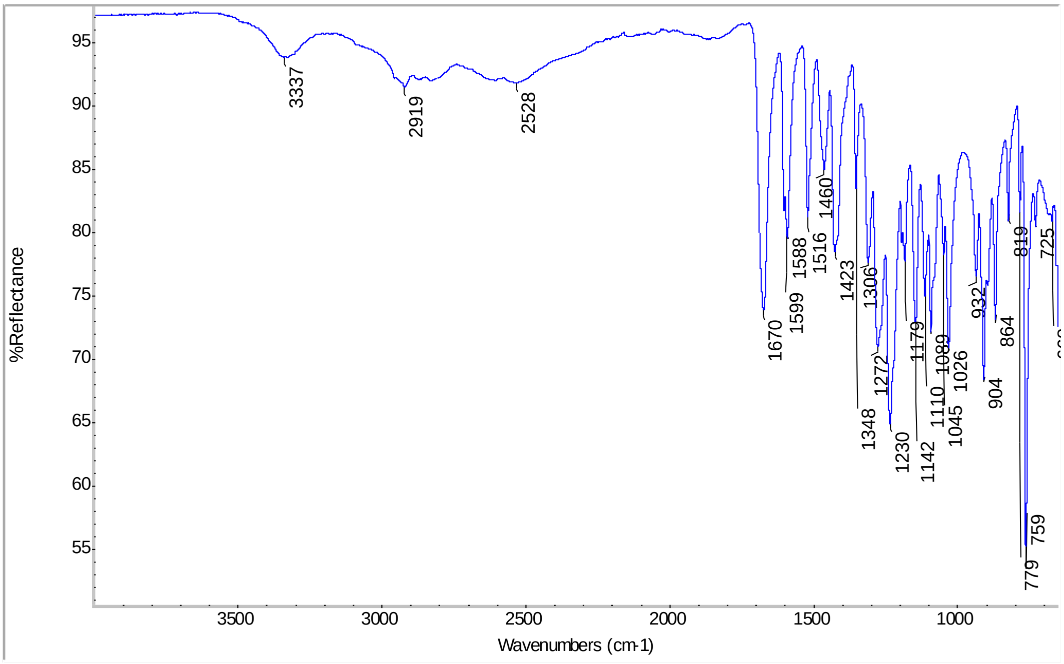


Figure 29: *IR of product from experiment 10*

As for the 4-(2-hydroxyethoxy)-benzoic acid in Chapter 5.1.2, this is analysed for a full elucidation. The main focus of this is to see whether the reaction has taken place at the hydroxy-group of the vanillic acid, producing the desired ether, or at the carboxylic acid, producing an ester instead. The two structures in question are shown in **Figure 30**:


4-(2-hydroxyethoxy)-3-methoxybenzoic acid 2-hydroxyethyl 4-hydroxy-3-methoxybenzoate

Figure 30: *Stuctures of the two possibilities of product*

The ^{1}H-NMR of the product from experiment 10 is shown in **Figure 31** and described in **Table 27**. This shows a fairly pure product, but with some minor traces of vanillic acid (not included in the table due to low intensities). There are also some indications of water in the sample as the hydroxy peak has an integral of 2 instead of 1. No traces of vanillic acid is seen in the ^{13}C-NMR (**Figure 32**, connected to the chemical environments of ^{1}H-NMR in **Table 28**), indicating that the amount of the starting material seen in the ^{1}H-NMR is very low. COSY-NMR is found in appendix F. This confirms the statement of which environments are close together and thus which peaks are the aromatic part and the two aliphatic parts.

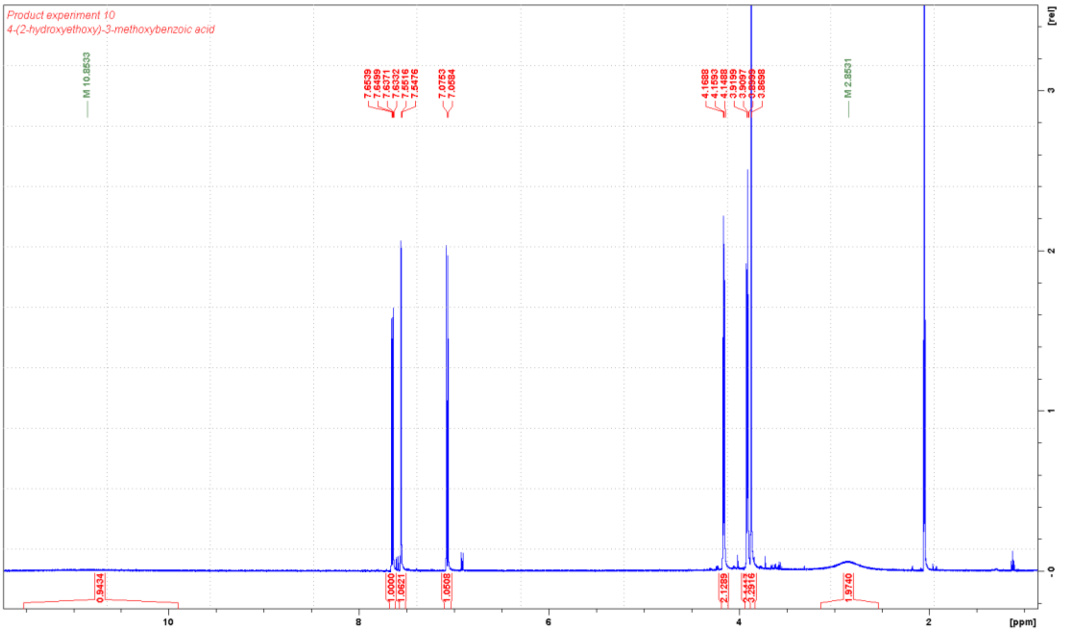


Figure 31: *^{1}H-NMR of product from experiment 10*

Table 27: *Analysis table of spectrum shown in* ***Figure 31****:*

Compound	Peak	Shift [ppm]	Multiplicity	J [Hz]	Integration [a]	Assigned
Product expt. 10	-	2.05	p	2.2	-	Acetone d_6
	A	2.85	br s	-	2 (1)	-OH (H_2O)
	B	3.87	s	-	3	-CH_3
	C	3.91	t	5.1	2	-$\underline{CH_2}$(-OH)
	D	4.16	t	5.2	2	(-O)-$\underline{CH_2}$
	E	7.07	d	8.5	1	Ar-H
	F	7.55	d	2.0	1	Ar-H
	G	7.64	dd	8.4, 2.0	1	Ar-H
	H	10.85	br s	-	1	-COOH

[a] Numbers in parentheses are what these integrals are supposed to be.

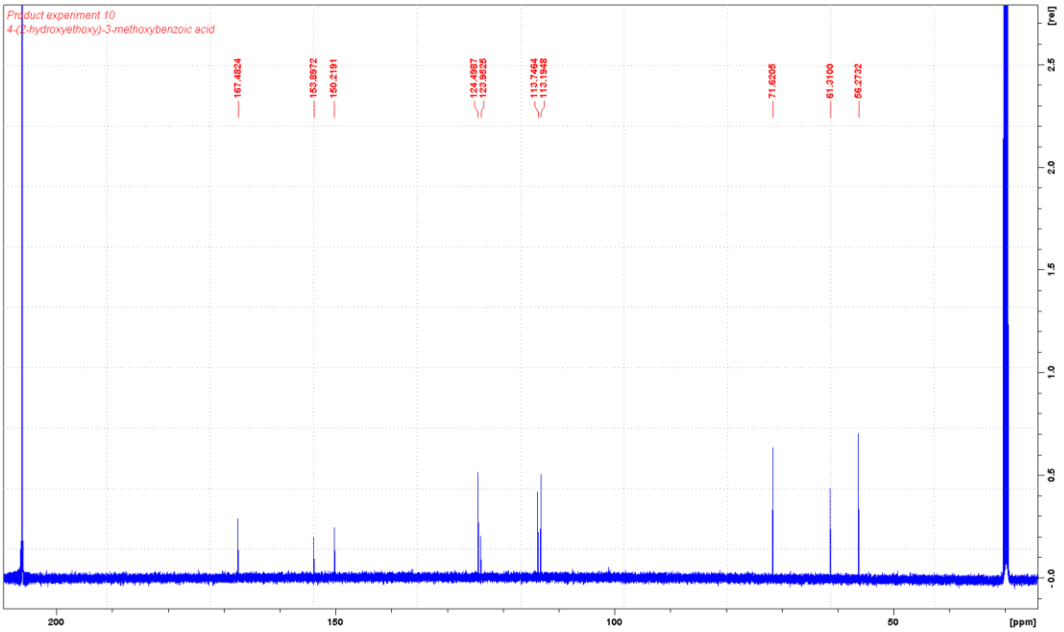


Figure 32: *^{13}C-NMR of product from experiment 10*

The HMBC-NMR shown in **Figure 33** shows cross peaks between ^{13}C- and ^{1}H-NMR. These are listed in **Table 29**. The carbonyl of the carboxylic acid (or ester) will only have a cross peak to two environments of the aromatic ring, and thus has to be the peak at 167.5. This is also a peak that is recognizable based on its shift value. If the reaction were to take place on the carboxylic acid, this carbon would have a ^{3}J-connection to the closest Hydrogen of the attached group. As HMBC is optimized for ^{3}J-connections, this would give a strong cross peak. There are no cross peak between these, indicating that the reaction took place at the hydroxy-group to produce the desired ether, and not at the carboxylic acid to produce an ester. The remaining cross peaks supports the structure of the ether, and the structure with the chemical environments is thus as shown in **Figure 34**:

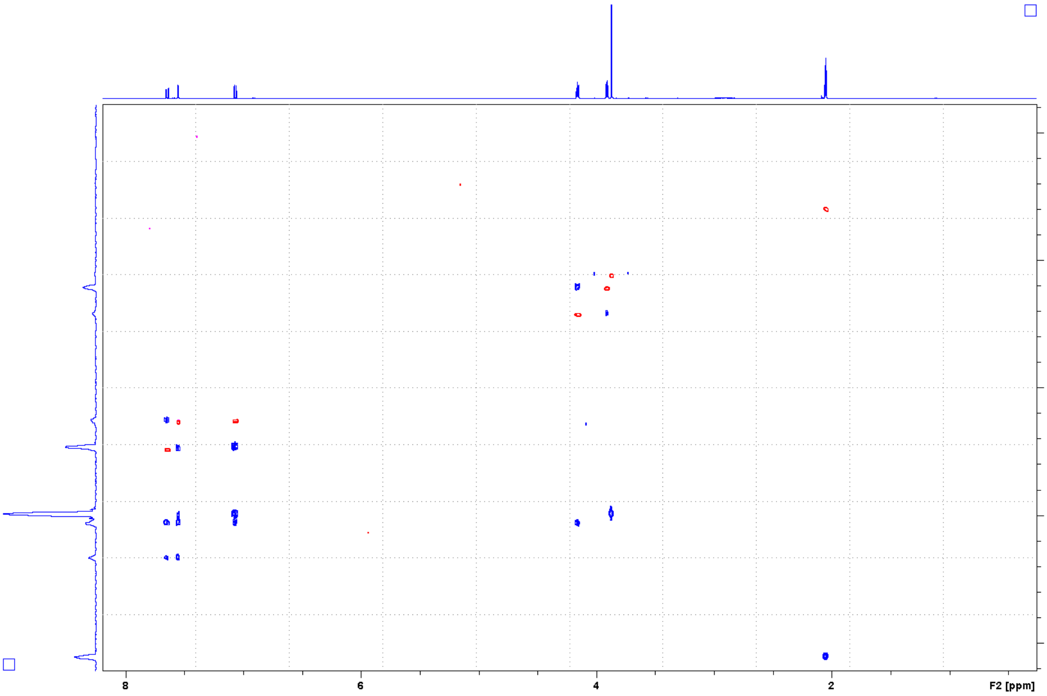


Figure 33: *HSQC- (red) and HMBC-NMR (blue) of product from experiment 10*

Table 28: *Relation between ^{1}H-NMR (**Figure 31**) and ^{13}C-NMR (**Figure 32**) based on HSQC-NMR (**Figure 33**):*

Peak	**^{1}H-NMR**				**^{13}C-NMR**
	Shift [ppm]	**Multiplicity**	**J [Hz]**	**Integration [a)]**	**Shift [ppm]**
Acetone d_6	2.05	p	2.2	-	29.92
A	2.85	br s	-	2 (1)	- (OH)
B	3.87	s	-	3	56.3
C	3.91	t	5.1	2	61.3
D	4.16	t	5.2	2	71.6
E	7.07	d	8.5	1	113.2
F	7.55	d	2.0	1	113.7
G	7.64	dd	8.4, 2.0	1	124.5
H	10.85	br s	-	1	- (OH)

[a)] Numbers in parentheses are what these integrals are supposed to be.

Table 29: *Cross peaks found in **Figure 33**:*

Carbon peak	Cross peak	Bond distance [a]	Deduction
B	H_B	^1J	Confirms relation found in **Table 28**
C	H_D	^2J	Confirms environments C and D to be located closely
D	H_C	^2J	Confirms environments C and D to be located closely
E	H_G	^2J	Confirms environments E and G to be located closely
F	H_G	^3J	Confirms environments F and G to be located closely
124.0	H_E	^3J	Aromatic carbon where the carboxylic acid is substituted
G	H_F	^3J	Confirms environments F and G to be located closely
150.2	H_B H_E H_F	^3J ^3J ^2J	Aromatic carbon where the methoxygroup is located
153.9	H_D H_E H_F H_G	^3J ^2J ^3J ^3J	Aromatic carbon where the 2-hydroxyethoxygroup is located. Shows that environment D is closer to the aromatic part than environment C, thus confirming the relative locations of C and D.
167.5	H_F H_G	^3J ^3J	Confirming the locations of environments G and F in ortho-position to the carboxylic acid.

[a] Based on how strong the cross peaks were relative to each other.

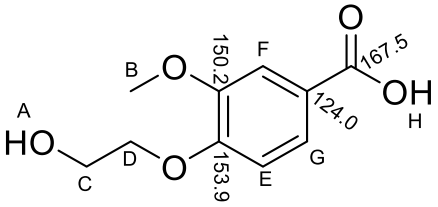
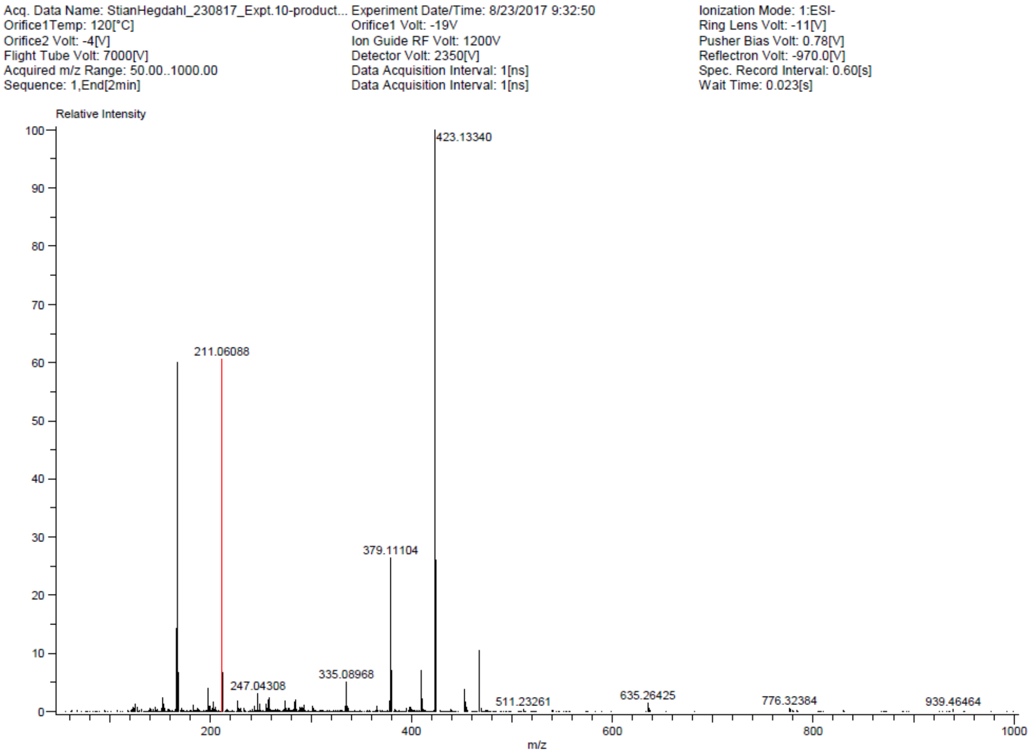


Figure 34: *4-(2-hydroxyethoxy)-3-methoxybenzoic acid, with chemical environments indicated*

The DART-MS of the product from experiment 10, shown in **Figure 35** and **Table 30** shows the expected $[M-1]^-$ and $[2M-1]^-$ within reasonable margins of error. In addition, two peaks at $[M-45]^-$ (assumed) and $[2M-45]^-$ are seen, which is the product after a cleavage of the carboxylic acid. This is again a sign that the reaction took place at the hydroxy-group as the cleaved group would otherwise be a larger difference than $[M-45]^-$.



Acq. Data Name: StianHegdahl_230817_Expt.10-product... Experiment Date/Time: 8/23/2017 9:32:50 Ionization Mode: 1:ESI-
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Orifice2 Volt: -4[V] Ion Guide RF Volt: 1200V Pusher Bias Volt: 0.78[V]
Flight Tube Volt: 7000[V] Detector Volt: 2350[V] Reflectron Volt: -970.0[V]
Acquired m/z Range: 50.00..1000.00 Data Acquisition Interval: 1[ns] Spec. Record Interval: 0.60[s]
Sequence: 1,End[2min] Data Acquisition Interval: 1[ns] Wait Time: 0.023[s]

Figure 35: *DART-MS of product from experiment 10*

Table 30: *Description of DART-MS found in* ***Figure 35****:*

Expt.	Found mass	Calculated mass	Mass difference [mmu]	Possible formula
10	211.06088	211.06065	0.23	$C_{10}H_{11}O_5$
	423.13340	423.12913	4.3	$C_{20}H_{23}O_{10}$

5.2 Polymerization

Table 31 shows the reaction conditions of the polymerizations, as well as the yields and the results of the DSC. As only parts of the polymers were dissolved in DCM/CF_3COOH, the non-soluble parts are set to sample X.1. Samples X.2 (in which X is the experiment number) are the parts that were not dissolved in $CHCl_3$, and samples X.3 are the samples that dissolved in $CHCl_3$ and precipitated in methanol. Based on the solubility of these samples, an assumption was made that samples X.1 had a higher average molecular weight than samples X.2, and that samples X.2 had a higher $\overline{\mathrm{Mw}}$ than samples X.3. This was supported by the estimation of molecular weights based on experiment 7, in which sample 7.2 has a higher $\overline{\mathrm{Mw}}$ than sample 7.3. The results of experiment 14, however, contradicts this hypothesis. A more detailed look into the thermic results are done in Chapters 5.2.1 and 5.2.2.

The estimations of the yields are based on the weight of the product divided by the weight of the imagined product if the polymerization were to result in one single polymer with 2 hydrogens and 1 oxygen removed from each of the monomeric units.

Table 31: *Polymerization and characterization based on DSC of 4-(2-hydroxyethoxy)-benzoic acid (R = H) and 4-(2-hydroxyethoxy)-3-methoxybenzoic acid (R = OMe):*

Expt./ Sample	R	Reaction conditions [a)]			Product				
		n(reactant) [mmol]	Reaction T [°C]	Reaction time [h]	T_g [°C]	T_m [°C]	ΔH_m [J/g]	$\overline{\mathrm{Mw}}$ [b)] [kg/mol]	Yield [%] [c)]
7.2	H	2.62	215	18	79	215	47	19	71.4 [d)]
7.3					78	214	48	18	
8.2	H	2.82	240	21	78	212	43	21	76.2
8.3					n.d.	n.d.	n.d.	n.d.	0.45
9.2	H	13.8	240	21	77	213	47	18	97.5
9.3					n.d.	n.d.	n.d.	n.d.	0.60
11.1	OMe	11.9	240	21	n.d.	271	109	n.d.	17.6
11.2					n.d.	271	122	n.d.	77.7
11.3					63	217 / 242	16 / 9	27 / 30	0.63
12.1	OMe	12.1	240	21	n.d.	266	120	n.d.	38.0
12.2					n.d.	265	94	n.d.	59.5
12.3					n.d.	n.d.	n.d.	n.d.	0.12
13.1	OMe	12.3	240	21	n.d.	269	126	n.d.	74.8
13.2					n.d.	264	108	n.d.	30.2
13.3					n.d.	n.d.	n.d.	n.d.	0.06
14.1	OMe	7.21	240	21	n.d.	n.d.	n.d.	n.d.	13.0
14.2					100	260	90	8	82.1
14.3					73	213	24	27	1.96

[a)] See **Scheme 4**. [b)] The $\overline{\mathrm{Mw}}$s are found by a model not yet published by Csaba Fodor (University of Groningen)[36]. [c)] The yields are estimations based on weight. More information is found below. [d)] The specific yields of samples 7.2 and 7.3 were not found. The yield given is the total of these.

