Study the effect of alkyl substitution of monomers on properties of polyesters

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Summary

Keywords: Polyester, Polymerization, Halogenation, Alkylation and Characterisation

This study concerned the synthesis of modified terephthalic acid monomers and branched dialcohols for the synthesis of polyesters with different properties.

Monomers were prepared by esterification of terephthalic acid (TPA) and the alkylation of the ester dimethyl terephthalate (DMT). If alkylation was unsucessful, TPA was brominated using *N*-bromosuccinimide (NBS) and other brominating agents. However, the bromination reactions were also unsuccessful. Therefore, oxidation reactions of 2-bromoparaxylene were conducted as an attempt to obtain the desired monomers, however a mixture of products was produced that were difficult to separate. Subsequently, the brominated TPA was bought, and the alkylation reactions were performed using tetramethyltin and other alkylating agents; however the alkylation reaction was once again unsuccessful.

Despite the difficulties encountered during monomer synthesis, polymerization of the obtained monomers was investigated. Polymer synthesised by the technique of condensation polymerization of branched diols and the brominated TPA. The unbranched diol monomers and unsubstituted DMT were used to synthesize reference polymers for comparison with the novel polymers produced in this study. The following diols were used: 1,2-propanediol, 2-methyl-1,3-propanediol, and 3-methyl-1,5-pentanediol*.* A batch reactor equipped with a mechanical stirrer connected to the vacuum pump was used as polymerization vessel. The polyesters were synthesised and they were characterised using IR and NMR. Additional polymer analysis was performed using Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), X-Ray Diffraction (XRD), Gel permeation Chromatography (GPC) and Scanning Electron Microscopy (SEM).

The results of the analyses indicated that the polymers became flexible and softer with an increasing number of methylene units in the main chain. Consequently, the melting point of the polymer decreased when there was branching present. SEM analyses showed that polymers were softer and had no hard edges, and the SEM also showed the catalyst inside the polymers. The decomposition temperature changed very slightly with alkyl substitution or the presence of bromide in benzene ring.

It was concluded that the benzene ring did not become activated as a number of methods were attempted unsuccessfully to facilitate reaction by either alkylation or bromination. The methyl branches on the diols were not held responsible for any changes in the properties of the polyesters. Bromination of the monomers resulted in polymers that were structurally amorphous and that demonstrated a low tensile strength.

Opsomming

Sleutelwoorde: Poliëster, Polimerisasie, Halogenering, Alkilering en Karakterisering

Die studie bied ‘n ondersoek na die sintese van die gewysigde asynsuurmonomere en vertakte dialkohole, vir die sintese van poliësters met verskillende eienskappe.

Monomere is berei deur die verestering van tereftaalsuur (TPA) en die alkilering van die ester dimetieltereftelaat (DMT). Onsuksesvolle alkileringsreaksies is egter waargeneem en in opvolgende reaksies, TPA gevolglik gebromineer met behulp van *N*-bromosuksienimied (NBS) en ander brominergsreagense. Hierdie bromineringsreaksies was egter ook onsuksesvol gewees. As moontlike probleemoplossing vir die onsuksevolle reaksies, is oksidasiereaksies van 2-bromoparaxileen onderneem. Hierdie reaksies het gelei tot ’n mengsel van produkte wat moeilik geskei kon word. Gevolglik is gebromineerde TPA aangeskaf om die alkileringsreaksies met behulp van tetrametieltin en ander alkileringsreagense uit te voer. Daar is egrer weereens onsuksesvolle reaksies waargeneem tydens hierdie benadering.

Ten spyte van die mislukte reaksies, is ’n aantal monomere tog suksesvol gesintetisteer. Polimere is gesintetiseer vanuit hierdie monomere deur middel van kondensasie-polimerisasie van vertakte diole en die gebromineerde TPA. Die onvertakte dioolmonomere en onveranderde DMT is gebruik om verwysingpolimere mee te sintetiseer om dit te vergelyk met die unieke polimere wat in hierdie studie berei is. Die volgende diole is gebruik: 1,2-propaandiool, 2-metiel-1,3-propaandiool, 3-metiel-1,5-pentandiool. ’n Reaktor wat toegerus is met ‘n meganiese roerder verbonde aan die vakuumpomp is gebruik. Die poliësters wat gesintetiseer is, is gekarakteriseer met behulp van Termogravimetriese Ontleding (TGA), Differensiële Skandeerkalorimetrie (DSC), X-Straaldiffraksie (XRD), Geldeursypelingschromatografie (GPC) en Skandeerelektronmikroskopie (SEM).

Die karakterisering van die polimere het aangetoon dat die polimere meer buigsaam en sagter geword het met ’n gepaardgaande toename in die toevoeging van metileenhede in die hoofketting. Die smeltpunt het gedaal nadat vertakking van die polimeerketting plaasgevind het. SEM-ontleding het getoon dat die polimere sagter is as die verwysingspolimeer en dat dit geen duidelike rande besit nie. Die SEM het ook die katalisator in die polimere getoon. Die ontbindingstemperatuur het effens verander met alkielvervanging of met die teenwoordigheid van bromiede in die benseenring.

Daar is tot die gevolgtrekking gekom dat die benseenring nie geaktiveer kon word nie ten spyte van die aanwending van verskeie pogings om aktivering te bewerkstellig. Alkilerings-

en bromeringsreaksies is dus in hierdie gevalle onsuksesvol gewees. Die vertakking van die diole deur middel van metielgroepe word nie verantwoordelik gehou vir die verandering van die poliëstereienskappe nie. Bromering van die monomere het poliësters met ‘n amorte struktuur en lae trekvastheid teweeggebring.

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List of abbreviations

4CBA : 4-carboxybenzaldehyde

BHET : Bis-hydroxyethyleneterephthalate

BrTPA : Bromoterephthalic acid

Cat. : Catalyst

CPhos : Biarylphosphine ligand

DABCO : 1,4-diazabicyclo[2.2.2]octane

DBDMH : 1,3-dibromo-S,S-dimethylhydanton

DBU : 1,8-diazabicyclo[5.4.0]undec-7-ene

DCE : 1, 2-dichloroethane

DCM : dichloromethane

DEG : Diethylene glycol

DMF : Dimethylformamide

DMT : Dimethylterephthalate

Dppe : 1,2-bis(diphenylphosphino)ethane

Dppf : 1,1-bis(diphenylphosphino)ferrocene

DSC : Differential scanning calorimetry

DTG : Differential thermogravimetric analysis

EG : Ethylene glycol

GCMS : Gas chromatography mass spectrometry

HMPA : hexamethylenephosphoramide

IR : Infrared spectroscopy

Maldi-TOF : Matrix–assisted laser desorption/ionization-time of flight

Min : Minute

MS	: Mass spectroscopy
NBS	: N-bromosuccinimide
NMR	: Nuclear magnetic resonance spectroscopy
Nv	: Not visible
P(1,2-P) 2-BrT	: Poly(1,2-propanediol) 2-bromoterephthalate
P(1,2-P)T	: Poly(1,2-propanediol) terephthalate
P(2-M)P2-BrT	: Poly(2-methyl)propylene 2-bromoterephthalate
P(2-M)PT	: Poly(2-methyl)propylene terephthalate
P(3-M)PM2-BrT	: Poly(3-methyl)pentamethylene 2-bromoterephthalate
P(3-M)PMT	: Poly(3-methyl)pentamethylene terephthalate
PAT	: Polyalkyl terephthalate
PE2-BrT	: Polyethylene 2-bromoterephthalate
PET	: Polyethylene terephthalate
PP2-BrT	: Polypropylene 2-bromoterephthalate
PPM2-BrT	: Polypentamethylene 2-bromoterephthalate
PPMT	: Polypentamethylene terephthalate
PPT	: Polypropylene terephthalate
rt	: Room temperature
SEM	: Scanning electron microscopy
TFA	: Trifluoroacetic acid
TGA	: Thermo gravimetric analysis
THF	: tetrahydrofuran
TPA	: Terephthalic acid

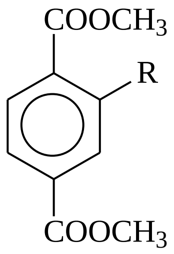
Chapter 1 Introduction

1.1 Aim

Polyesters of unsubstituted diacids (e.g. terephthalic acid) and various unbranched diols (Figure 1.2 D, E and F) are to be prepared as reference polymers. Polyesters of aryl substituted diacids (Figure 1.1) and the diols in Figure 1.2 are then to be produced and compared to the first mentioned products. By comparing the properties of the polyesters, the effect of different substituent groups can be determined. It could be envisaged that different properties may lead to new fields of application for this family of polyesters

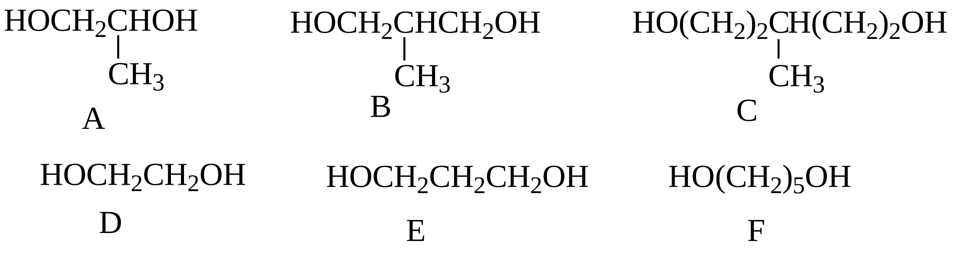
New and reported methods will be used in order to:

- Prepare monomers by alyklation of the benzene ring of the diacid and diacid ester;
- Synthesise polymers using alkylated diacids and the branched diols that are already available;
- Characterize the products; and
- Determine structure/properties relationship.