Table 32 shows the appearances of the products. A trend is seen from samples X.1 to X.3 that the polymer becomes lighter, going in general from a dark brown, to a grey and onto a beige powder for experiments 11 – 13. The same trend is seen of the remaining experiments as well. Some changes are between them, but a darker sample X.1 and a lighter sample X.3 is generally seen. Sample 14.1 was the largest exception, as this was a black solid mass that stuck to its filter paper. A picture of this is attached in appendix C.

***Table 32:** Appearances of products of polymerizations:*

Sample	Appearance	Sample	Appearance
7.2	Off-white powder	12.1	Brown powder
7.3	White powder	12.2	Grey powder
8.2	Brown powder	12.3	n.d. (only traces)
8.3	White powder	13.1	Brown powder
9.2	Beige powder and brown sheets	13.2	Grey powder
9.3	n.d.	13.3	n.d. (only traces)
11.1	Brown powder	14.1	Black solid
11.2	Grey powder	14.2	Grey powder
11.3	n.d. (only traces)	14.3	Beige powder

5.2.1 Starting with 4-(2-hydroxyethoxy)-benzoic Acid

Experiments 7, 8 and 9 were using 4-(2-hydroxyethoxy)-benzoic acid from experiment 5 as a monomer. As seen in **Table 6**, the total yields of these three experiments were 71.4 %, 76.7 and 98.1 %, respectively. This polymer did not result in a sample X.1 as all batches were completely dissolved in DCM/CF_3COOH. Sample 9.2 showed two different colors, as seen in **Table 32**. These were separated manually and analysed individually and are mentioned as “sample 9.2 – beige powder” and “sample 9.2 – brown part”. In general, the products of these experiments go from a darker color to a lighter color from samples X.2 to samples X.3

The IR spectrum of sample 7.3, shown in **Figure 36**, shows no signs of a stretch from -OH, neither from a hydroxy-group nor a carboxylic acid. This gives an indication that the polymer has been formed, at least until a degree of polymerization in which the end groups are not detectable by IR. A literature search was done to find a level of detection, either in terms of chain length of oligomers / polymers, or in terms of concentration, but none were found. The IR shows a peak at 2954, indicating the aliphatic group of the ester. In addition, the peak indicating the carbonyl has been shifted from 1677 cm^{-1} of the monomer to 1712 cm^{-1} of the polymer, indicating a change from the carboxylic acid of the monomer, to an ester in the polymer. The IR spectra of all samples from experiments 7 – 9 shows the same trends. These are found in appendix E.

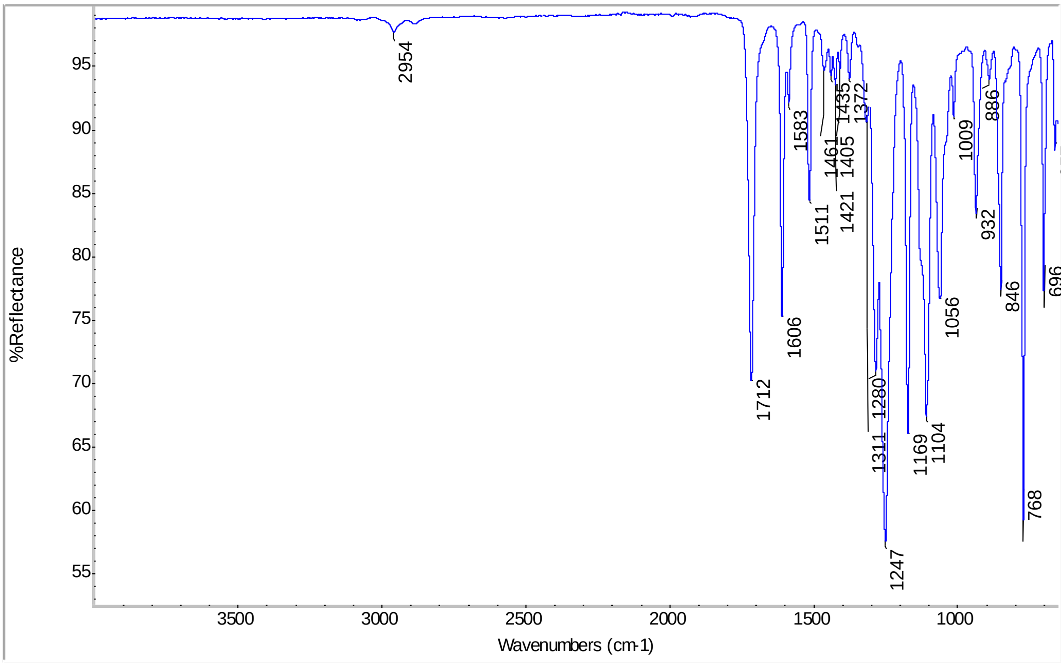

Figure 36: *IR of sample 7.3*

The results from the DSC are found in **Table 31**. The glass transition temperatures, as well as the melting temperatures and the enthalpies of melting, are quite similar to each other, however some changes are found, which gives different estimations of $\overline{\mathrm{Mw}}$. As mentioned in Chapter 5.2, sample 7.2 is estimated to have a higher average molecular weight than sample 7.3, which corresponds with an assumption that the easier soluble polymers are of smaller Mw. Samples 8.2 and 9.2 were of such small amounts that these were not analysed by DSC.

Samples 7.2, 8.2 and 9.2 were sent to GPC analysis, but the measurements were shut down by the GPC instrument due to the increasing pressure on the column. All samples were injected several times, but were shut down every time. A new column has been ordered, but did not arrive in time.

Sample 7.3 was analysed by NMR to find an estimate of the molecular weight. This was done by looking at the diffusion coefficient, given on the y-axis of **Figure 37**, and plotting this into a standard curve made from polymers with known sizes. The peak used for this estimate was the one at 1.24 ppm as the other two are DMSO d_6 and water. A diffusion coefficient of $2 * 10^{-10}$ m^2/s was measured, which resulted in an estimate of the average molecular weight between 10 and 20 kDa. This corresponds with the estimate of 18 kg/mol based on DSC from **Table 31**.

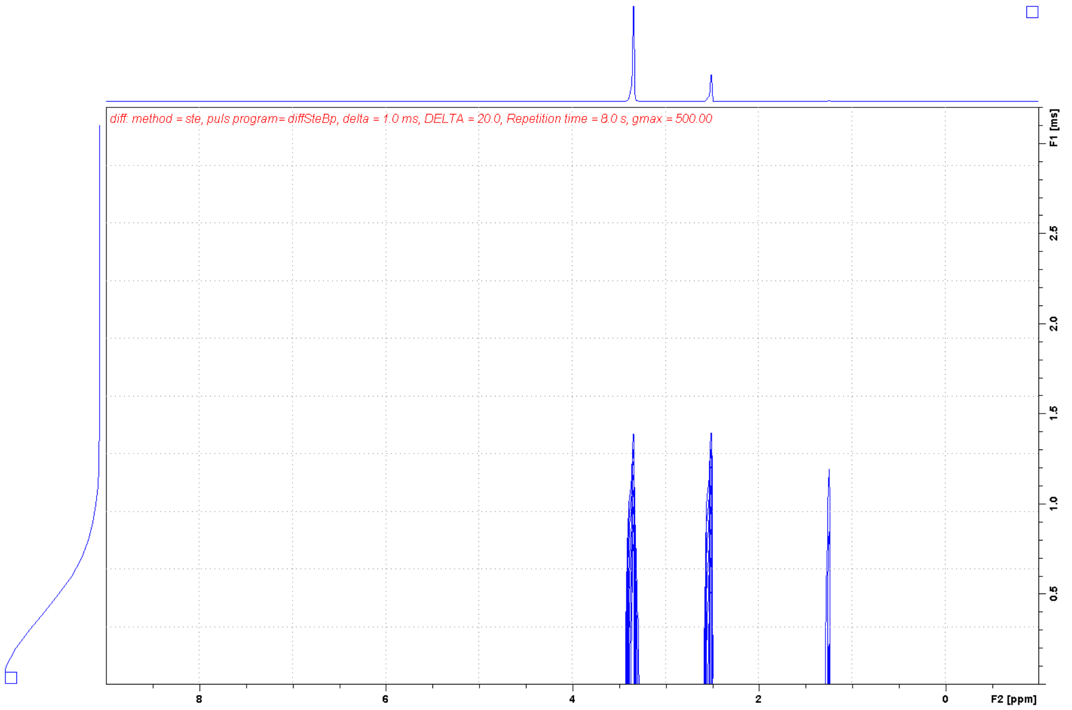

Figure 37: *DOSY-NMR, of sample 7.3*

Elemental analysis was done of samples 9.2 – beige powder and 9.2 – brown part. A table showing the analysis results is shown in **Table 33**. This shows a difference in the mol% of carbon and oxygen from the beige powder to the brown parts, however these numbers don't correspond to the monomeric unit, nor the oligomer or polymer, indicating an impurity in the samples, making all these numbers wrong as the mol% of oxygen is calculated based on an assumption that no other nuclei is present, and as these are percentages based on the total mass analysed, and in that any impurities as well.

Table 33: *Results from elemental analysis of samples from experiment 9:*

Sample	N [mol%]	C [mol%]	S [mol%] a)	H [mol%]	O [mol%] b)
9.2 – beige powder	0.0517	44.0	0.00583	37.3	18.7
9.2 – beige powder, 2nd run	0.0616	43.7	0.0102	37.9	18.4
9.2 – brown part	0.0681	42.6	0.0162	36.3	21.0
Calculated for monomer, oligomer and polymer					
n =	**N [mol%]**	**C [mol%]**	**S [mol%] a)**	**H [mol%]**	**O [mol%] b)**
1 (monomer)	0	39.1	0	43.5	17.4
10	0	44.3	0	40.4	15.3
20 000 (stabilized)	0	45.0	0	40.0	15.0

a) The instrument is not calibrated for S. b) The amount of oxygen is calculated based on the other percentages subtracted from 100 %.

Figure 38 shows a solid-phase ^{13}C-NMR of sample 9.2 – beige powder. This spectrum shows 9 peaks at roughly the same positions that the peaks of the monomeric unit were seen. A splitting of the two chemically identical carbon environments of the aromatic ring has happened as the product is now more locked to its physical position instead of turning around its own axis freely.

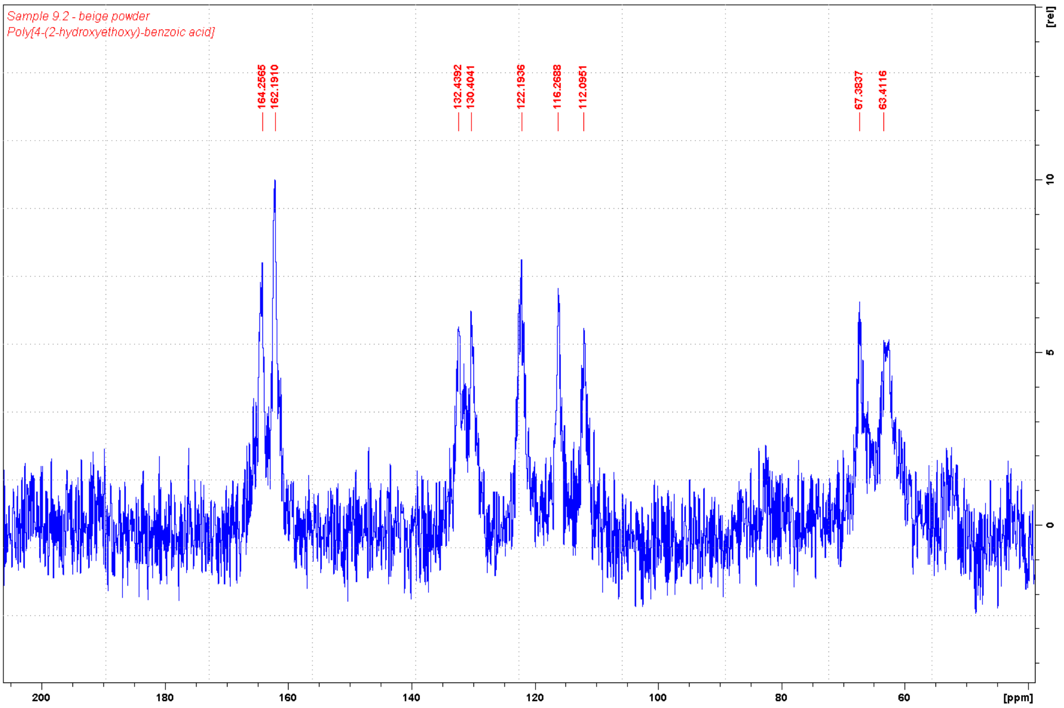

Figure 38: *Solid-phase ^{13}C-NMR of sample 9.2 – beige powder*

5.2.2 Starting with 4-(2-hydroxyethoxy)-3-methoxybenzoic Acid

Experiments 11 – 14 were using 4-(2-hydroxyethoxy)-3-methoxybenzoic acid from experiment 10 as a monomer. As seen in **Table 7**, the total yields of these experiments were 96.0 %, 97.7 %, 105 % and 97.0 %, respectively. As explained in Chapter 5.2, these numbers are estimates and thus somewhat uncertain.

Table 31 shows the yields of each sample individually, and a significant change in the relative yield of sample X.1 is seen from experiment 11 to 12, and further to 13. Experiment 12 and 13 were done in a rotary evaporator, which seems to have an effect on these relative yields, as the yields of 12.1 and 13.1 is a lot larger than that of 11.1. Experiment 14 however, contradicts this observation with the lowest yield of sample X.1 of all four experiments.

During experiment 14, some changes from the other experiments were noted. Firstly, the stirring was not as efficient as for the previous two experiments as there were now less chemicals in the round bottomed flask, resulting in the compound sticking to the round bottomed flask instead of being vigorously stirred by the combination of rotation from the rotary evaporator and the magnetic stirrer. Secondly sample 14.1 is, as seen in **Table 32**, different from the other samples X.1 as it was a black substance that stuck to the filter paper, instead of a brown powder like the rest. In addition, the filtrates during the workup had a light-yellow color, while this was blank for the previous experiments.

Table 31 shows the results from DSC. Due to the missing T_g, no $\overline{\mathrm{Mw}}$ could be estimated for experiments 11 – 13. Sample 11.3 has a T_g of 63 °C, T_m of 217 / 242 °C and ΔH_m of 16 / 9 J/g. These numbers are somewhat odd as the melting temperature and enthalpy of melting has two values. As seen in appendix D, the DSC of sample 11.3 does not look as though it worked properly. Based on this, the results of this DSC analysis is not given focus as it seems to not give a good representation. By looking at the yield, it is seen that a very small amount was received, and this might not have been enough to do a proper analysis by DSC. A difference is seen of the ΔH_m from samples X.1 to samples X.2, as this is increasing for experiment 11, but decreasing for experiment 12. This does not correspond to the hypothesis that samples X.1 are of larger $\overline{\mathrm{Mw}}$ than samples X.2, as one of these indicate a lower molecular weight for sample X.1 than for sample X.2. The hypothesis is also contradicted by the results from experiment 14, in which sample 14.3 has a higher $\overline{\mathrm{Mw}}$ than sample 14.2.

The IR spectra of samples 11.1 – 11.3 are seen in **Figure 39**. Neither of these show any traces of the end groups as neither the OH-stretch from the carboxylic acid, nor the hydroxyl-group is visible. This indicates a degree of polymerization high enough for the end groups to be non-detectable by IR. A peak at 2962 / 2963 cm^{-1} indicates the aliphatic group of the ester, whose carbonyl stretch can be seen at 1702 – 1706 cm^{-1}. This has shifted towards higher wavenumbers compared to the carboxylic acid of the monomer as this was seen at 1670 cm^{-1}. No tailing effect towards this wavenumber is seen, again giving some indications to the degree of polymerization. The C=C double bond of the aromat can be seen at 1598 – 1600 cm^{-1}. The same trends described here can be seen for the samples from experiments 12 – 14 as well. The spectra from these experiments are found in appendix E. The spectrum of sample 14.1 has one extra peak at 1786 cm^{-1}, which has not been identified.

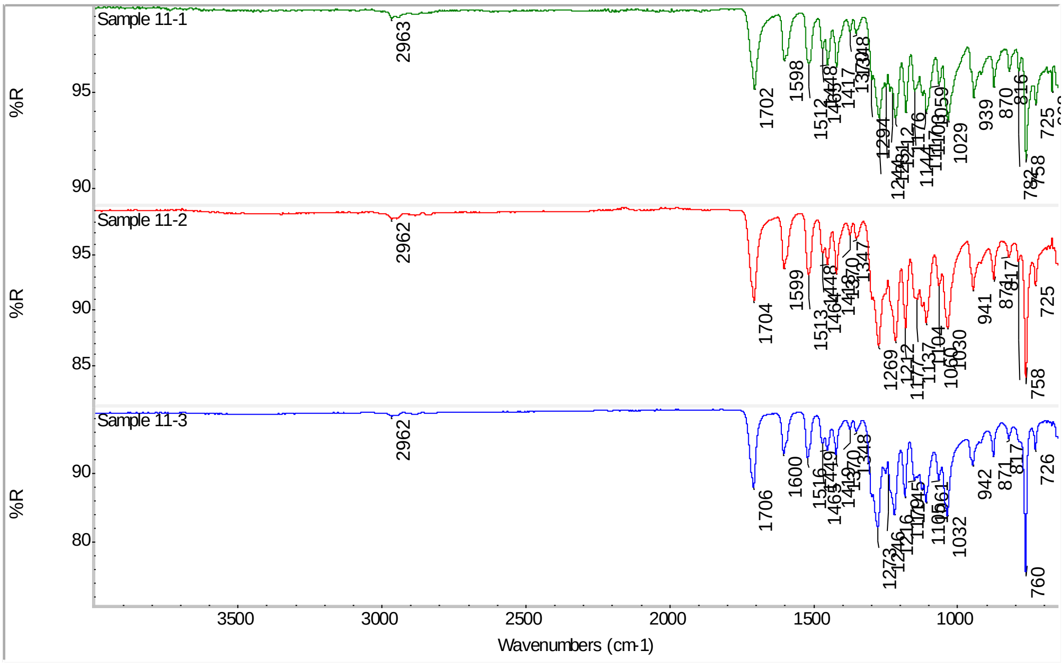

Figure 39: *IR of products from experiment 11 (sample 11.1 in green, sample 11.2 in red, sample 11.3 in blue)*

As the reaction is done with the monomer and the catalyst, not much can contribute to the impurities of the polymers. To see whether the catalyst is still in either of the samples, samples 11.1 – 11.3 were analysed by DART-MS to look for the catalyst in specific. This showed no traces of the catalyst, indicating the samples to be relatively pure.

5.2.3 Crystallinity Indications

The IR analyses from all the polymerizations were combined to look for trends that might indicate more or less crystallinity relative to the other samples. As samples X.1 proved to be less soluble than samples X.2, which again were less soluble than samples X.3, in addition to a missing T_g from the DSC of experiments 11 – 13, a hypothesis was formed that samples X.1 has a higher degree of crystallinity than the remaining samples, and samples X.3 is more amorphous.

Figure 40 and **Figure 41** show the carbonyl peak for experiments 7 – 9 and experiments 11 – 14, respectively. The position of each peak is presented graphically in **Figure 42**, and by looking at both experiment 11, 12 and 13, the position of the carbonyl peak is increasing in frequency from samples X.1 to X.3. This is also the case for sample 14.2 to 14.3, however sample 14.1 has a higher wavenumber than sample 14.2, which contradicts this trend. Sample 14.1, together with sample 13.3, was taken on a filter paper and a glass filter paper, respectively. Spectra of pure filter paper and glass filter paper was taken to subtract from the spectra of the samples (spectra of both pure filter papers and samples

13.3 and 14.1 before subtraction are included in appendix E), however this makes the acquisition different from the remaining spectra. Experiment 7 only have sample 7.3 analysed, however this has the highest wavenumber of all recorded spectra. From experiment 8, the same trend is seen as previously, where sample 8.3 has a higher frequency than sample 8.2. In experiment 9 this is not the case as sample 9.2 – beige powder and sample 9.3 has about the same frequency, though this being a bit lower for sample 9.2 – brown part. In total, the position of the carbonyl peak seems to support the hypothesis of crystallinity with some exceptions.

By looking at the peak width at half the peak height, shown in **Figure 43**, no clear trends are visible, thus contradicting the hypothesis mentioned above.

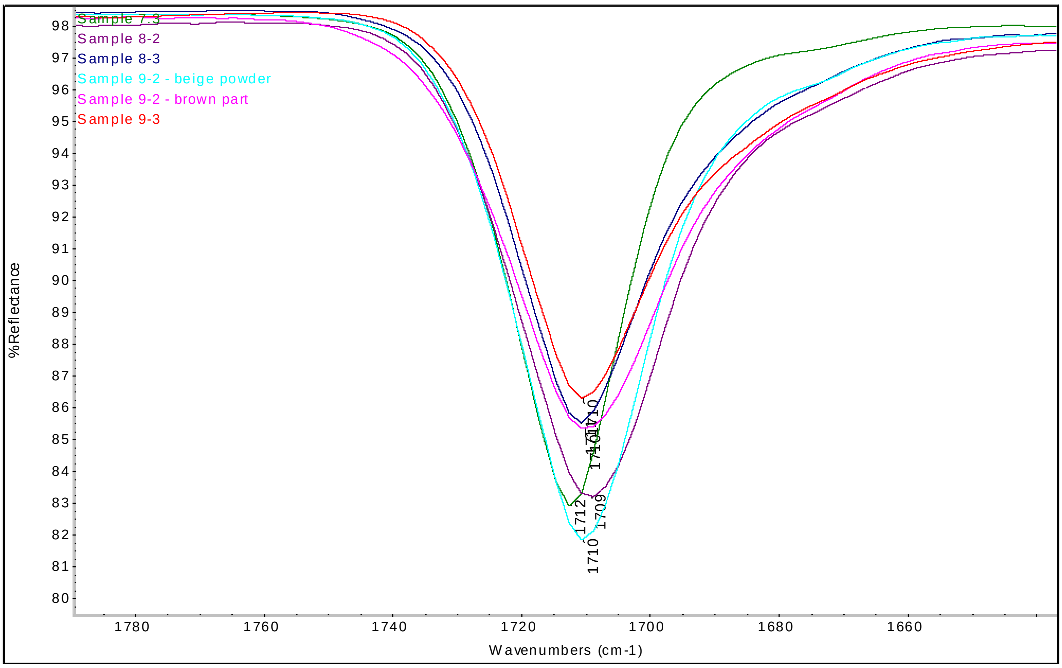

Figure 40: *IR of all products from experiments 7 – 9, showing only the peak of the carbonyl*

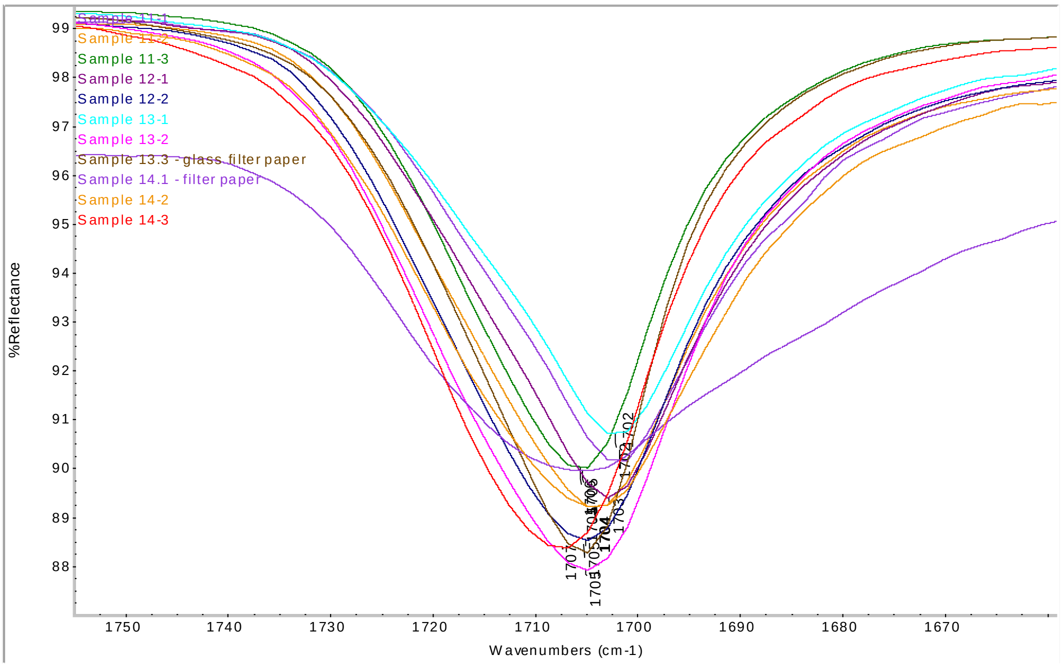

Figure 41: *IR of all products from experiments 11 – 14, showing only the peak of the carbonyl*

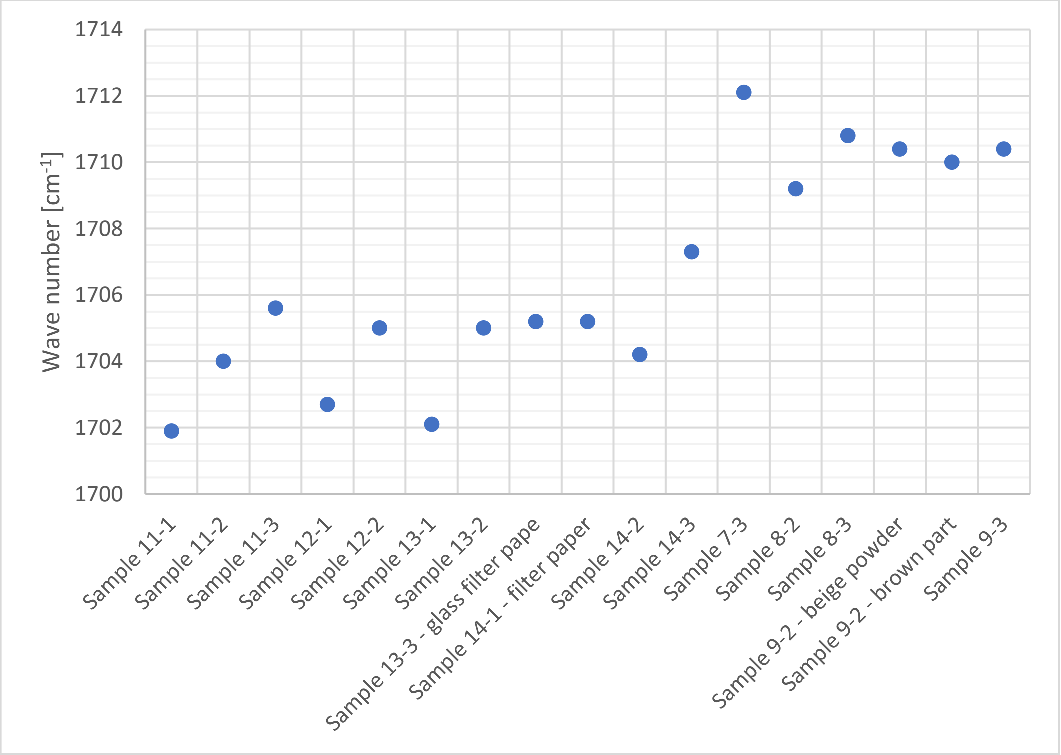

Figure 42: *Position of the carbonyl peak for all polymers*

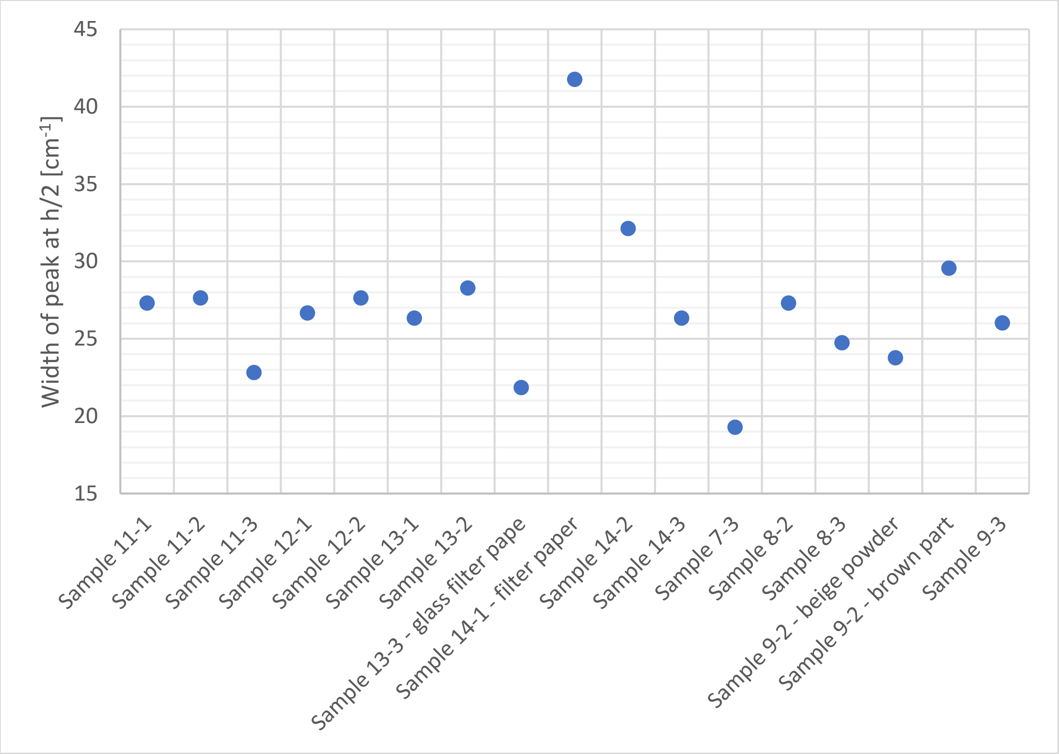

Figure 43: *Peak width at h/2 for all polymers*

6 Discussion

This chapter will discuss the results given in Chapter 5, first from the monomer synthesis, and later from the polymerization, followed by an overall comparison with the results published by Mialon et. al. Lastly, a discussion of the environmental friendliness of the process is discussed.

6.1 Monomer Synthesis

The monomer synthesis was performed 7 times with adjustments of the experimental variables, first to find a working method and then to increase the yields. The discussion of the monomer syntheses will thus be divided into the preliminary experiments, focusing on adjusting variables to find a working method, and full-scale experiments, focusing on adjusting the variables to increase the yields and to produce the monomer for further reaction. The structure elucidations will also be discussed, before a discussion regarding the reproducibility of the synthesis, and lastly the factors that reduced the yields.

6.1.1 Preliminary Experiments

The preliminary experiments were started by attempting to duplicate the work of Mialon et. al.[21]. This was tried twice, in equal scale and after a scale reduction (see Chapter 4.1.1), but neither of the experiments were successful. Analyses of the products in experiments 1 and 2 showed it to be the same as the starting material, though they were somewhat more impure than when starting. The parts of the products that were insoluble in acetone are assumed to be salt residues, based on the melting point analysis. As the product of later experiments have proved soluble in acetone, the conclusion is that experiments 1 and 2 did not result in the desired ether. Several variables were changed as a result of this, and the starting material was changed from vanillic acid to 4-hydroxybenzoic acid. This was due to the lower price of the 4-hydroxybenzoic acid compared to vanillic acid together with an assumption that the methoxy group should not change the reaction by too large of a factor. Experiments 3 and 4 improved, and the product was obtained, however in low yields, as seen in **Table 10**. The analyses show a clear indication of the desired product, however the starting material is also present. The exception of this is sample 4.8, which shows a pure product with only minor impurities, as detected by DART-MS (see **Figure 18**). As no other analyses found these impurities, the MS instrument was controlled for impurities by checking the MS from the TIC just before the sample was applied, but no impurities were found.

The range of analyses done for each experiment was also varied. Although melting point analysis, IR, and NMR gave results, several other methods of analysis were tried. GC-FID and GC-MS did not provide any result, as no product was detected due to lack of volatility. DART-MS on the other hand, provided extra confirmation regarding the product, and was used in future experiments.

The overall outcome of the preliminary experiments was that experiments 1 and 2 did not yield the desired product, while experiment 3 and 4 gave low yields, however these products were impure as there were found starting material residues as well.

6.1.2 Full-Scale Experiments

Experiments 3 and 4 were partly successful in that the product had been achieved, however in small yields and with various amounts of the starting material. Experiments 5 and 6 were done in the attempt of an increased yield of the product, by increasing the relative amount of 2-chloroethanol, and by changing the starting material from 4-hydroxybenzoic acid to methyl 4-hydroxybenzoate (see Chapter 4.1.3). Experiment 5 was considered a success, yielding 49.7 % of the desired product. Analyses of the product resulted in a pure product, with no visible residue from the starting material, nor its carboxylic acid derivative.

A comparative experiment was done in experiment 6, exchanging the 2-chloroethanol and sodium iodide with 2-bromoethanol. This resulted in a reduced yield of 38.2 % (**Table 10**). Compared to the yield of experiment 5, this indicated that the catalyst did help the reaction as the bromine would otherwise be a better leaving group and thus increase the yield. An important variable to note between these experiments, is that experiment 6 was done in a smaller scale than experiment 5.

The switch from 4-hydroxybenzoic acid to methyl 4-hydroxybenzoate from experiment 4 to 5 had resulted in an increased yield, however it is assumed that this were due to the increase of the relative amount of 2-chloroethanol, and to the improved techniques used due to more experience of the procedure. These assumptions are done because the first reaction that takes place is the deprotonation of the carboxylic acid (see Chapter 1.4.1), or the cleavage of the ester. From this point onwards, the reactions are the same. As the next monomer synthesis aimed to try the reaction with the -3-methoxy-group on the aromatic ring, the assumption mentioned above supported the choice of using vanillic acid instead of using methyl vanillate for experiment 10.

Experiment 10 yielded 50.7 % of the product. The analyses of the product from this experiment showed the desired composition, with some minor traces of the starting material (see **Figure 31**). These traces were so small that no further purification was done. The products of experiments 5 and 10 were used for further polymerization for experiments 7 – 9 and 11 – 14, respectively.

The overall outcome of the full-scale experiments is a successful preparation of both the 4-(2-hydroxyethoxy)-benzoic acid in experiments 5 and 6, and of 4-(2-hydroxyethoxy)-3-methoxybenzoic acid in experiment 10.

6.1.3 Structure Elucidation

The elucidation of the crude product (sample taken from process 1G in **Figure 9**) from experiment 4, and of the product from experiment 10 provided information regarding the attached groups and their localization on the structures. One question was whether the 2-chloroethanol would react with the hydroxy-group or the carboxylic acid. The elucidation resulted in a clear conclusion that the product of the reaction was the desired ether and not the ester, as shown in **Figure 34**. This was supported by the MS of the products from experiments 5 and 6, as these showed a peak of $[M-45]^-$ (see **Figure 27** and **Figure 28**), which is the loss of a -COOH. This loss was also seen at the MS of experiment 10 (see **Figure 35**). It was also supported by observations of the carbonyl group of the IR, as this would have shifted towards higher wavenumbers if the product were the ester, and by the reaction itself, as the ester would react with the NaOH to produce the alkoxide again, as for the starting material.

The ^{1}H-NMR of the product from experiments 3 – 6 and 10 (see **Figure 25** and **Table 23** for experiments 5 and 6, and **Figure 31** and **Table 27** for experiment 10) did not match the published data from Mialon et. al.[21] as closely as expected, however due to the number of analyses done to confirm the compounds, the product is still considered to be the desired ether.

6.1.4 Reproducibility

Due to time limitations, the reproducibility of the monomer synthesis was not tested directly, as no experiment was run twice. Two quite similar experiments were however run, experiment 5 and experiment 10, which correspond closely. There is one important difference between these experiments, as experiment 5 was done starting from methyl 4-hydroxybenzoate while experiment 10 was done starting from vanillic acid (see Chapters 5.1.3 and 5.1.4). As the sodium hydroxide produces an alkoxide ion (see Chapter 1.4) from both the carboxylic acid and the ester even before the 2-chloroethanol is added, this variable should in theory be of no concern. As for the methoxy-group in experiment 10 compared to experiment 5, this is an unknown factor, and a variable to be aware of. The yields of these experiments are however quite similar, which, if these two variables are insignificant, could indicate that the synthesis is reproducible.

6.1.5 Loss Factors

The maximum yield of these experiments was 51 %. Several variables might contribute to this. Firstly, the conversion is not complete. The reaction was left for 3 days, but there was still starting material left that did not react. This was determined by NMR of the final products, such as experiments 3, 4 and 10, where some starting material was left in the sample. NMR of crude products, and also from sample 4.10, which is the evaporated filtrate after acidification (process 1G in **Figure 9**) from experiment 4, have also given this indication. In addition, side reactions might occur. In Chapter 5.1.2.2, ethylene glycol and 1,2-dichloroethane was found, which indicates a side reaction from the 2-chloroethanol, shown in **Scheme 5**. This was corrected with an increased amount of 2-chloroethanol starting from experiment 5. Any oligomer of ethylene glycol might be produced by this reaction and by this reduce the amount of 2-chloroethanol left for the intended reaction.

There is also a possibility that the 2-chloroethanol reacts with itself to produce ethylene oxide and HCl, however this ethylene oxide can produce the same product as the 2-chloroethane with the carboxylic acid, thus making no problem to the reaction, nor any impurities.

Another possibility is that the product again reacts with 2-chloroethanol in a new Williamson ether synthesis to produce 4-(2-(2-hydroxyethoxy)-ethoxy)-3-R-benzoic acid (in which R = H for experiments 1 – 6 and OMe for experiment 10), shown in **Figure 44**. This is suspected not to be removed during purification, and thus be a contamination in the final product. When looking for this compound in particular in the NMR analyses done, some very minor traces were seen, however these were so small that no definite conclusion could be made.

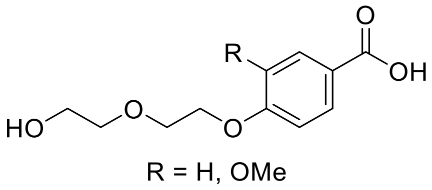

Figure 44: *Structure of possible side product*

6.2 Polymerization

The polymerization was performed 7 times. The aim was to increase the average molecular weight, by adjusting the variables to increase the total molecular weight. Based on the assumption that samples X.1 were of highest average molecular weight due to the solubility of the samples (see **Figure 10**), this would also increase the relative amount of samples X.1. The discussion will focus on the reactions and a comparison between the two methods of polymerization, before discussing the analysis results and the uncertainty of these. Further, the difficulty of reproducibility is discussed, and the hypothesis of crystallinity of the products themselves, but also within the stages of products. Then the contributions to a reduced yield and to a different relative yield of the three stages of product is discussed, before the similarities of the experiments are explained.

6.2.1 Reactions

Experiment 7 was done on an exploratory basis to establish a method for later polymerizations. Only a part of the product was taken aside for dissolving in chloroform (see procedure, Chapter 4.2.1 and process 2F – 2I in **Figure 10**). When the method was proven to work, the remaining part was dissolved in chloroform as well, but by this time it product did not dissolve in chloroform at all. A hypothesis to explain this observation is that the product had crystallized. For the analyses, the product initially separated by solubility was used.

Experiments 7 and 8 were done in a smaller scale than the others. Experiment 9 showed that by increasing the volume of the round bottomed flask, the loss of product was a lot smaller (see **Table 31**), confirming the observations that some reactant was lost because of the vacuum during the reaction, especially when the vacuum was reduced.
Experiment 11 compared to experiment 12 and 13 indicate that method 2, using the rotary evaporator for the polymerization (see Chapter 4.2.2), gives higher yields for sample X.1, and lower yields for samples X.2 and X.3 (see **Figure 10** for flowchart of the polymerization process, and **Table 31** for relative yields of the samples). Experiment 14 contradicted this indication by having the lowest yield of sample X.1 of all these polymerizations. This experiment had however been observed to differ from the others, both as the stirring had a reduced efficiency, as sample X.1 differed from the remaining ones, and as the filtrates showed a yellow color compared to the clear liquids of the previous experiments. Thus, experiments 13 is considered the most successful one.