R = Br; CH_3; C_2H_5; C_4H_9

Figure 1.1 Substituted DMT monomers



$HOCH_2CH(CH_3)OH$ (A)

$HOCH_2CH(CH_3)CH_2OH$ (B)

$HO(CH_2)_2CH(CH_3)(CH_2)_2OH$ (C)

$HOCH_2CH_2OH$ (D)

$HOCH_2CH_2CH_2OH$ (E)

$HO(CH_2)_5OH$ (F)

Figure 1.2 Branched diol monomers 1,2-propanediol (A), 2-methyl-1,3-propanediol (B), 3-methyl-1,5-pentanediol (C), ethylene glycol (D), 1,3-propanediol (E) and 1,5-pentanediol (F).

1.2 Introduction to polyesters

The first to produce polyesters were Carothers and co-workers. [1] [2] Polyesters are produced by a condensation reaction that occurs between two or more functional groups, namely carboxylic acid (or an ester) and alcohol functional groups. [3] Some reactions involve the substitution of the methoxy group, for example in the reaction of dimethyl terephthalate (DMT) with ethylene glycol for the production of polyethylene terephthalate (PET).

About 9 million tons of PET was produced in 1994, and this number has been steadily increasing towards 37 million tons by 2004. This rise clearly indicates the demand for this product. [1, 4] The main end uses for PET are fibres, packaging, and films. In this study PET, polypropylene terephthalate (PPT) and polypentamethylene terephthalate (PPMT) are used as reference polyesters to the new polyesters with branched diol and diacid monomers.

The produced polyesters are characterised and properties are studied by means of Infrared Spectroscopy (IR), Nuclear Magnetic Resonance Spectroscopy (NMR), Differential Thermogrametric Analysis (DTG), Differential Scanning Calorimetry (DSC), Gel-permeation Chromatography (GPC), X-ray Diffraction Spectroscopy (XRD) and Scanning Electron Microscopy (SEM).

1.3 References

[1] K. Pang, R. Kotek and A. Tonelli, *Progress in Polymer Science* **2006**, *31*, 1009-1037.

[2] W. H. Carothers, *Journal of the American Chemical Society* **1929**, *51*, 2548-2559.

[3] P. J. Flory, *Chemical Reviews* **1946**, *39*, 137-197.

[4] a) X. Zuo, F. Niu, K. Snavely, B. Subramaniam and D. H. Busch, *Green Chemistry* **2010**, *12*, 260; b) F.-A. El-Toufaili, J.-P. Wiegner, G. Feix and K.-H. Reichert, *Thermochimica Acta* **2005**, *432*, 99-105.

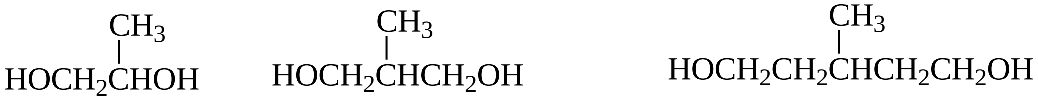
Chapter 2 Literature Survey

2.1 Introduction

PET has been manufactured by ICI (UK, 1949) and Du Pont (USA, 1953). [1] Also, in 1949, Whinfield and Dickson developed the technology for polyester manufacturing. [1] According to Flory [2], any condensation reaction could be used for the production of polyesters, as long as the prerequisite is met by the monomers, namely that they must have the functional groups that are mentioned above. Polyesters produced from glyocols and diacids are representative of the linear polyesters. The ones that are produced from glycerol and dibasic acids are three-dimensional; this difference in structure of the two polymers is responsible for their different properties. [2]

2.2 Synthesis methodology for the preparation of monomers

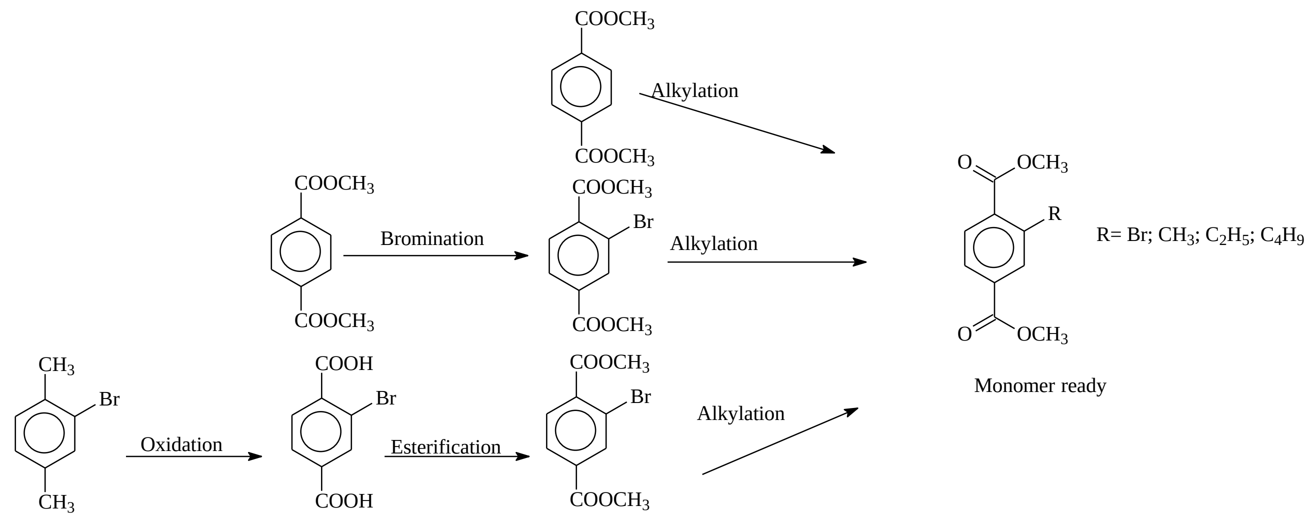
The monomers in Figure 2.1 below that are used as the dialcohols are commercially available and will therefore not be prepared for this study. They will be reacted with the monomers in Scheme 2.1 to produce polyesters with different properties as also noted by Flory [2].