6.2.2 Comparing Method 1 and Method 2

The method was changed into using a rotary evaporator for the polymerization to increase the effect of the stirring as this seemed to be a key factor for the reaction. A hypothesis was formed that the longer the stirring lasts, the longer the reaction will keep going. The rotary evaporator was thus tested, with positive results regarding the relative amount of sample X.1, which has been assumed to have the highest $\overline{\mathrm{Mw}}$ based on the solubility of the samples (see flowchart, **Figure 10**). This was, however, contradicted by the results of experiment 14 (see **Table 31**).

During the experiments using the rotary evaporator (Chapter 4.2.2), the magnet was observed to behave differently, as it sometimes was stirring normally at the bottom of the flask, while other times was turning with the round bottomed flask from the rotation of the rotary evaporator. A third behavior was something in between, where the magnet would stick to the round bottomed flask halfway up, but fall back down and continue stirring. The stirring was changing between these three pathways without any visible pattern.

From the limited number of experiments performed here, the best option seems to be the second method, using the rotary evaporator for the reaction (see Chapter 4.2.2). Also from a laboratory technical focus, this method was preferred as the crude product were not stuck to the glass flask, as it was for the first method (Chapter 4.2.1).

6.2.3 Analytical Results

As the IR spectra of the polymers showed no sign of the end groups (see **Figure 36** and **Figure 39**), this supported that the degree of polymerization was at least of a certain length, making the end groups such a small part of the polymer that they are no longer detectable by IR.

In experiment 7, the DSC indicated, as assumed in Chapter 6.2, that sample X.2 is of higher molecular weight than sample X.3 (see **Table 31**), however this assumption is contradicted by experiment 14, where the estimates show a larger polymer for sample 14.3 than for 14.2. Sample 14.2 is analysed by DSC twice with similar results. These results, together with the solubility of the samples (see Chapter 4.2.1), provide uncertainty as to which sample has the highest average molecular weight. A hypothesis is therefore made that the solubilities are not necessarily connected to the $\overline{\mathrm{Mw}}$. A similar $\overline{\mathrm{Mw}}$ is seen for samples 7.3 and 9.2. A difference in the $\overline{\mathrm{Mw}}$ of these should be expected by the previous hypothesis as this is two different fractions of the polymer. There is a considerable uncertainty to this estimate however, partly due to the high heating rate of the DSC that it is based on. More about this is found in Chapter 6.2.3.1. This heating rate also provides some problems for the estimations that sample 7.1 has a higher average molecular weight than sample 7.2 (see **Table 31**), as these are quite similar, and the uncertainty of the estimate is larger than the difference between the samples.

Several of the analyses did not show a T_g and were therefore not given an estimate of $\overline{\mathrm{Mw}}$. There are several possible reasons to the missing glass transition temperatures, the first being that the T_g might be below the starting temperature of the analysis. As the analysis has a quite high heating rate, the T_g might have been missed in the process as well, as this is just a small change to the heat flow.

The solid-phase NMR of sample 9.2 – beige powder showed the expected peaks, and in general the spectrum was similar to the monomer (see **Figure 38** for the solid-phase NMR and **Figure 26** and **Table 24** for the NMR of the monomer). The additional peaks are from the chemical environments that were identical in the monomer but differ in the polymer. The shifts of these peaks still seem similar for the polymer, however due to this being a solid-phase NMR and the product being a polymer, a free spinning state is not achieved, which is required for separating the two environments.

The DOSY-NMR of sample 7.3 (**Figure 37**) resulted in an estimate of the average molecular weight of between 10 and 20 kDa, which corresponds with the estimate of 18 kDa based on the estimations from DSC. For a more precise analysis, a standard curve should be made from polymers that are more similar to the product of this thesis than the polystyrene and poly(methyl methacrlyate) used by Guo, X. et. al.[42] A standard curve based on polyesters with both aromatic and aliphatic parts, such as PET, would be preferable.

The elemental analysis of samples 9.2 beige powder and 9.2 brown part did not give interpretable results, as the percentages did not fit a polymer of any length (see **Table 33**). According to the carbon percentage, the product should be an oligomer with n between 1 and 10, however this is not confirmed by either the hydrogen, nor the oxygen percentages. The hydrogen percentages indicate a higher percentage than for a highly polymerized polymer (the numbers indicated for n = 20,000 are the same as for n = 200,000), and the oxygen percentages indicate a lower percentage, and thus a lower degree of polymerization, than for the monomer itself. All this gives a clear indication that elemental analysis does not have sufficient precision to give relevant information regarding the degree of polymerization. As explained in Chapter 5.2.1, the numbers might have been wrong due to impurities in the sample, however the amount of impurities are limited, as found by DART-MS of the products from experiment 11 (see below). In addition, no literature is found that uses elemental analysis to get indications of molecular weight of a polymer.

As the only chemicals added to the reaction of the polymerization were the monomer and the catalyst, the number of possible impurities in the product is limited. As the catalyst had proven soluble in the solvents during experiments 7 – 9, it is logical to suspect that samples X.1 should not contain any impurities from the catalyst. This was checked for all three stages of samples from experiment 11 by DART-MS, which showed no traces of the catalyst in either sample. The analysis was done by analysing the catalyst itself to find the settings needed for fragmentation of this, and to find the fragments that is to be looked for in the samples. This was found to be $Sb_4O_5^-$, which was not found in the samples, thus giving clear indications of all the catalyst having been removed efficiently by the workup.

The GPC was not able to give any results from experiments 7 – 9 due to an increasing pressure in the column, which blocked the only available possibility of finding the $\overline{\mathrm{Mw}}$ by analysis.

6.2.3.1 Uncertainty of DSC and DSC-Based Estimation

The DSC has a method uncertainty of ± 1 °C for the T_m and T_g, and ± 5 J/g for the ΔH_m. For the derived estimates of $\overline{\mathrm{Mw}}$, this gives an uncertainty of ± 3000 g/mol. This is only based on the analytical data; the uncertainty of the estimation model itself further increases the range. To make this uncertainty smaller, the analysis could be performed with a slower heating rate. The uncertainty of the estimation of $\overline{\mathrm{Mw}}$ from DSC data itself is not known, as the model is proprietary and not yet published, and so cannot be evaluated here.

6.2.4 Reproducibility

The reproducibility of the polymerization, using the second method described in the experimental part, was tested in experiments 12 and 13. These proved to differ by the relative yields of samples X.1, X.2 and X.3 by a large factor, which increased the relative amount of sample X.1 (see **Table 31**). This showed that testing the reproducibility of the polymerization is not easily done. Another polymerization was tried, however due to time limitations it was scaled down, using what was left of the product from experiment 10. This experiment did not reproduce the results from either of the two previous experiments, confirming the difficulties of reproducibility. For this last experiment, a change in the stirring was observed as this was not as vigorous as for the previous two experiments, which might indicate that this is a key factor, as assumed in Chapter 6.2.1.

6.2.5 Crystallinity

A hypothesis that samples X.1 (insoluble in DCM/CF_3COOH, see **Figure 10**) were of a more crystalline state than the remaining, and that samples X.3 (soluble in chloroform) were more amorphous than the others, was made. This was based on the solubility of each sample due to the crude product from experiment 7 not being soluble in chloroform for the second batch of dissolution, after being partly soluble for the first batch (see Chapter 6.2.1). An overall higher level of crystallinity was also indicated for the poly[4-(2-hydroxyethoxy)-3-methoxybenzoic acid]. This hypothesis was supported when the DSC did not find a T_g for either of the samples from experiments 11 – 13, however this has not been verified further.

An evaluation of the relative crystallinity of the samples was done by looking at the carbonyl peaks from the IR spectra from all the polymers and comparing them, as seen in **Figure 40** to **Figure 43**. The positions of the peaks gave indications of a higher crystallinity for samples X.1 and a lower degree of crystallinity for samples X.3. As for the width of the peaks, no trends were seen, thus contradicting the indications of a difference in crystallinity. No definite conclusion can be drawn by this. As the literature is based on PET, it is unknown whether the same trends are expected of the polymers synthesized in this thesis. PET and the polymers produced here are fairly similar, which supports that this might apply to some degree in this case as well.

6.2.6 Loss Factors

The conversions of the reactions themselves are expected to be 100 % as all the monomer should react to some degree, even if only to an oligomer. Even so, yields of 100 % are never obtained, and there are several factors that might contribute to this. Firstly, the reaction takes place at 50 mbar, which makes it possible that some of the powder is sucked out of the flask, especially when the pressure is reduced. This could be seen during the first experiments, as the adaptor that connected the flask to the vacuum was covered with a white powder. To minimize this effect, the pressure was lowered by small steps until the desired pressure was obtained.

Secondly, the yields are estimations based on the mass of the starting material, with 2 moles of hydrogen and 1 mole of oxygen removed for each mole of starting material, for the formation of water (see **Scheme 4**), which evaporates and is removed from the reaction. This is an assumption which is more inaccurate the lower the degree of polymerization is, as each produced polymer molecule contains 2 hydrogens and 1 oxygen atom more than this estimate. The estimated average molecular weights are thus not used to find the yields due to the uncertainty of these estimates (see Chapter 6.2.3.1).

6.2.6.1 Contributions to a Different Relative Yield

The reasons for a reduced yield mentioned above describes the uncertainty of the total yield, however there are also some factors that will affect the relative yield of samples X.1, X.2 and X.3. These factors will be discussed in this chapter.

Firstly, the temperature of the oil bath was off its set value to some extent. The largest observed difference was 8 °C below the set temperature, however as the reaction went overnight, this might have been larger at some point without it being observed. This might provide a variation in the degree of polymerization, and thus a different relative yield of each of the products. However, such a small temperature change will probably not do much change to the reaction.

Secondly, as the first stage of product is not totally dissolved in the solvents that have been used, all transfers include recovery of solid products, and are not quantitative transfers with the help of a solvent. This will increase the loss by transfer. This concerns both the first transfer of all soluble products and during filtration (processes 2B and 2C from the flowchart given in **Figure 10**). A factor here is therefore how thorough the transfer is.

Another point of uncertainty is the dissolving in DCM / CF_3COOH. As DCM evaporates quite fast, the ratio between these is not necessarily 1/1 at the time of filtration, thus changing the solvent composition for the dissolution. This may increase or decrease the solubility, depending on the ratio at the time of filtration and thus separated from the solvent. This is not as relevant for experiments 7 – 9 (producing poly[4-(2-hydroxyethoxy)-benzoic acid]) as for the others, as these were completely dissolved.

In addition, comparing experiments 12 – 14, experiment 12 was a first try using the rotary evaporator, while experiments 13 and 14 used the previously tested method found in experiment 12, thus improving the techniques of the procedure.

Lastly, for experiments 11 – 14, the equipment used from the reaction and until sample X.1 was filtered off (processes 2A until and including 2C in **Figure 10**) did not get completely clean after the process. As the same equipment was used every time, this became a source of contamination. These contaminations would be the polymer of the previous synthesis, making the possibility that some polymer from the previous experiment could be included in the results of the ongoing experiment. This is a factor for experiments 12 – 14, as experiment 11 was done in clean equipment. To minimize this case, the equipment was cleaned several times between the experiments, both with different solvents (DCM/CF_3COOH, $CHCl_3$, acetone), scrubbed thoroughly soap and water, and in a sodosil bath to make sure that any remaining contaminations to the equipment was thoroughly stuck to the glassware and thus hard to transfer at a later experiment.

6.2.7 Similarities

To ensure that the experiments are as comparable as possible, the equipment used was the same for each experiment. The only exceptions to this are the new equipment for upscaling after experiment 8, the new equipment needed for doing the reaction as method number 2 (in Chapter 4.2.2) describes instead of method number 1 (from Chapter 4.2.1), and equipment used only once, such as filter papers. The temperature and pressure settings were increased and decreased by the same steps. The stirring was set to the same settings, but as the rotary evaporator has no exact settings for this, this was done to a visually equal level of stirring. As the DCM/CF_3COOH mixture could change its ratio if the DCM evaporated, a new batch was made for every experiment, and the solvents were always added in the same order. As far as possible, the time used for dissolving the product and until filtration was kept the same for each experiment. All containers that contained the solvent mixture were kept in closed containers as much as possible, and all solvents were used in the same amount until and including the point of filtration for all experiments. For experiment 14, this was somewhat different due to the change of scale. The equipment used was still the same. The amount of solvents and the time used for dissolving and filtrations were reduced, but not by as much as to the same scale.

6.3 Overall Comparison of Results

This Chapter will compare the results of the monomer synthesis and of the polymerization of this thesis to those of Mialon et. al.[21].

The monomer synthesis was not reproduced when the factors were kept the same, nor when scaled down (see Chapter 5.1.1 for all results, see **Figure 13** for ^{1}H-spectra). In addition, these experiments gave problems regarding the solubility of the solids in the limited amount of solvents as they were just barely soluble. When the factors had been changed to give a functioning synthesis, the yield of 72 % published by Mialon et. al. was still not achieved as experiment 10 yielded 51 % (see **Table 10**). As for experiments 3 – 6, starting with 4-hydroxybenzoic acid, these achieved a maximum yield of 50 %, while Mialon et. al. achieved 57 %. As mentioned in Chapter 6.1.3, the ^{1}H-NMR of experiments 3 – 6 (see **Table 15** for experiments 3 and 4, and **Table 23** for experiments 5 and 6) and 10 (see **Table 27**) did not match the published data from Mialon et. al. The deviation of the peaks is not equal for all chemical environments, removing the possibility that the calibrations could have differed. Two differences are found between the analyses, as Mialon et. al. used a 300 MHz NMR and $CDCl_3$ as the solvent during acquisition of the spectra. The spectra in this thesis was taken on a 500 MHz NMR (see Chapter 4.3.1), using acetone-d_6 for solvent. No impurities have been mentioned by Mialon et. al. for comparison.[21]

The polymerizations of both products gave a higher total yield than reported by Mialon et. al., who published a yield of 70 and 79 %, respectively, while the work of this thesis yielded 98 and 96 – 105 %, respectively (see **Table 31**). No product is mentioned as insoluble in DCM/CF_3COOH in the article, as for samples X.1. Samples X.2 and X.3 (insoluble in chloroform and soluble in chloroform, respectively, see **Figure 10**) were not separated in the article, thus making a change to the thermal analysis and to the average molecular weight, regarding which fractions are analysed. Mialon et. al. reports a T_g of 80 °C and a T_m of 203 °C for poly[4-(2-hydroxyethoxy)-benzoic acid], which is the polymer produced in experiments 7 – 9 of this thesis. DSC of these polymers gave T_g of 77 – 79 °C and T_m of 212 – 215 °C (see **Table 31**). T_g has a close proximity to the values reported by Mialon, but a somewhat higher T_m. Mialon reports an average molecular weight of 23.9 kg/mol, found by GPC, while the ones estimated in this thesis are 18 – 21 kg/mol. These numbers have a close enough proximity to be considered the same, the uncertainty of the estimate taken into consideration.

Poly[4-(2-hydroxyethoxy)-3-methoxybenzoic acid], produced in experiments 11 – 14 of this thesis gave T_m in the rage of 213 – 271 °C and T_g in the range of 73 (63) – 100 °C, while most analyses were not able to find a T_g (see **Table 31**). Mialon et. al. reports of a T_m of 239 °C and a T_g of 71 °C. The T_m is within the range found in this thesis, while T_g is close to the T_g of sample 14.3. Due to the lack of determined glass transition temperatures, no clear conclusion can be reached regarding the similarity of the products.

In total, the results published by Mialon et. al. are in general achieved in this thesis as well.

6.4 Environmental Friendliness of the Process

The synthesis described here is done based on potentially lignin derived building blocks, but for the product to be environmentally friendly, all chemicals used should be given this focus, not only the building blocks themselves. The building blocks, being the vanillic acid and the 2-chloroethanol, can be derived from biomass. Vanillin is produced from lignin at Borregaard, as mentioned in Chapter 1.2.1.4, and

2-chloroethanol can be produced from ethylene glycol,[43] which might be derived from biomass, as used by Coca-Cola Company (see Chapter 1.3). The solvents used for the monomer synthesis is water and ethanol (see **Scheme 3**), which are both environmentally friendly, and the catalyst is sodium iodide. This is a salt industrially made by an acidic iodide that is reacted with sodium hydroxide,[53] which is possible to do while avoiding petroleum-derived chemicals. During the workup, diethyl ether is used. This can be produced from ethanol and sulphuric acid[54], both of which can be produced in a renewable manner.

As for the polymerization, the building block is the monomer produced in the monomer synthesis. The catalyst used, antimony trioxide (see **Scheme 4**), is found in nature as a mineral.[55] As for the solvents, none are used in the synthesis directly, however THF is used to homogenize the monomer and the catalyst (see Chapter 4.2.1). This is generally produced from petroleum-derived 1,4-butanediol.[54] Both DCM and chloroform (used in the workup, see **Figure 10**) should be easily produced from methane, which is a natural gas, and trifluoroacetic acid is a derivative of acetic acid, which can be produced from ethanol. Methanol, used for precipitations, can be produced from syngas.[7]

Electricity is used for the reactions, both for heating, stirring, evaporation etc. The environmental friendliness of the electricity is dependent on how the electricity is produced. In Norway, where the experiments have taken place, most electricity is produced by hydropower,[56] which is an environmental friendly solution.

As a result, all compounds used are relatively environmental friendly, or can be produced in an environmentally friendly manner if produced from e.g. bioethanol instead of ethanol derived from petroleum. THF is the exception, however this could be exchanged to any other solvent as long as the solvent dissolves both the monomer and the catalyst. For a larger scale, all solvent could also be distilled and thus used several times, for an even more environmentally friendly process.

6.5 Possibilities of Replacing PET

As stated in the title of this thesis, the goal of the project is to develop a product that can replace PET in as many daily usages as possible. For this to be true, the T_g and T_m of the product need to be in the same area as for PET. Industrial PET has T_g of 69 °C and T_m of 280 °C, as stated in Chapter 2. The T_g of the final product was in most cases not found, but in the cases where it was found, this was 73 (63) – 100 °C (**Table 31**), and the T_m was in the range of 213 – 271 °C. The glass transition temperatures that are found are close to the one of PET, and most temperatures of melting were in the higher part of the range mentioned above, which is also close to the one of PET, making a replacement possible.

In addition, the plastic properties themselves have to be tested. This includes tests like flexibility, impact properties and viscosity. If these tests are close enough to the required values, additives can be added to the polymer to get these results as wanted. These tests have not yet been performed, and so at this state it cannot be concluded whether the final product is a suitable replacement for PET.

7 Conclusion

4-(2-hydroxyethoxy)-3-methoxybenzoic acid was successfully synthesized from vanillic acid after some adjustment to the method provided by Mialon et. al., providing a sufficient yield (51 %) of the monomer. The product proved to be relatively pure, except for some traces of the starting material and some water. Some minor traces of 4-(2-(2-hydroxyethoxy)-ethoxy)-3-methoxybenzoic acid are indicated, but in such a small amount that no definite conclusion could be made regarding its presence.

Polymerization from this monomer to poly[4-(2-hydroxyethoxy)-3-methoxybenzoic acid] was done, however the analysis of the product gave indications that the average molecular weight was not as high as required. A new method was implemented, where the polymerization was carried out in a rotary evaporator to provide better stirring conditions.

The method of utilizing the rotary evaporator proved to work better than the previous method, both from a laboratory technical view, and from the limited number of analyses of the products. A problem to the newly acquired method was the stirring uniformity, as the results seemed to vary.

The yields of the monomer synthesis were close to those published by Mialon et. al. The analysis results had some deviations, however, due to a thorough elucidation, the product is still concluded to be as desired. As for the polymerization, the yields achieved were better than those published by Mialon et. al., and the analysis results had a close proximity for some samples, while other samples did not give analytical values.

Overall, the approach seems promising for the development of environmentally friendly substitutes for petroleum based PET, but further studies are needed to confirm this.

8 Further Work

These following factors can be improved:

- Duplication of more experiments of the monomer synthesis, especially for the comparison between experiment 5 and 6 for a better comparison of 2-chloroethanol and sodium iodide as catalyst compared to 2-bromoethanol, and duplication of experiment 10 to control the reproducibility.
- Further work to the second method of polymerization to find a way to better control the stirring while keeping it on a vigorous level. Test the reproducibility of the method with this improvement.
- Do GPC analysis with a new column, and DSC with a lower heating rate. Testing of the final plastic to find whether this product could replace PET in some commercial usages given the right additives would be interesting.