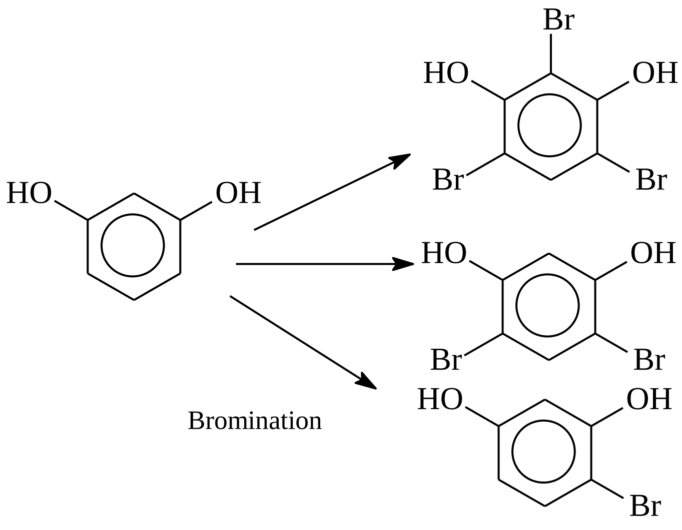
$HOCH_2\overset{\overset{CH_3}{|}}{C}HOH$ $HOCH_2\overset{\overset{CH_3}{|}}{C}HCH_2OH$ $HOCH_2CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2OH$

Figure 2.1 The dialcohols

The required monomers must have a side chain. An example of this would be a monomer such as terephthalic acid or dimethyl terephthalate with a substituent on it, as shown in Scheme 2.1, and the dialcohol with the substituent on it, as shown in Figure 2.1. The aromatic dialcohols will also be used after adding a single bromide or more on them as seen in Scheme 2.2, after which they will be polymerised with the monomer prepared as seen in Scheme 2.1.



Scheme 2.1 Preparation of substituted terephthalic acid (terephthalate) monomers



Scheme 2.2 Aromatic dialcohol monomers

Steps for the preparation of monomers:

2-alkyl terephthalic acid or 2-alkyl dimethyterephthalate

Method 1: Alkylation of dimethylterphthalate (DMT) and obtain a monomer.

Method 2: Bromination of DMT, alkylation of brominated DMT; lastly, obtain a monomer.

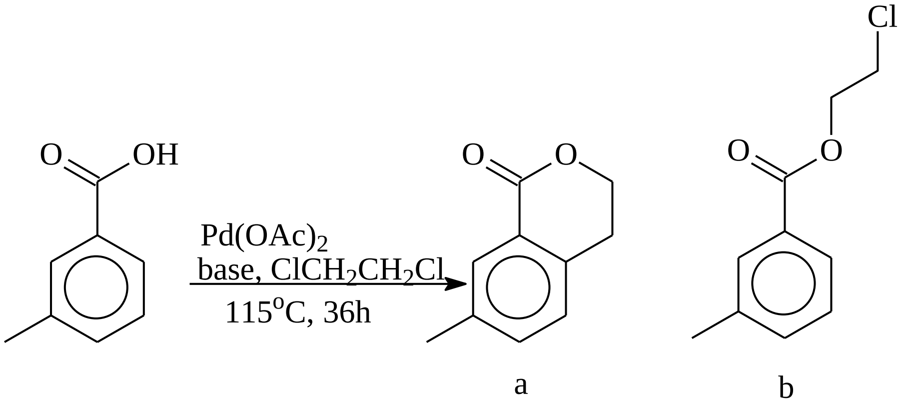
Method 3: Oxidation of 2-bromo paraxylene to 2-bromo terephthalic acid, esterification of 2-bromoterephthalic acid to 2-bromo dimethylterephthalate, alkylation of 2-bromo dimethylterephthalate to 2-alkyl dimethylterephthalate. At this stage the monomer is ready for polymerisation.

2.3 Preparation of monomers

2.3.1 Alkylation

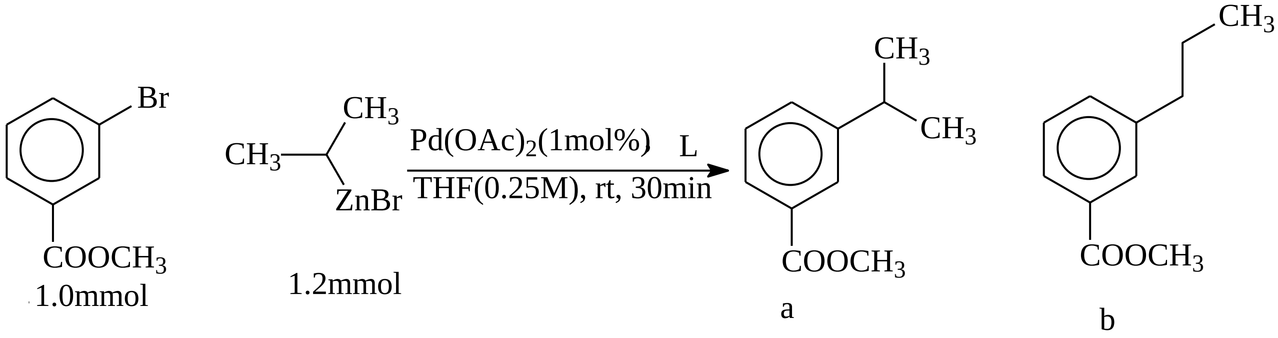
Monomers are required to be alkylated with a methyl, ethyl or propyl and butyl. To this end, a number of alkylation methods have been identified. Methods of *ortho* alkylations will be used to synthesise the monomers. In a survival guide for directed metalation, it is stated that direct metalation group (DMG) is a Lewis basic half that interacts with the Lewis acidic cation (Li^+), allowing the disproportionation by the alkyl-metal from the nearest *ortho*-position. [3] [4] [5] The alkyl lithium that is used in the *ortho* alkylation processes is prepared using sodium: lithium alloys and alkyl chloride, for example butyl chloride. [6] [7]

Palladium acetate catalyst is used for the *ortho*-alkylation of benzoic acids, without any co-oxidant being used. [8] Different alkyl halides such as dibromomethane and chloropentane are used as alkylating agents and the bases used are K_2HPO_4, Na_2HPO_4, and K_3PO_4 at different concentrations. [8] The preferred base for the reaction is K_2HPO_4. The reaction mixture is stirred for 36 hours at 115°C. The product is purified with column chromatography. For the reaction equation, see Scheme 2.3. The expected yield is of 82% of product a, and little bit of b, which is the undesired product.



Scheme 2.3 Alkylation of 3-methylbenzoic acid

In the above reaction, the temperature is raised to 140°C, with different reagents, for the alkylating or lactonisation reaction of the benzoic acid. The coordination of the cation K^+ with a carboxylate group forces the Pd^{II} center to chelate in the *ortho* C-H bonds for benzoic acid and beta C-H bonds for aliphatic acids. [8] According to Han and Buchwald [9], in the reaction equation shown in Scheme 2.4, an aryl halide is coupled with an alkyl metal to produce an alkylaryl, in the so-called Neggishi Coupling. Palladium acetate ($Pd(OAc)_2$) catalyses the reaction of isopropyl with aryl halide with tetrahydrofuran (THF) as the solvent. The reaction is performed at 0°C to room temperature, for 30 minutes.



Scheme 2.4 Alkylation of 3-bromomethylbenzoate

The products a and b (94% yield) are formed in the ratio of 46:1 a:b.

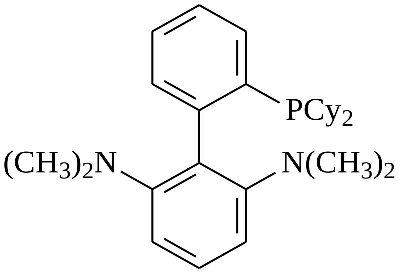
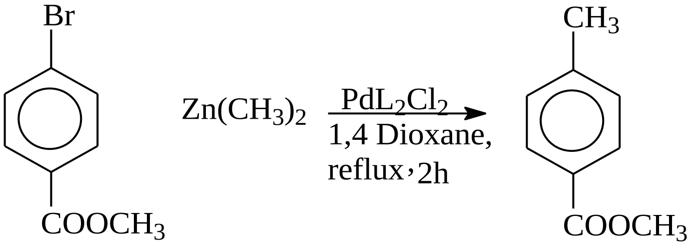


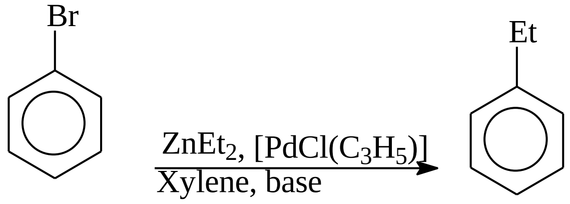
Figure 2.2: The biarylphosphine ligand (CPhos).