There are also some larger areas that needs more focus:

- Once the reproducibility is improved and the GPC is set, a systematic investigation of the effect of stirring compared to the degree of polymerization could be done to check whether this is a relevant factor, or whether there are any other influences from the rotary evaporator that increased the relative yield of samples X.1 for experiments 12 and 13.
- A study of different catalysts to the polymerization compared to the yields and degree of polymerization would be interesting. The degree of polymerization should be given more focus and ways to improve this should be implemented in a continued study.
- Reducing energy is also a priority, so checking whether the temperature or time could be lowered in the syntheses without this influencing the outcome is relevant. (If the monomer synthesis has reached its maximum conversion after 1 day or the polymerization could be done at 200 ^{o}C, this could save some electricity and thus be a greener option.) To save time while doing all of these adjustments, a multivariate experimental design would be efficient.
- As plastic is used in a scale of 10^8 tons every year, an increase in scale is necessary. Scaling the experiments up to check the outcome of a bigger scale would be interesting. During these upscaled versions, and especially if scaling up to a larger level, the previously mentioned point of reducing the time and temperatures becomes of great importance.
- DOSY-NMR was taken to give an estimate of Mw. An interesting study would be to use this further to produce a standard curve based on similar polymers, and use this to give better estimations of the molecular weight.

- Start a focus on other possibilities of biobased plastic, such as a synthesis of terephthalic acid from 4-hydroxybenzoic acid (and thus *p*-coumaryl alcohol), which could be reacted by known methods to PET. A problem of this synthesis would be the amount of *p*-coumaryl alcohol in biomass, as seen in **Table 1**, so a calculation on how much biomass would be needed to provide a certain quantity of biobased plastic should also be considered for this method.

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Appendix A – Master’s Project Original Description

Master's project opportunity: “Future aromatic biopolymers from lignin“

Start date: Preferably September – October 2015

Norner is a global, independent Polymer Institute with leading expertise in materials and polymers for the whole plastics and packaging value chains. Norner provides research and innovative solutions for the polymer industry and has a comprehensive scientific lab for development and testing of plastic materials. Norners clients are companies within a broad specter of industries. Examples of clients are Statoil, Scania, Unilever, Borealis and ABB. Norner is located in Stathelle, Norway, has 50+ employers and is currently growing.

Development of new bioplastics is a focused area for Norner, to take a role in the forefront within green chemistry for a sustainable future. Lignin is one of the most abundant naturally occurring feedstock for renewable aromatic chemicals and polymers, and is currently attracting huge interest in both the academe and industry. The complex structure of lignin requires development of novel technology for efficient degradation to obtain well-defined oligomers and monomers. In the OXYPOL project, Norner together with several partners addresses the bio-based plastics value chain using biocatalysis for the degradation of lignin into aromatic building blocks and the subsequent controlled polymerization of these aromatic precursors into bio-based polymers, using both biocatalysis and conventional catalysis to produce thermoplastic polymers, notably polyesters.

Scope and objective: The objective of this diploma work is to produce a range of thermoplastic polymers using selected lignin based monomers and conventional catalysts. Suitable monomers will be available either directly from commercial sources, or by simple synthesis modification of commercially available chemicals. The work will include literature search for suitable synthesis methods, major synthesis work and construction/assembling of equipment. The work will be conducted at Bergen University but will also comprise necessary visits and short term stays at Norner in Stathelle.

Deliverables:

i) Master thesis
ii) Products: Aromatic polyesters made from potential lignin based building blocks, in sufficient quantity for basic characterization and testing

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Appendix B – Practical Information Regarding Setup of Rotary Evaporator

To be able to flush the setup with nitrogen, a gas trap was added to the system. The nitrogen tube was connected to the vacuum outlet-valve, with the collector flask removed for nitrogen outlet, as seen in **Figure 11** in Chapter 4.2.2. For this to work, instead of the nitrogen evacuating the system before entering the round bottomed flask, a tube is present from the vacuum outlet valve to below the outlet to the collector flask, forcing the nitrogen to a point below this flask and into the round bottomed flask. This tube is shown in the figure below.

When changing from flushing the system with nitrogen to applying vacuum, the collector flask was connected, thus making the nitrogen go through the gas trap. The vacuum pressure valve was closed and the vacuum was applied to the system.

Appendix C – Picture of Samples

Sample 14.1

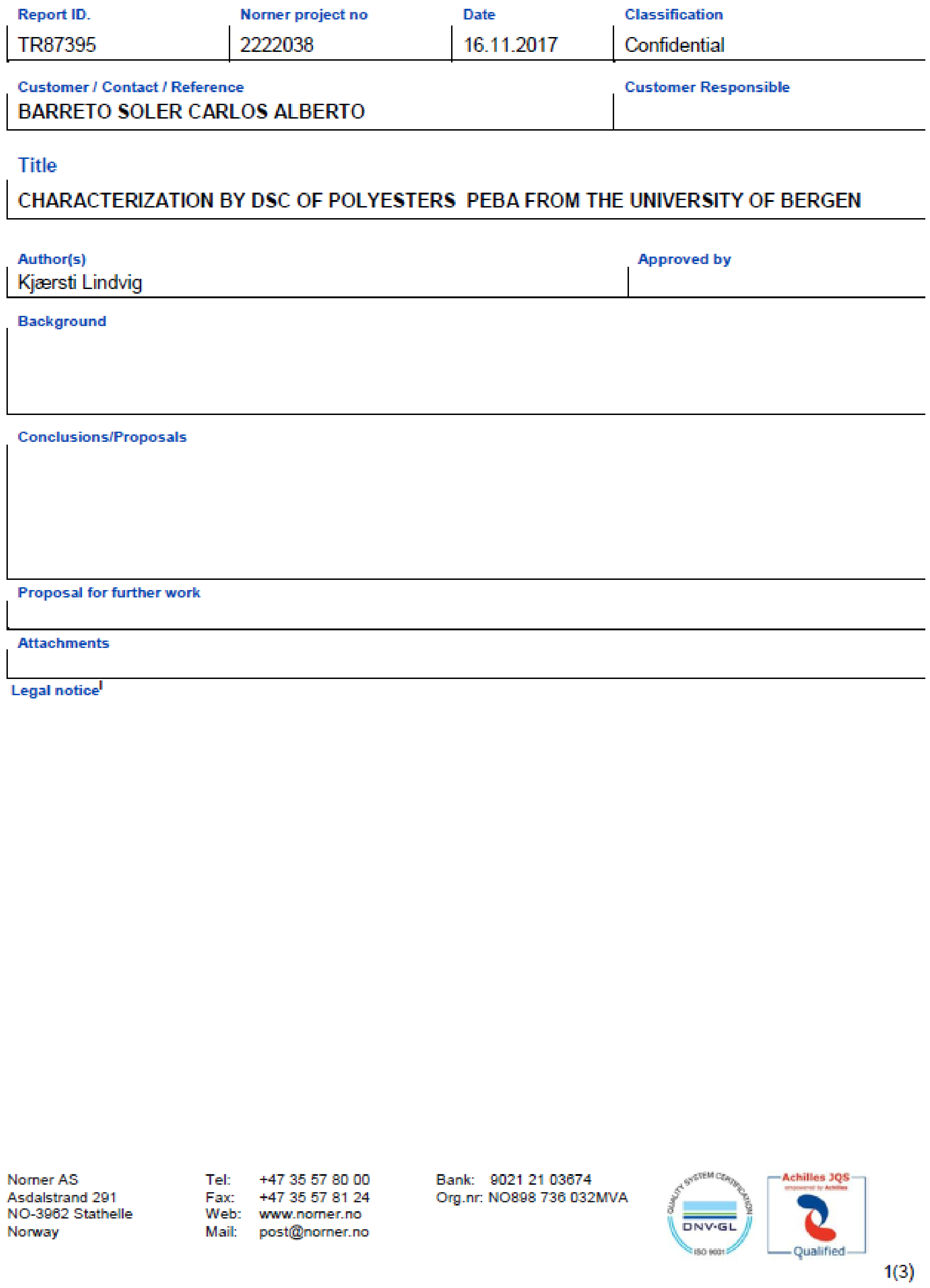
Sample 12.1 – a representation of samples X.1

Sample 12.2 – a representation of samples X.2

Sample 12.3 – a representation of samples X.3

Appendix D – DSC Test Reports

Experiment 7:



Report ID.	Norner project no	Date	Classification
TR87395	2222038	16.11.2017	Confidential

Customer / Contact / Reference	Customer Responsible
BARRETO SOLER CARLOS ALBERTO	

Title

CHARACTERIZATION BY DSC OF POLYESTERS PEBA FROM THE UNIVERSITY OF BERGEN

Author(s)	Approved by
Kjærsti Lindvig	

Background

Conclusions/Proposals

Proposal for further work

Attachments

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1(3)

1 Introduction

Characterization by DSC of Polyesters- PEBA- From University of Bergen.

2 Experiment description and results

2.1.1 Differential Scanning Calorimetriy, DSC

Method	Differential Scanning Calorimetry DSC – According to ISO11357-3- 2013 Determination of temperature and enthalpy of melting and crystallization
Definitions	DSC is a technique to verify the melting and crystallization behavior of a material subjected to heat under controlled temperature program and atmosphere. There are two crucibles in the furnace; one with sample and one empty, and the difference in heat flow between these is the response of the material being analyzed.
Instrument	Netzsch 204-F1
Specimen type	Direct on crude and purified material
Test conditions	1.Heating 30 to 230°C/240°C Cooling 230 to 30°C 2. Heating 30 to 250°C /240°C Heating /Cooling rate : 20°C/min Evaluation of Tg and Tm is performed at 2nd heating segment Parallels: 1
Method uncertainty	T_m and T_c ±1°C, Enthalpy ± 5 J/g

Table 1 - Table of properties

	Unit	POL-CRUDE-EXP7	POL-PURIF-EXP7
Tg - mid	°C	79	78
Temperature of melting	°C	215	214
Enthalpy of melting	J/g	47	48

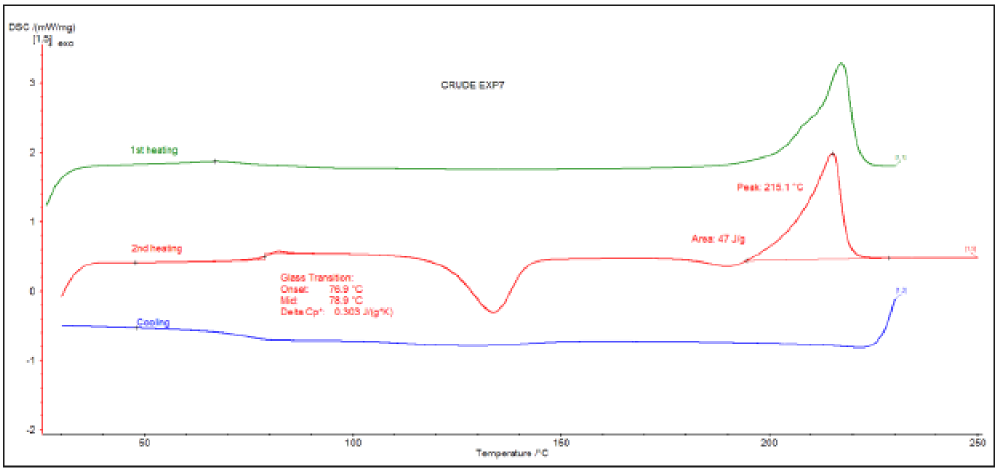

Figure 1 – DSC dynamic scan of CRUDE EXP7

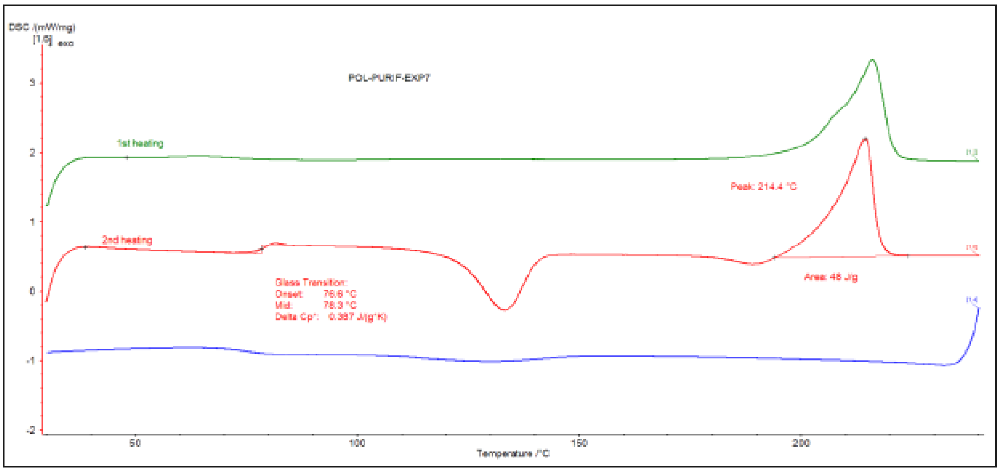

Figure 2 -DSC dynamic scan of PURIFIED EXP7

3 Discussion and Conclusions

4 Proposals for further work

---

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Experiments 8 and 9:

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BARRETO SOLER CARLOS ALBERTO	

Title

CHARACTERIZATION BY DSC OF POLYESTERS PEBA produced by Norner

Author(s)	Approved by
Kjærsti Lindvig	

Background

Conclusions/Proposals

Proposal for further work

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1(4)

1 Introduction

Characterization by DSC of Polyesters- PEBA- produced by Norner and from University of Bergen

2 Experiment description and results

2.1.1 Differential Scanning Calorimetriy, DSC

Method	Differential Scanning Calorimetry DSC – According to ISO11357-3- 2013 Determination of temperature and enthalpy of melting and crystallization
Definitions	DSC is a technique to verify the melting and crystallization behavior of a material subjected to heat under controlled temperature program and atmosphere. There are two crucibles in the furnace; one with sample and one empty, and the difference in heat flow between these is the response of the material being analyzed.
Instrument	Netzsch 204-F1
Specimen type	The samples have been compressed by KBr-press and also tested direct on lump
Test conditions	1.Heating 30 to 230°C/240°C Cooling 230 to -30°C 2. Heating -30 to 250°C /240°C Heating /Cooling rate : 20°C/min Evaluation of Tg and Tm is performed at 2nd heating segment Parallels: 2
Method uncertainty	T_m and T_c ±1°C, Enthalpy ± 5 J/g

Table 1 - Table of DSC of samples from UIB

	Sample prep	Tg mid	Tg- ΔCp	Melting temp	Enthalpy of melting	Crystallization temperature
UIB-POL-PURIF-EXP8.1	Compressed	78	0.15	212	43	132.5
UIB-POL-PURIF-EXP9.1	Compressed	77	0.19	213	47	119

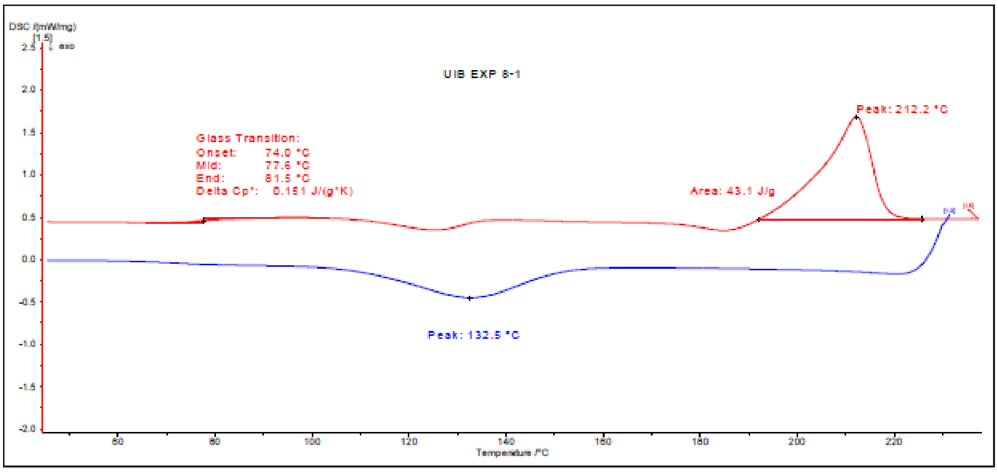

Figure 1 -DSC dynamic scan of UIB-POL-PURIF-EXP8.1

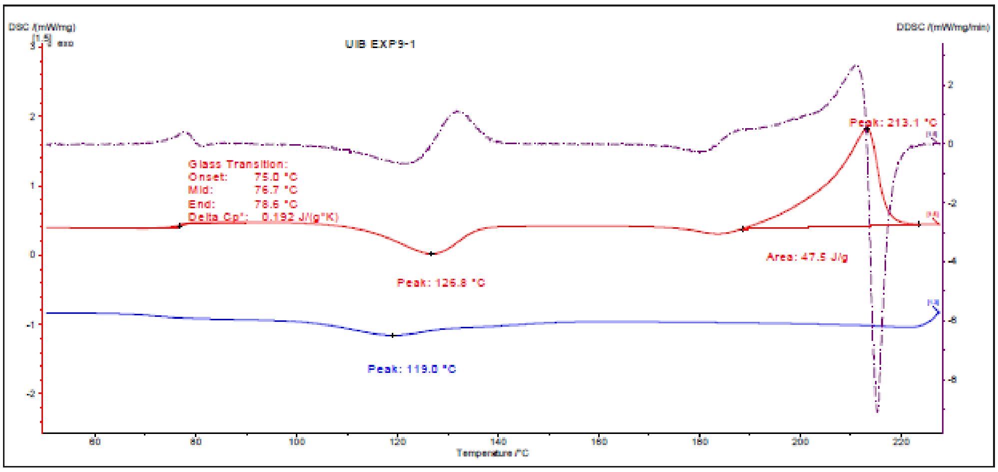

Figure 2 – DSC dynamic scan of UIB-POL-PURIF-EXP9.1

Table 3 - Table of MW parameters estimated from DSC (Tg and Enthalpy of melting)

				MW estimation			
	Sample prep	**Tg mid**	**Enthalpy of melting**	Model	Mn	Mw	PDI
UIB-POL-PURIF-EXP8.1	Compressed	78	43	DSC NORNER	9884	20492	2,07325
UIB-POL-PURIF-EXP9.1	Compressed	77	47	DSC NORNER	8962	18126	2,02254

3 Discussion and Conclusions

4 Proposals for further work

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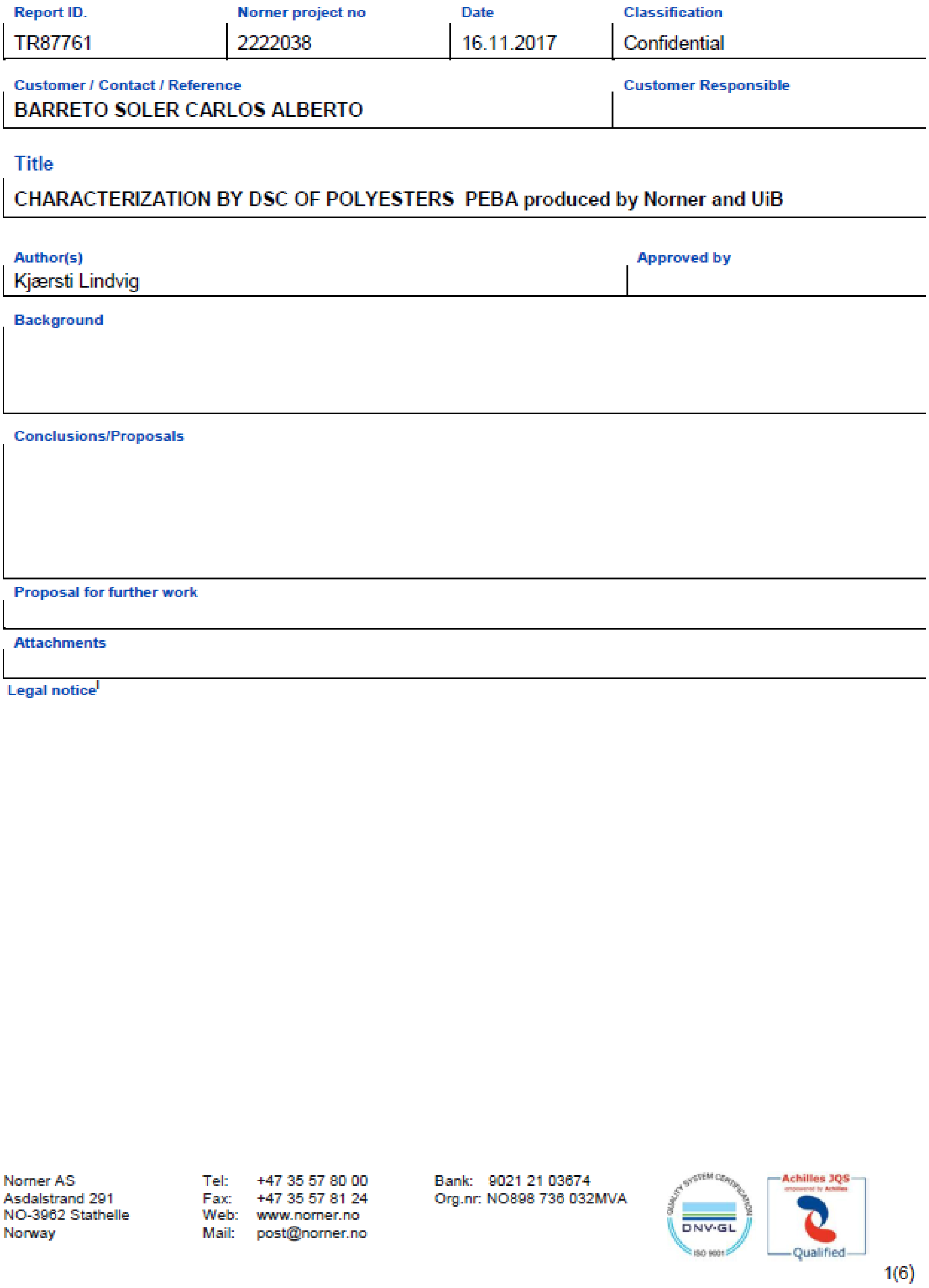
[1] ***Legal notice***