Wang et al. [10] and Herbert [11] used dimethyl zinc in toluene with palladium catalyst (PdL_2X_2) for the conversion of 4-bromobenzoic acid to the 4-methyl benzoic acid and 4-bromomthylbenzoate to 4-methyl methylbenzoate (see Scheme 2.5). The yield is 95% with catalyst palladium-1,2-bis(diphenylphosphino)ethane chloride ($Pd(dppe)Cl_2$). [11] Another catalyst that may be used is palladium-1,1-bis(diphenylphosphino)ferrocene chloride ($Pd(dppf)Cl_2$). [12] [13] [14]



Scheme 2.5 Alkylation of 4-bromomethlylbenzoate

Kondolff et al. [15] also use alkyl Zn reagents to alkylate aryl halides. Xylene is used as the solvent and the reaction is allowed to run for 18 hours under argon, and the yield is 100%. The reaction temperature is 70°C. With THF as the solvent, the yield becomes 70%.

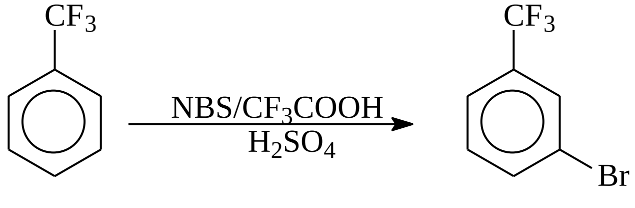


Scheme 2.6 Alkylation of bromobenzene

Tetrakis triphenylphosphine palladium(0) is also used with tetrabutyltin as an alkylating agent. [16] Grignard reagents are also used in the cross-coupling reaction with bromobenzene. [17] Alkylation can also be done using Friedel-Crafts reactions to produce substituted aromatic compounds. [18] The catalysts used here are $AlCl_3$ as Lewis acids and H_2SO_4 as Brönsted acid. [18]

2.3.2 Halogenation

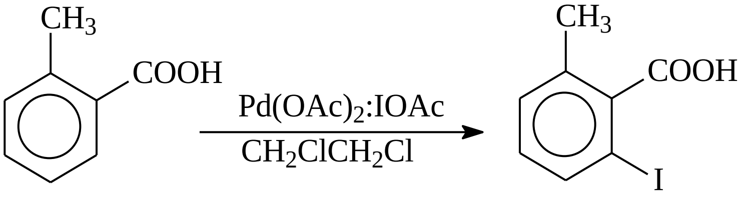
Bromo-aromatics are useful intermediates during the synthesis, but the aromatic ring is deactivated. [19] The available methods for the bromination of deactivated aromatic compounds use toxic, hazardous reagents and/or harsh conditions of reaction. [19] Reagents that have become known and which use N-bromosuccinimide (NBS) or the 1,3-dibromo-s,s-dimethylhydanton (DBDMH) are among the most useful for carrying out such these reactions[19] (see Scheme 2.7). It has been reported that the use of trifluoroacetic acid (TFA) as solvent, with H_2SO_4 as the catalyst, and NBS as the active source of electrophilic bromine, seems to be an ideal medium for bromination, of deactivated aromatic compounds such as nitrobenzene, methylbenzoate, and trifluoromethylbenzene. [19-20] [21]



Scheme 2.7 Bromination of trifluoromethyl benzene (yield of 81%)

Mei et al. [22] performed C-H bond iodination using a palladium acetate catalyst for the mono-selective *ortho*-halogenation of carboxylic acids (see Scheme 2.8). The C-H activation is achieved by means of inorganic salts and organic bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,4-diazabicyclo[2.2.2]octane (DABCO). In this reaction, iodoacetate (IOAc) oxidises the aryl palladium (II) intermediate to palladium (IV), which then undergoes reductive elimination to yield the desired product. The reaction is done with both the acid and the acid ester, and the yields were 5% for acid and 85% for the ester. [22]

NBS is also used for a selective mono-bromination of aromatic hydrocarbons, and dimethylformamide (DMF) is used as a solvent in this electrophilic substitution. [20a] NBS-DMF solution is added to a solution of substrate, and the solution is stirred at room temperature for 24 hours. [20a]



Scheme 2.8 Iodination of 2-methyl benzoic acid

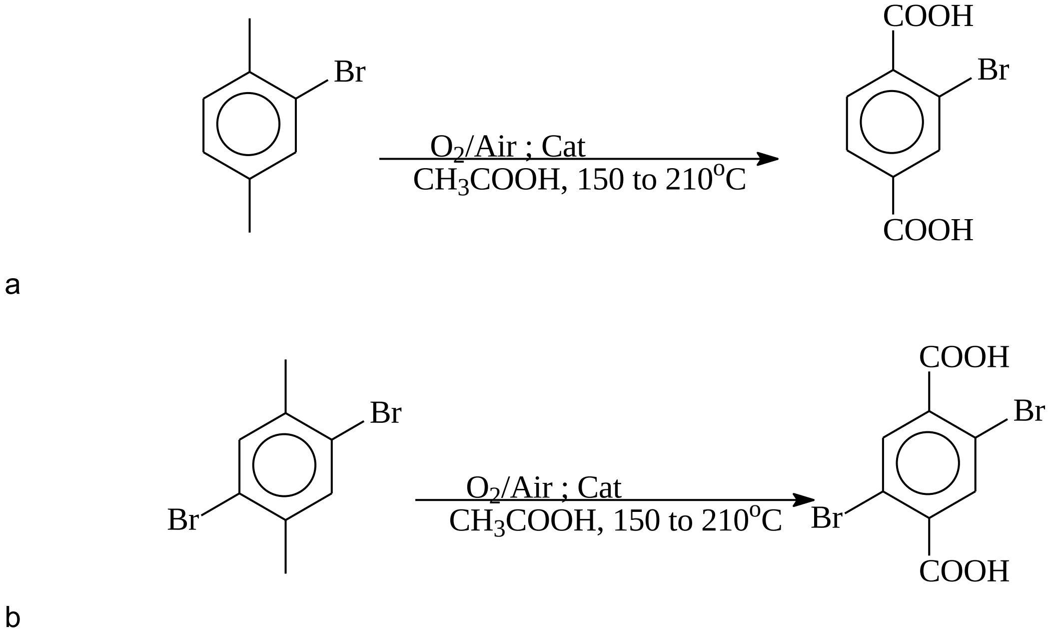
Most bromination reactions are regioselective. Methanol is used to facilitate other bromination reactions. The active species that generates Br^+ is methyl hypobromite (MeOBr). [23] In this reaction, the substrate (aromatic compound) is reacted with MeOBr to yield a brominated product.

Other interesting reactions include the C-H oxygenation reaction of aromatic compounds using palladium acetate/pyridine catalysts. [24] The hydrogen is substituted by acetate in these reactions. The hydroxylation reactions of aromatic compounds using palladium acetate catalysts to produce alcohols are also important. [25]

2.3.3 Oxidation

The oxidation of halogenated dimethyl benzene is another method that could be considered to produce aromatic diacids that could be alkylated in order to produce the desired monomers. Ritter [26] has developed a multicomponent catalyst system containing

$Co(Oac)_2.4H_2O$, $Mn(Oac)_2.4H_2O$, $Zr(Oac)_4$ and NaBr, to produce the diacids (see Scheme 2.9).



Scheme 2.9 Oxidation of halogenated dimethyl benzenes a and b.

These processes have an effect on product yield, as it was found that a semi-continuous process produces higher yields (85%) than a batch process (70%). [26] The oxidation process is a two-stage oxidation process. Oxygen-containing gas is supplied continuously under pressure while the reaction mixture is heated to a temperature of between 120°C and 150°C with continuous stirring. During this process, the first reactive methyl is oxidised to carboxylic acid. [26] The duration of the oxidation step depends on the temperature of the reaction mixture, the amount of catalyst, the pressure and the extent of mixing. [26]

During the second stage of the process, the reaction mixture is heated from 150°C to 180°C, resulting in the remaining methyl group being oxidised into a carboxylic acid group. This duration ranges from 1 to 15 hours. [26]

In the continuous oxidation process, the product mixture containing the partially oxidised halogenated dimethyl benzene may be continuously removed from the first oxidation reaction zone, and fed to the second reaction zone at the second reaction temperature. [26] The product mixture containing the desired diacid is then continuously removed from the second reaction zone. The reaction mixture is cooled and the precipitated product is recovered by means of suction filtration. The formation of by-products is minimised by avoiding low oxygen concentrations throughout the process. This also improves product yield and purity. [26]

In the semi-continuous process, the reagents and catalysts are fed hourly into the oxidation reactor. The reactor is connected to the distillation tower and air is introduced at 200°C and 17.65 bars. The mixture of acetic acid and water as by-product is distilled at a tower top temperature of 170°C. [27] The exhaust gas and water are removed from the tower top. The acetic acid is recycled and the water content is kept at 4 to 5% by weight. [27a] After the residence time of 53 minutes in the reactor, the reaction mixture is filtered.

In all the oxidation experiments 4-carboxybenzaldehyde (4CBA) is the impurity that is present in highest concentration. [26-27, 28]

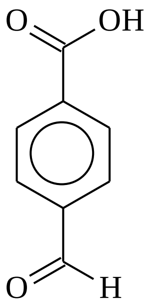


Figure 2.3 4-carboxybenzaldehyde (4CBA)

Yoshiro Yokota [27]a used cobalt acetate as the catalyst, under different reaction conditions. The reagents are fed into the bubbling column-type stainless steel pressure reactor with a gas inlet at the lower portion. These reagents are fed at such a rate that the average residence time of 8 hours is achieved. The inside temperature of the reactor is kept at 120°C, while air is fed at a rate of 3 mL/s under pressure of 10 kg/cm^2 (9.81bar). [28] Bawn and Wright [29] use the oxygen intake by the reaction in order to measure the rate of reaction.