Experiments 11 and 12:



Report ID.	**Norner project no**	**Date**	**Classification**
TR87761	2222038	16.11.2017	Confidential

Customer / Contact / Reference
BARRETO SOLER CARLOS ALBERTO

Customer Responsible

Title
CHARACTERIZATION BY DSC OF POLYESTERS PEBA produced by Norner and UiB

Author(s)
Kjærsti Lindvig

Approved by

Background

Conclusions/Proposals

Proposal for further work

Attachments

Legal notice[i]

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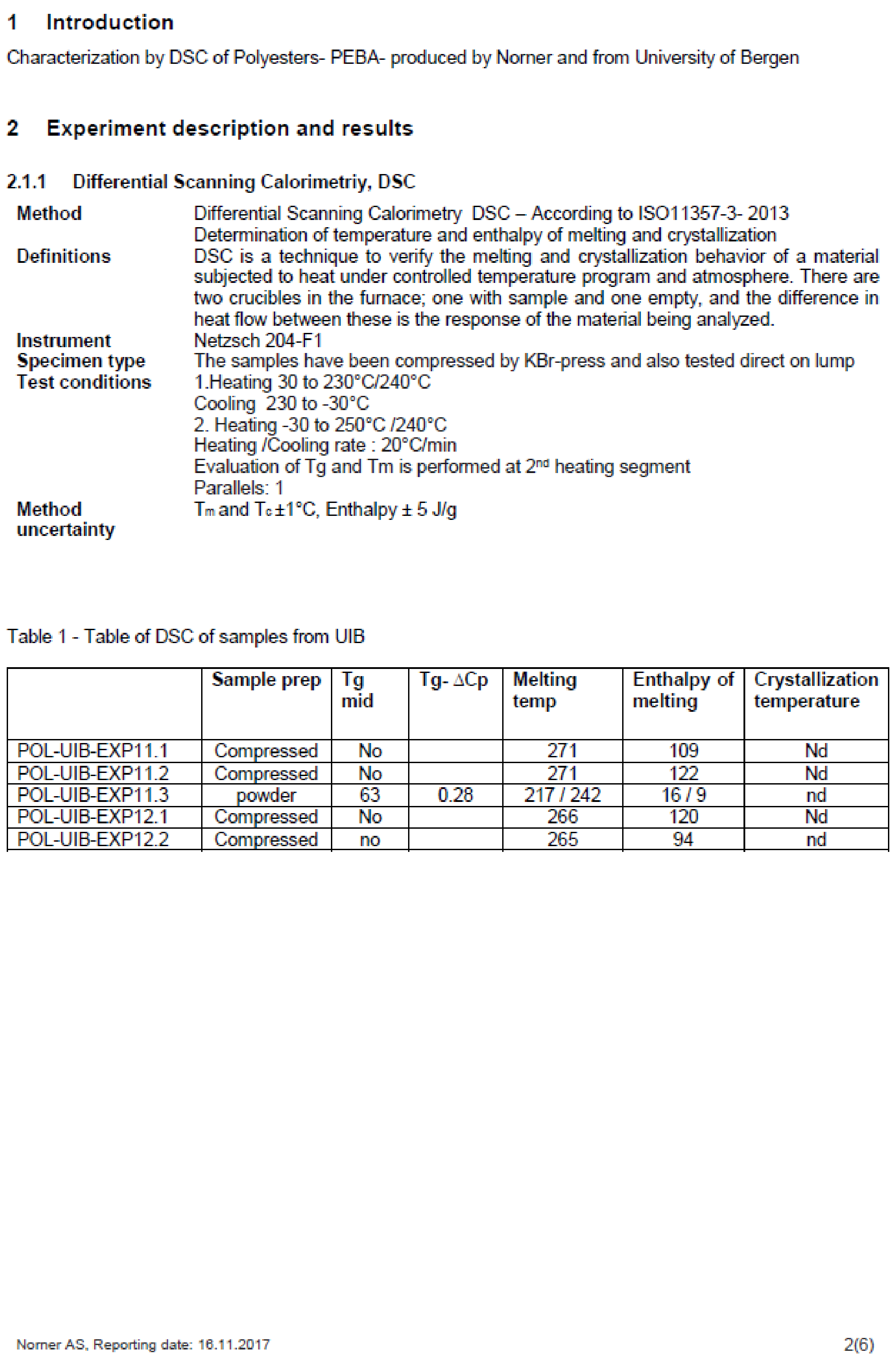
1(6)



1 Introduction

Characterization by DSC of Polyesters- PEBA- produced by Norner and from University of Bergen

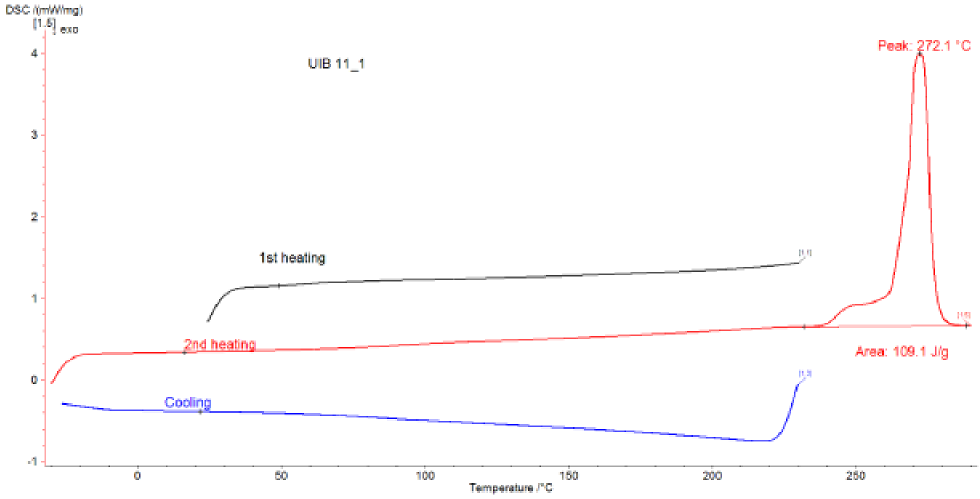
2 Experiment description and results

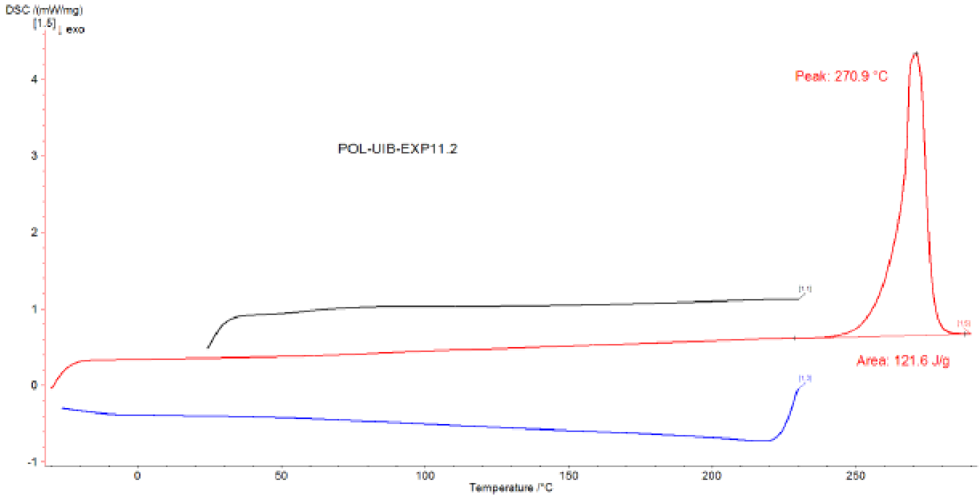
2.1.1 Differential Scanning Calorimetriy, DSC

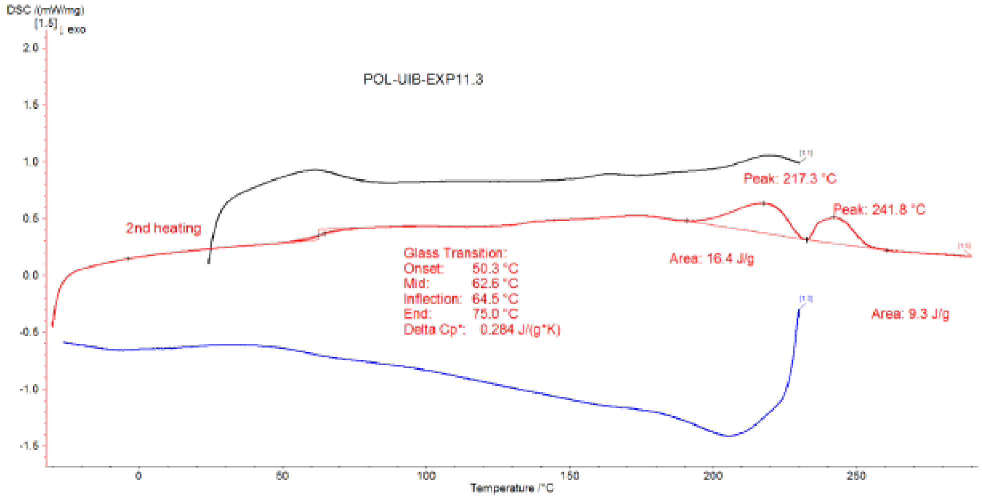
Method	Differential Scanning Calorimetry DSC – According to ISO11357-3- 2013 Determination of temperature and enthalpy of melting and crystallization
Definitions	DSC is a technique to verify the melting and crystallization behavior of a material subjected to heat under controlled temperature program and atmosphere. There are two crucibles in the furnace; one with sample and one empty, and the difference in heat flow between these is the response of the material being analyzed.
Instrument	Netzsch 204-F1
Specimen type	The samples have been compressed by KBr-press and also tested direct on lump
Test conditions	1.Heating 30 to 230°C/240°C Cooling 230 to -30°C 2. Heating -30 to 250°C /240°C Heating /Cooling rate : 20°C/min Evaluation of Tg and Tm is performed at 2nd heating segment Parallels: 1
Method uncertainty	T_m and T_c ±1°C, Enthalpy ± 5 J/g

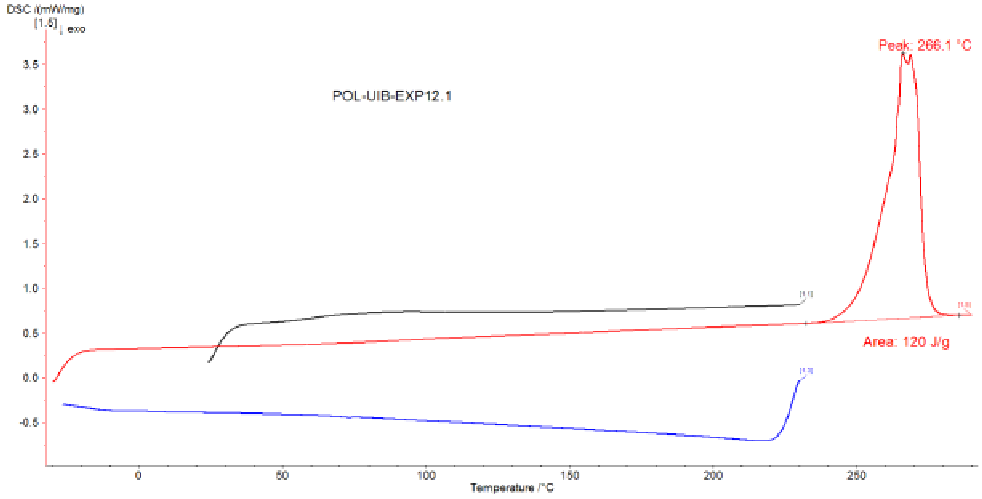
Table 1 - Table of DSC of samples from UIB

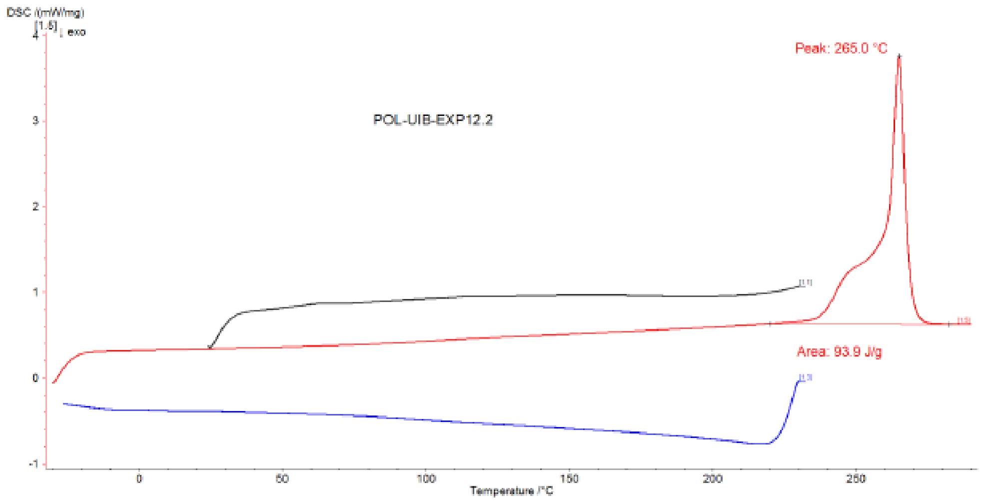
	Sample prep	**Tg mid**	**Tg- ΔCp**	**Melting temp**	**Enthalpy of melting**	**Crystallization temperature**
POL-UIB-EXP11.1	Compressed	No		271	109	Nd
POL-UIB-EXP11.2	Compressed	No		271	122	Nd
POL-UIB-EXP11.3	powder	63	0.28	217 / 242	16 / 9	nd
POL-UIB-EXP12.1	Compressed	No		266	120	Nd
POL-UIB-EXP12.2	Compressed	no		265	94	nd


DSC /(mW/mg)
[1.5] ↓ exo
UIB 11_1
Peak: 272.1 °C
1st heating
2nd heating
Cooling
Area: 109.1 J/g
4
3
2
1
0
-1
0
50
100
150
200
250
Temperature /°C


DSC /(mW/mg)
[1.5] ↓ exo
Peak: 270.9 °C
POL-UIB-EXP11.2
Area: 121.6 J/g
4
3
2
1
0
-1
0
50
100
150
200
250
Temperature /°C


DSC /(mW/mg)
[1.5] ↓ exo
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
POL-UIB-EXP11.3
2nd heating
Peak: 217.3 °C
Peak: 241.8 °C
Area: 16.4 J/g
Area: 9.3 J/g
Glass Transition:
Onset: 50.3 °C
Mid: 62.6 °C
Inflection: 64.5 °C
End: 75.0 °C
Delta Cp*: 0.284 J/(g*K)
0
50
100
150
200
250
Temperature /°C


DSC /(mW/mg)
[1.5] ↓ exo
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
POL-UIB-EXP12.1
Peak: 266.1 °C
Area: 120 J/g
0
50
100
150
200
250
Temperature /°C



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Experiments 13 and 14:

This test report has been adjusted as more tests, not related to this thesis, were shown. The results of these tests have been removed.

1 Introduction

Characterization by DSC of Polyesters- PEBA- produced by Norner and from University of Bergen

2 Experiment description and results

2.1.1 Differential Scanning Calorimetriy, DSC

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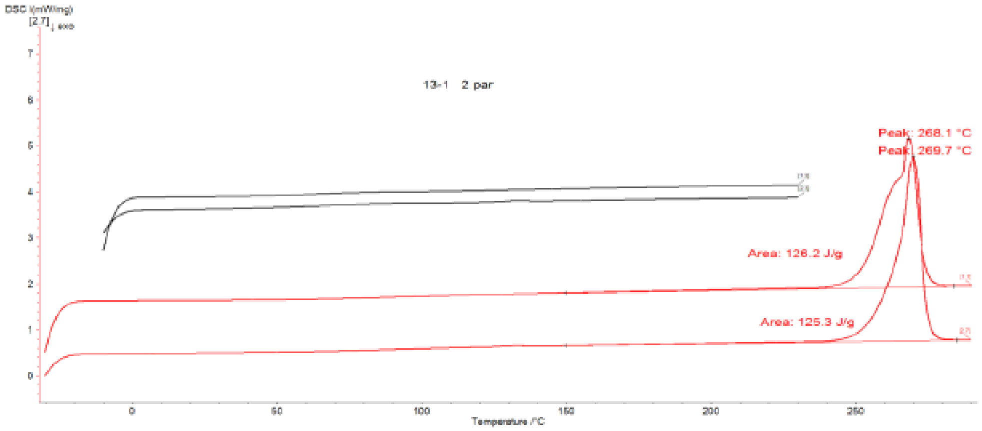
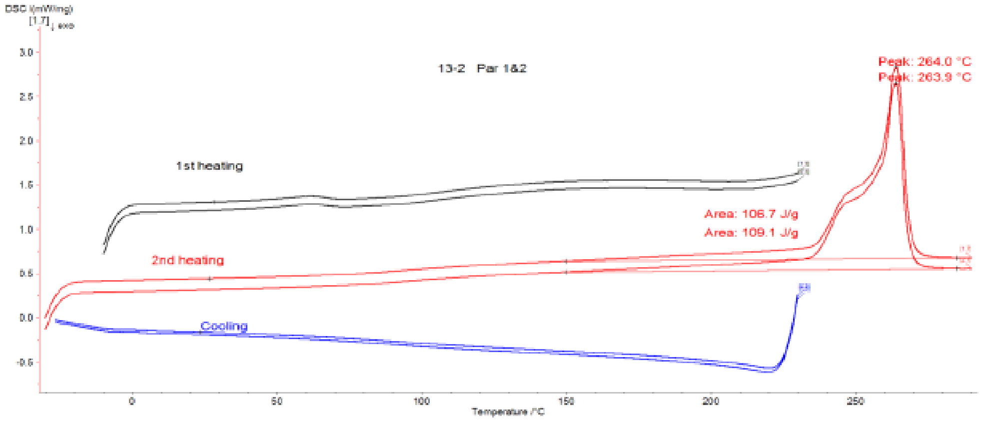
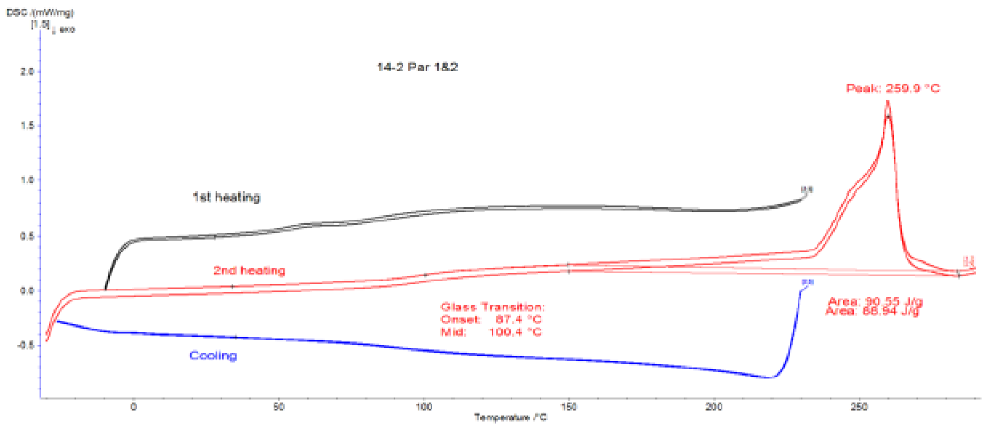
Specimen type	The samples have been compressed by KBr-press, 0,1g material
Test conditions	1.Heating 30 to 230°C/240°C Cooling 230 to -30°C 2. Heating -30 to 270°C Heating /Cooling rate : 20°C/min Evaluation of Tg and Tm is performed at 2nd heating segment Parallels: 2
Method uncertainty	T_m and T_c ±1°C, Enthalpy ± 5 J/g

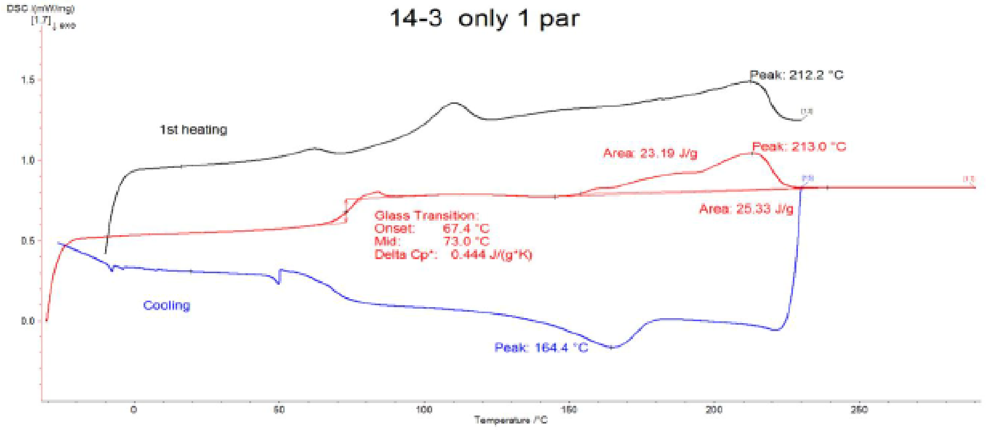
Table 2 - Table of DSC of samples from UIB

	Sample prep	**Tg mid**	**Tg- ΔCp**	**Melting temp**	**Enthalpy of melting**	**Crystallization temperature**
POL-UIB-EXP13.1	Compressed			269	126	
POL-UIB-EXP13.2	Compressed			264	108	
POL-UIB-EXP14.2	Compressed	100		260	90	
POL-UIB-EXP14.3	Compressed	73	0,44	213	24	164


DSC /(mW/mg)
[2.7] ↓ exo
13-1 2 par
Peak: 268.1 °C
Peak: 269.7 °C
Area: 126.2 J/g
Area: 125.3 J/g
7
6
5
4
3
2
1
0
0
50
100
150
200
250
Temperature /°C


DSC /(mW/mg)
[1.7] ↓ exo
13-2 Par 1&2
Peak: 264.0 °C
Peak: 263.9 °C
1st heating
Area: 106.7 J/g
Area: 109.1 J/g
2nd heating
Cooling
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
0
50
100
150
200
250
Temperature /°C





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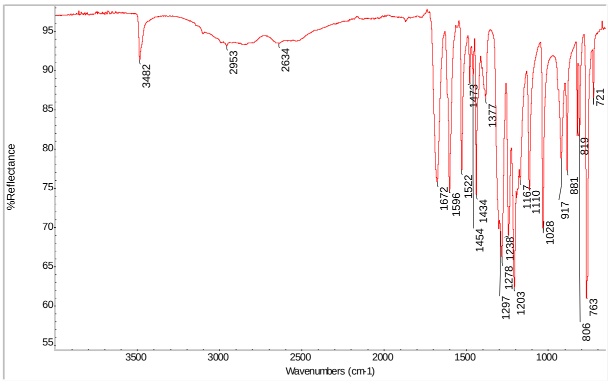
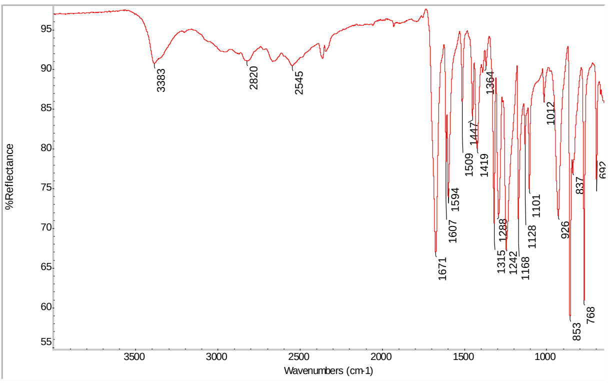
Appendix E – IR-spectra

Starting Materials

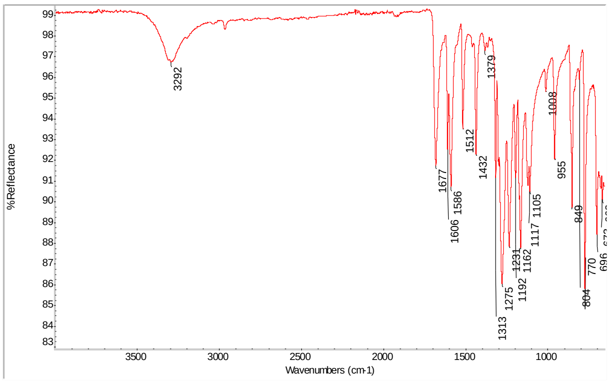
Vanillic acid



4-hydroxybenzoic acid

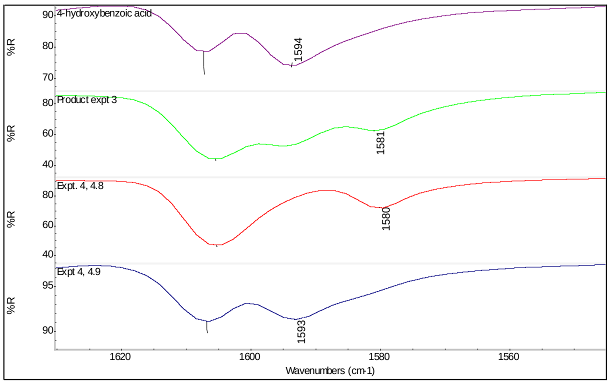


Methyl 4-hydroxybenzoate

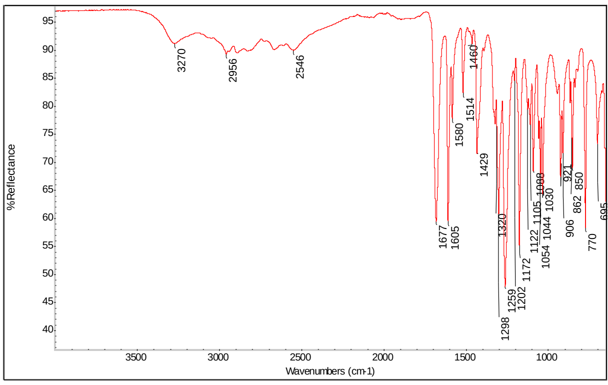


Monomers

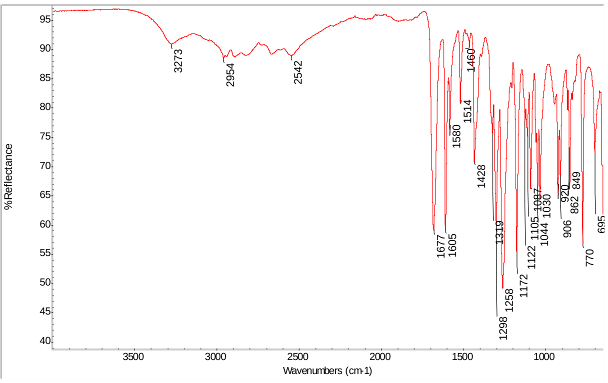
4-hydroxybenzoic acid (purple), prod. Expt 3 (green), sample 4.8 (red), sample 4.9 (blue)



Product expt. 5

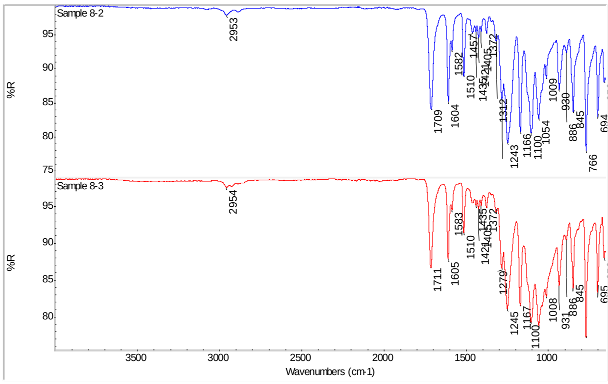


Product expt. 6

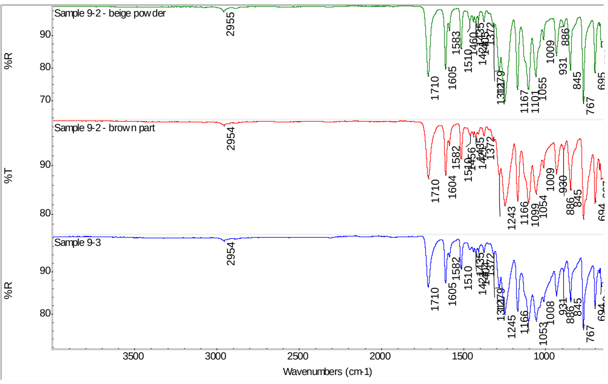


Polymers

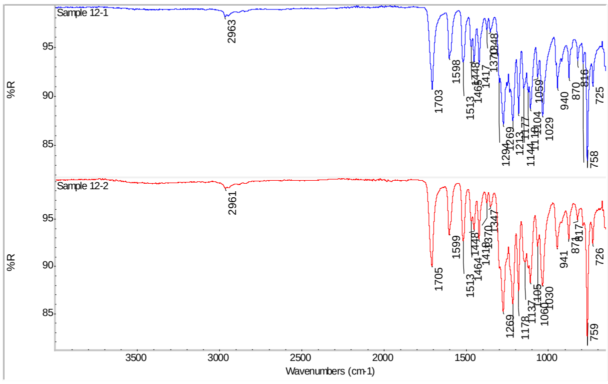
Sample 8.2 (blue) and 8.3 (red)



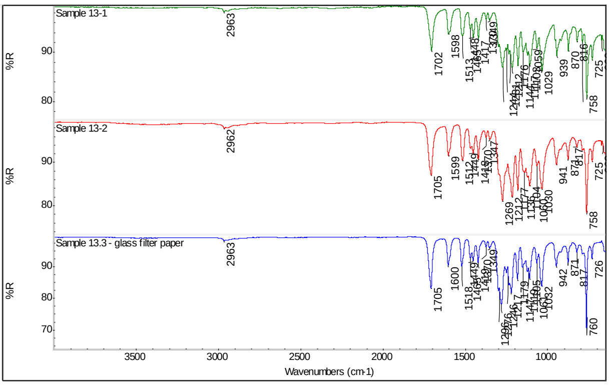
Sample 9.2 – beige (green), 9.2 brown (red) and 9.3 (blue)



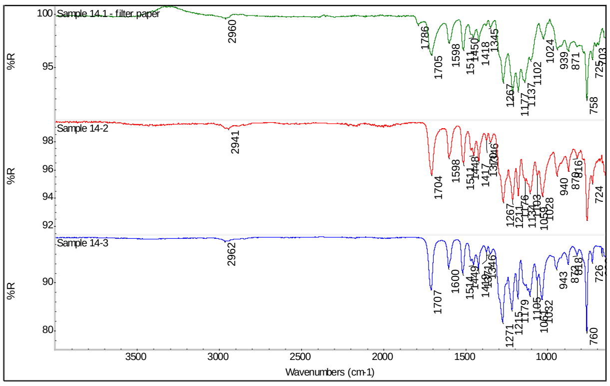
Sample 12.1 (blue) and 12.2 (red)



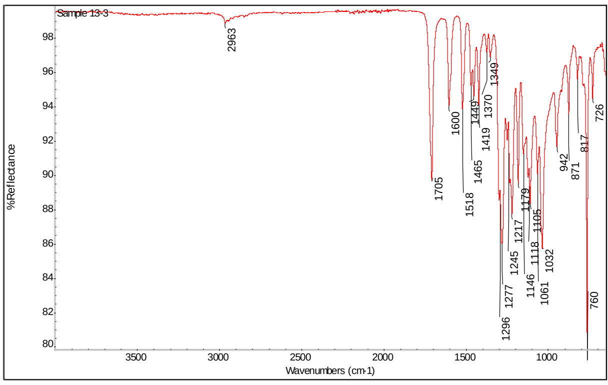
Sample 13.1 (green), 13.2 (red) and 13.3 (blue)



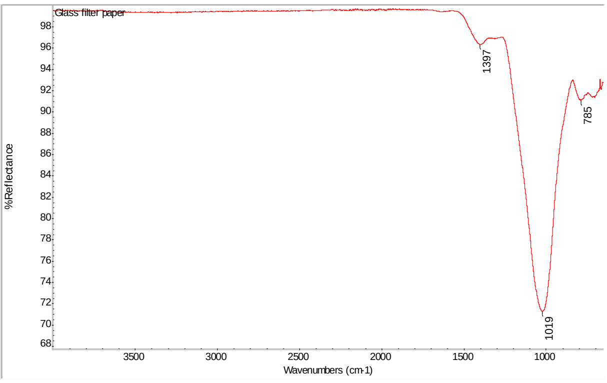
Sample 14.1 – filter paper (green), 14.2 (red) and 14.3 (blue)



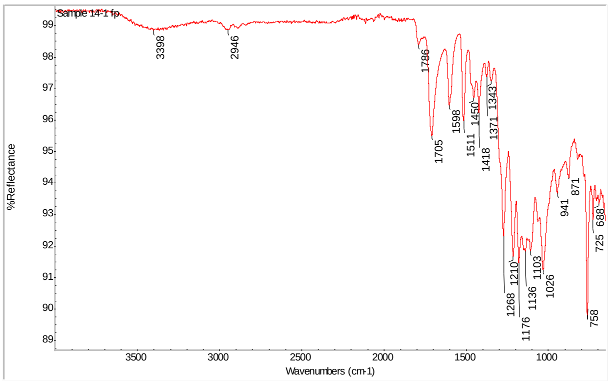
Sample 13.3 on glass filter paper



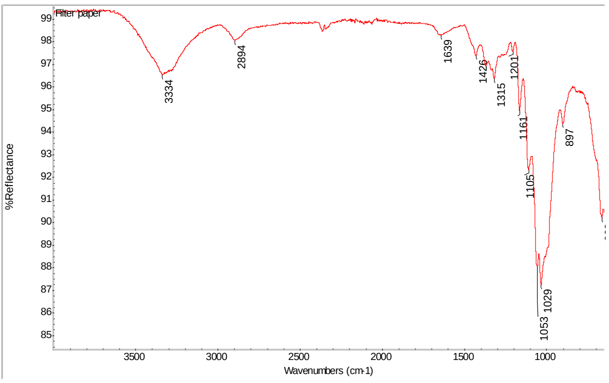
Glass filter paper



Sample 14.1 on filter paper



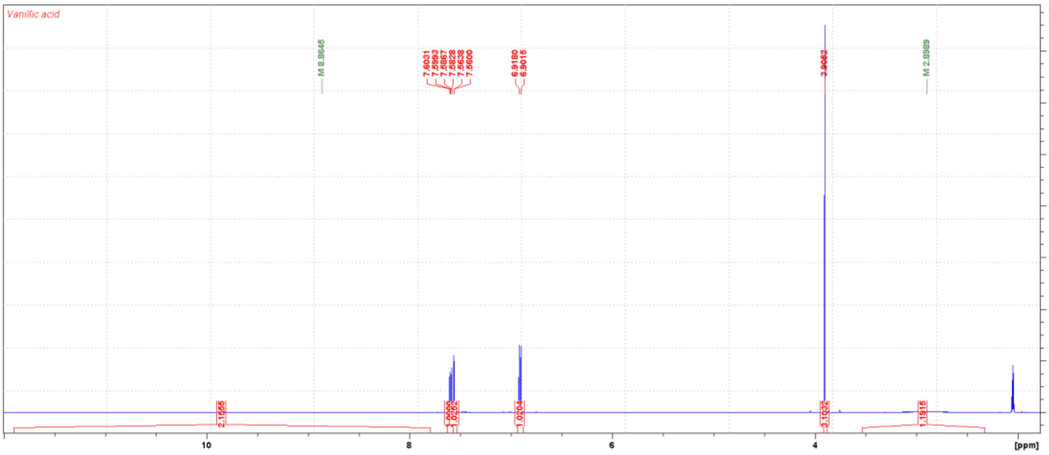
Filter paper



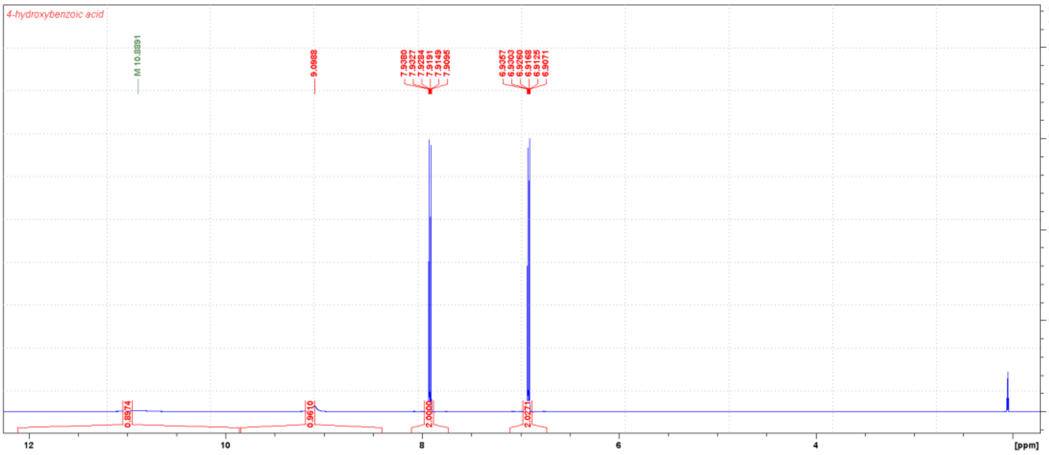
Appendix F – NMR-spectra

Starting Materials

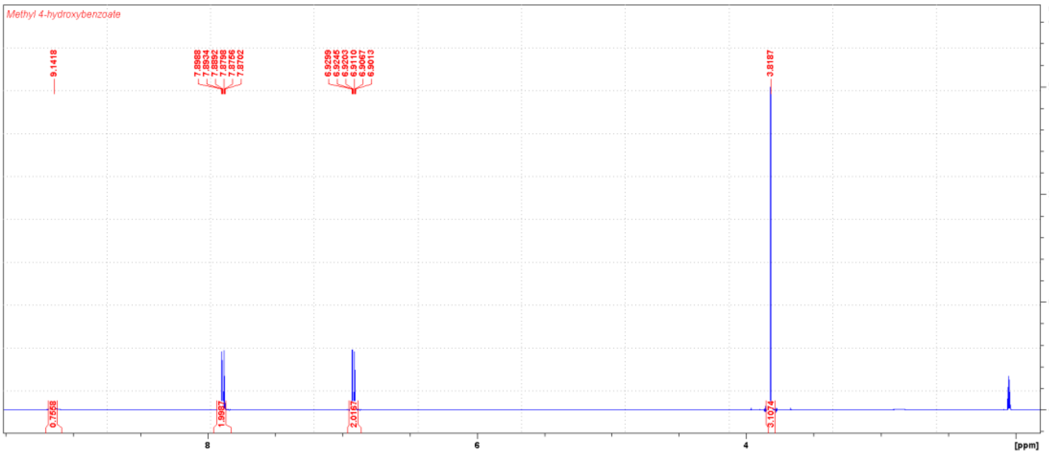
^{1}H-NMR, Vanillic acid



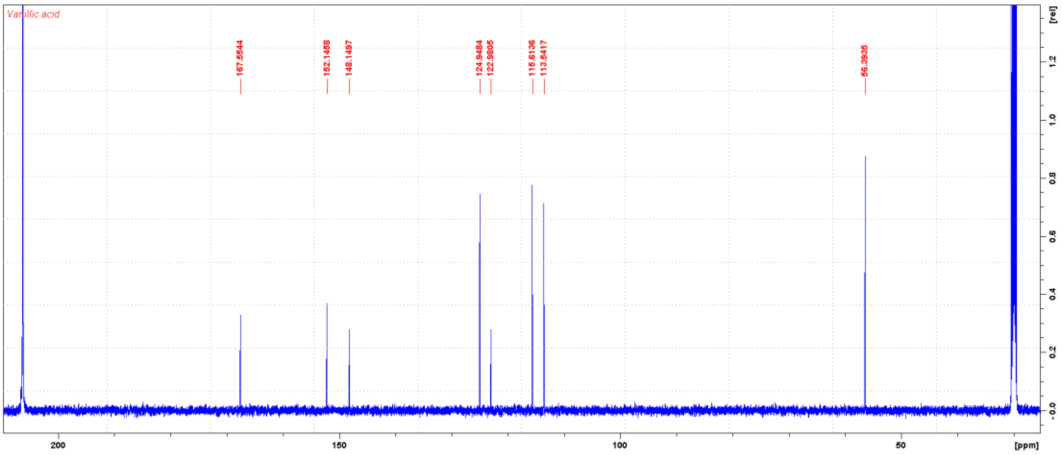
^{1}H-NMR, 4-hydroxybenzoic acid



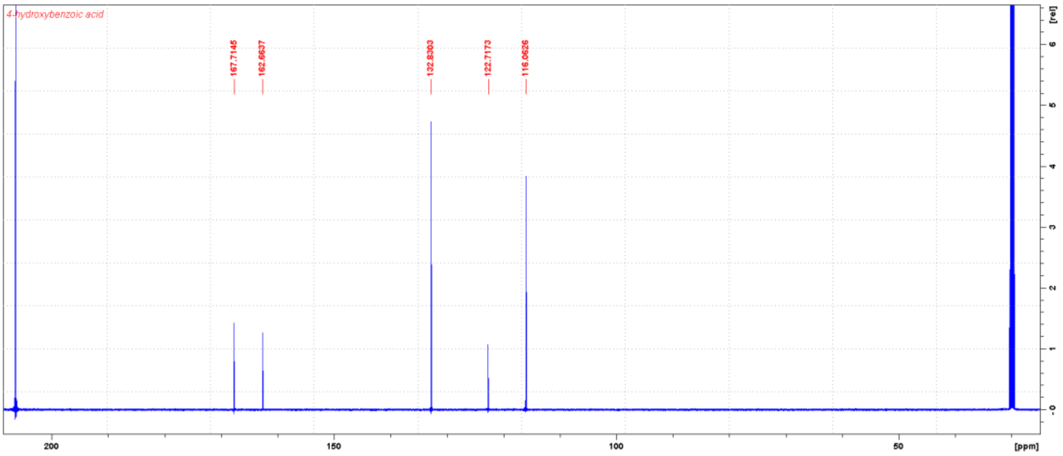
^{1}H-NMR, Methyl 4-hydroxybenzoate



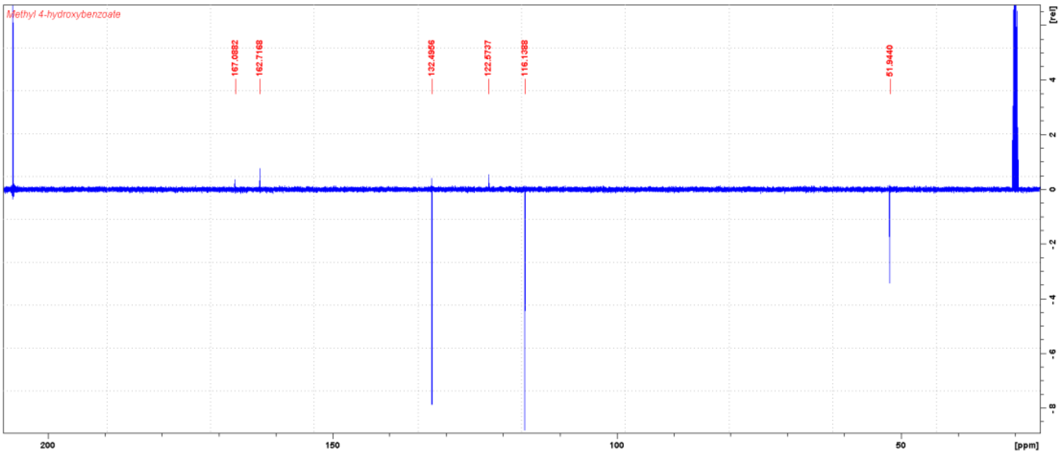
^{13}C-NMR, Vanillic acid



^{13}C-NMR, 4-hydroxybnenzoic acid

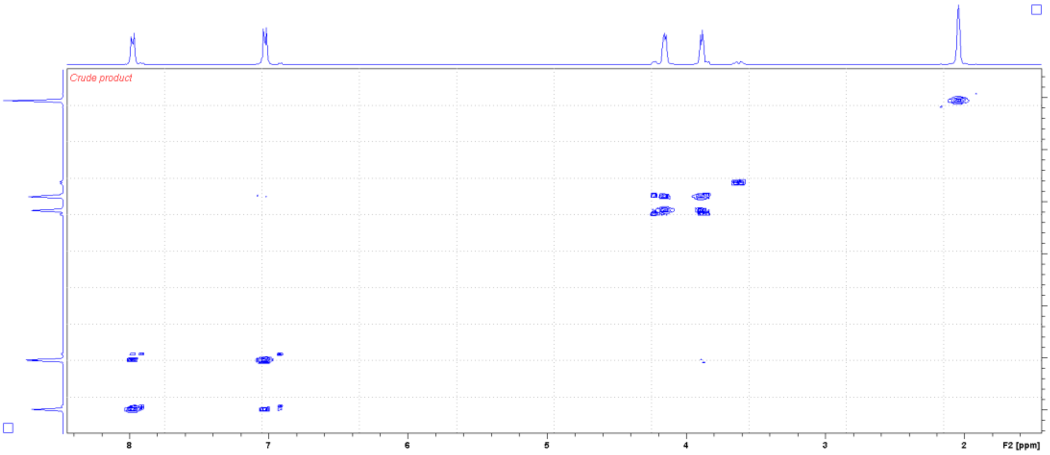


CAPT-NMR, Methyl 4-hydroxybenzoate

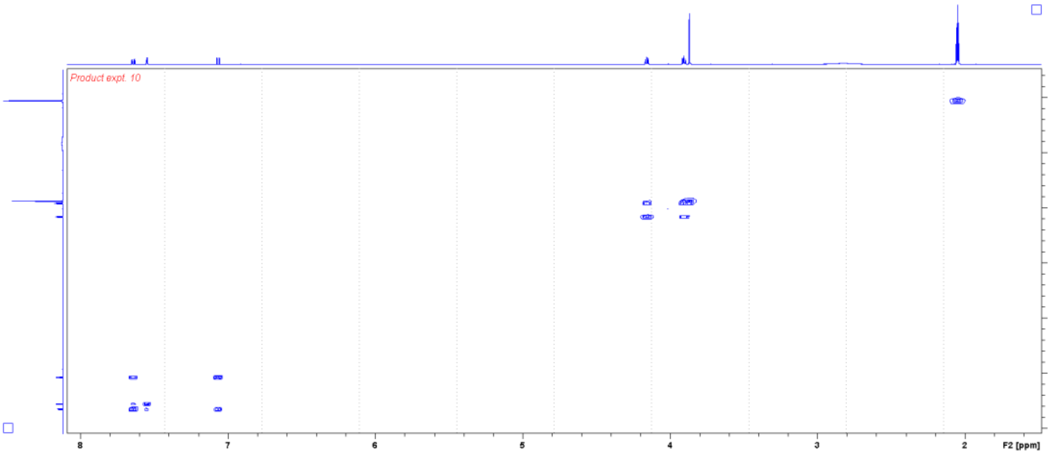


Monomers

COSY-NMR, crude product expt. 4

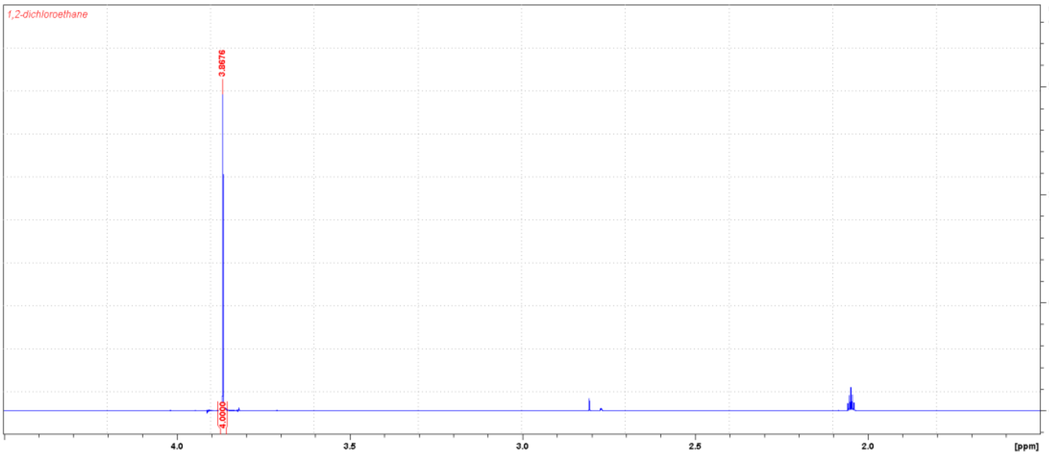


COSY-NMR, product expt. 10

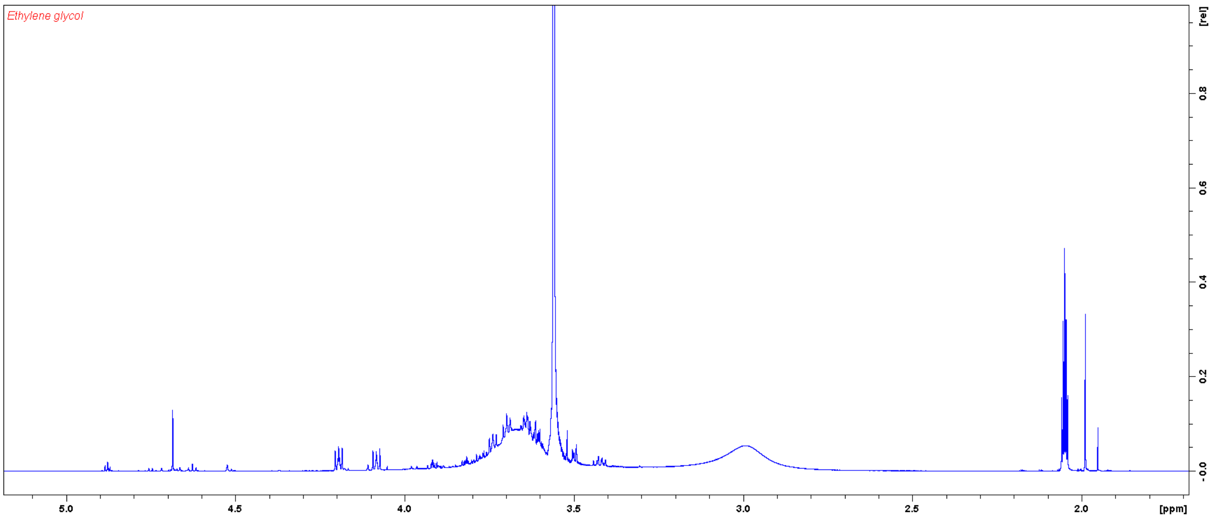


Compounds for Side Reaction Comparison

^{1}H-NMR, 1,2-dichloroethane

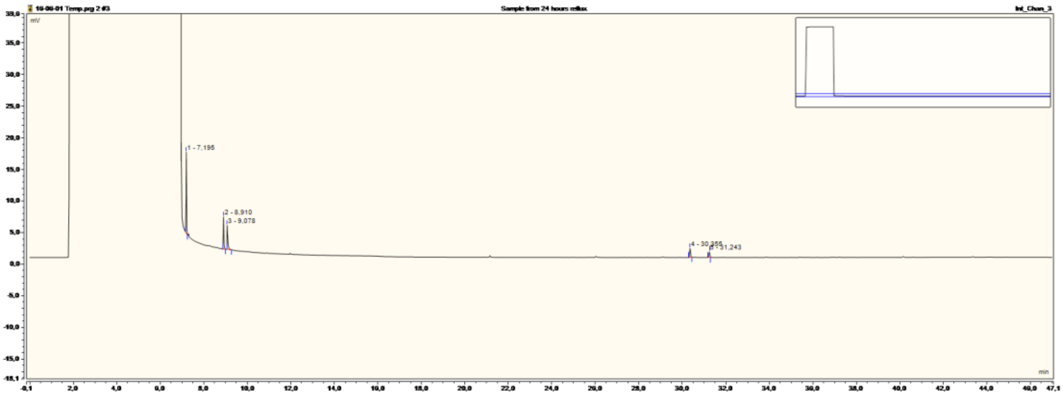


^{1}H-NMR, ethylene glycol

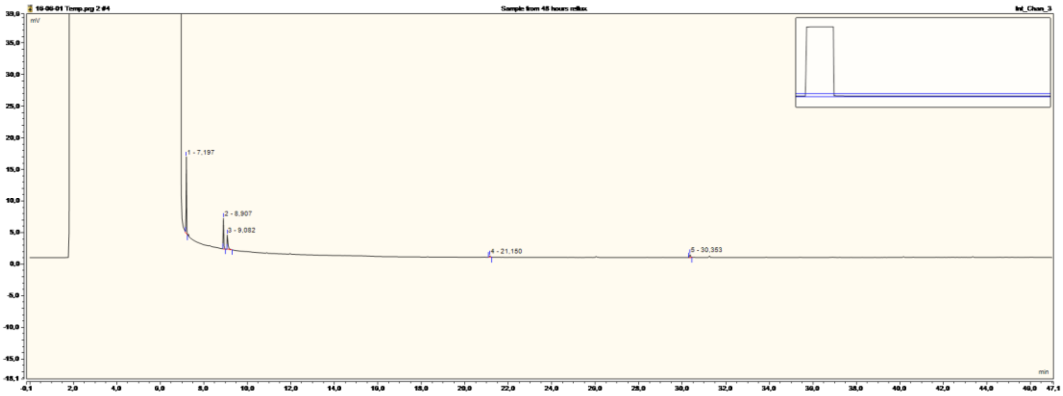


Appendix G – GC-FID

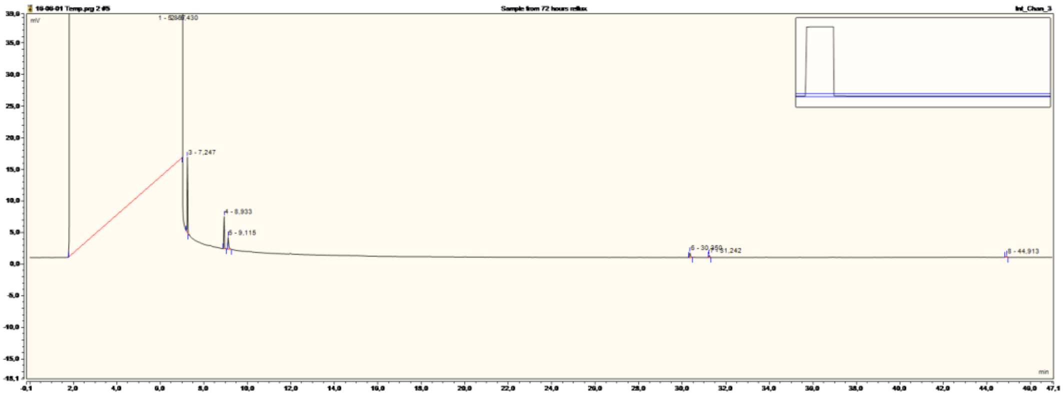
Expt. 3 – sample after 24 hours reflux



Expt. 3 – sample after 48 hours reflux



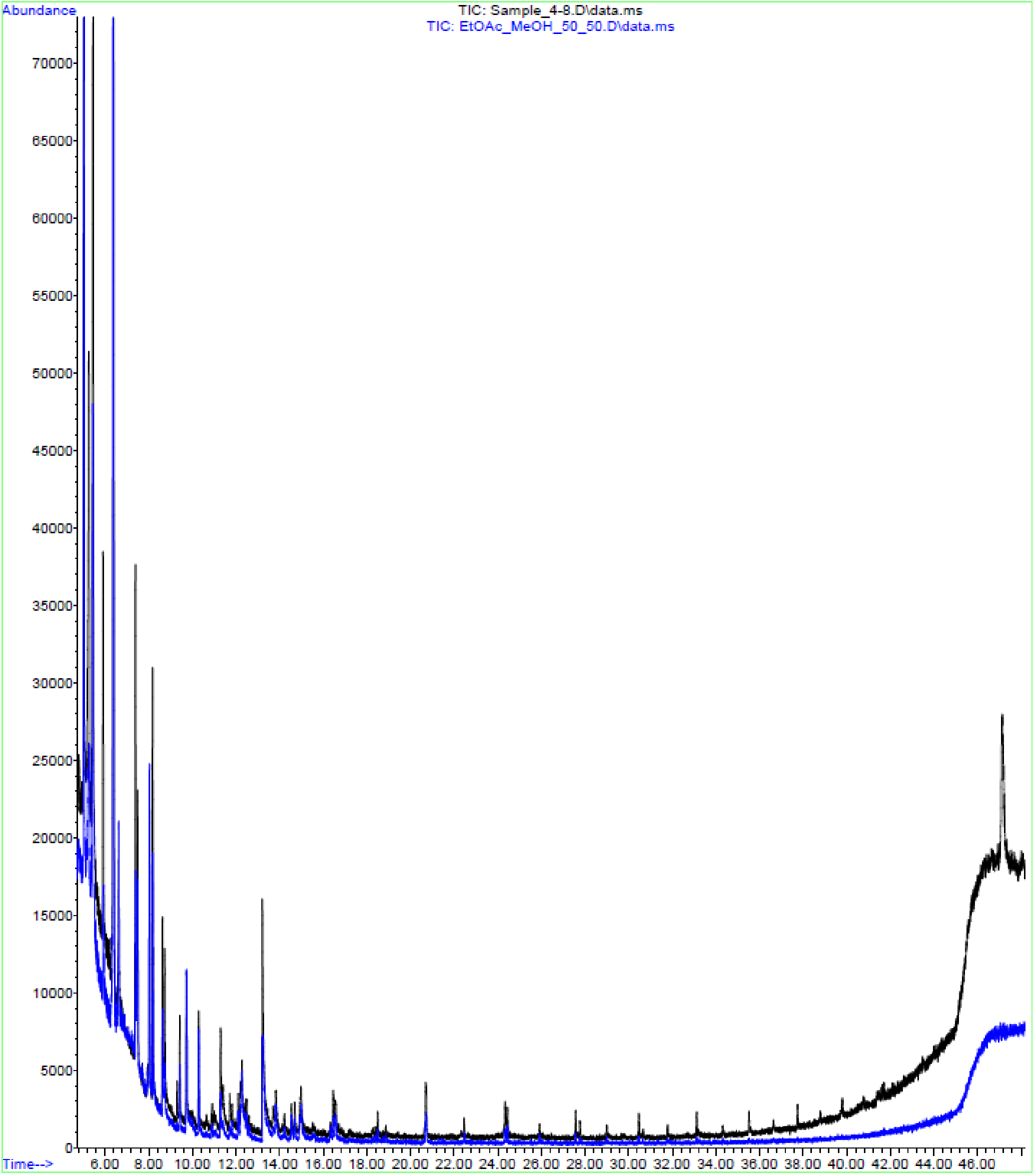
Expt. 3 – sample after 72 hours reflux



Appendix H – GC-MS

GC sample 4.8

File :C:\gcms\1\data\SHH170202\Sample_4-8.D
Operator : SHH
Acquired : 02 Feb 17 08:16 am using AcqMethod TANJA2.M
Instrument : GCMS5977-1
Sample Name: Sample_4-8
Misc Info :
Vial Number: 1



MS sample 4.8, average of 47.095 to 47.162 min

File   :C:\gcms\1\data\SHH170202\Sample_4-8.D
Operator   : SHH
Acquired   : 02 Feb 2017 08:16   using AcqMethod TANJA2.M
Instrument :   GCMS5977-1
Sample Name: Sample_4-8
Misc Info :
Vial Number: 1