2.4 Polyesters and their synthesis

2.4.1 Polyethylene terephthalate (PET)

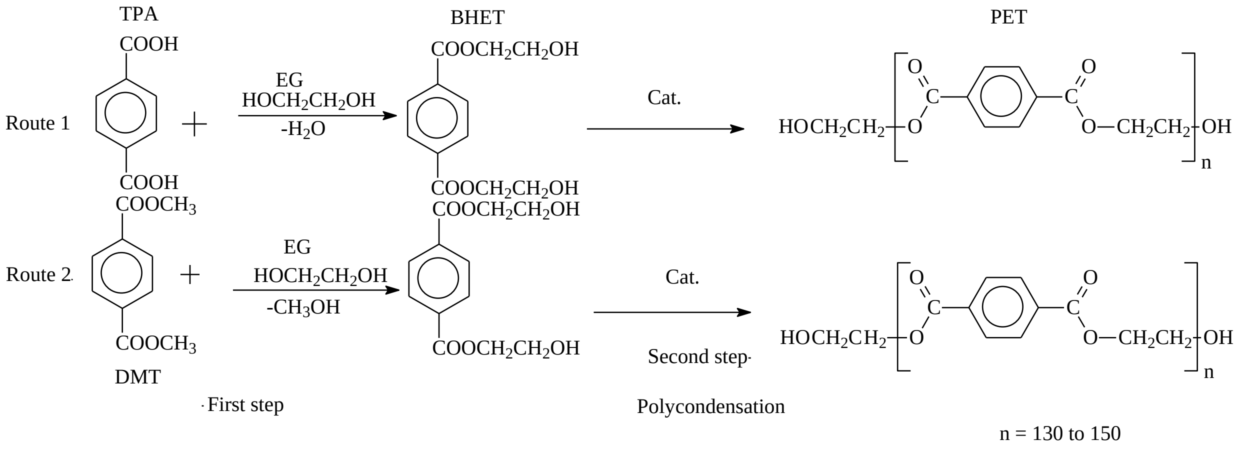
The raw materials for PET are terephthalic acid (TPA) or dimethylterephthalate (DMT) and ethylene glycol (EG). [30] TPA is not preferred as the monomer because of purity problems, but more recently pure TPA has been used as monomer to replace DMT. [1] The purer TPA is provided by Amoco. [1] The most common impurity in the crude TPA is 4-carborxybenzaldehyde (4-CBA), which is very difficult to remove from TPA as its structure is similar to that of TPA. During polymerisation, 4-CBA acts as chain terminator. Another problem concerning the use of TPA as the monomer is that the reaction of TPA with ethylene glycol is too slow for use in commercial production of PET. [31]

Solid DMT is melted and mixed with EG in a mixer before it is added into the reactor at 140°C. As the condensation reaction continues, methanol is formed, and evaporates together with some of the unreacted EG. EG is separated in the distillation column and recycled to the reactor. [32] At this stage, the molar ratio of DMT to EG in the feed is usually about 2:1, and the condensation reaction occurs mainly between 140 and 240°C at atmospheric pressure. The temperature path followed for the trans-esterification reaction in the industrial processes shows a constant increase in temperature from 140 + 30°Ch^{-1} giving a conversion of 95% after 2.5 hours. [32] Zinc acetate catalyst is used so that the reaction can be completed in a reasonable reactor residence time. [32]

The two routes of manufacturing for PET are

1) The direct esterification of terephthalic acid (TPA) with ethylene glycol (EG), to form an intermediate diester and oligomers, is followed by polycondensation to form the PET.[33]
2) The trans-esterification of dimethylterephthalate ester (DMT) with ethylene glycol (EG), to form an intermediate diester and oligomers, is followed by polycondensation to form the PET. [33]

Basically, the two routes are similar after the formation of diester, bis-hydroxy ethylene terephthalate (BHET) and oligomers.



Scheme 2.10 Process for polymerisation of PET [1]

The first step

Route 1: In this polymerisation process, the direct esterification, monomers are TPA and EG, with a molar ratio of 1:1.5-3.0 TPA:EG. The temperature is 170 – 210°C. No catalyst is used because TPA catalyses the reaction. [1] The product is bis-(2-hydroxyethyl)terephthalate (BHET), and water is the by-product.

Route 2: In this polymerisation process, the trans-esterification reaction, monomers are DMT and EG, used in a molar ratio of 1:2.1 – 2.3 DMT:EG. A slow stream of nitrogen is purged. The temperature of reaction is 170 – 210°C. [1] The product bis-(2-hydroxyethyl) terephthalate (BHET) is formed while the by-product is methanol. The heating is done under atmospheric pressure, and in both routes the by-products are evaporated. The reaction rate for this step is low due to the low reaction temperature. [32] The increase in temperature for condensation polymerisation indicates that the reactivity ratios for monomers decrease. [34]

The second step

BHET is gradually heated to 280°C, while the pressure is reduced to less than 1 mmHg. The reaction time for both esterification and polycondensation ranges from 5 to 10 hours. At faster stirring speeds and higher reaction temperatures, the reaction time is shortened. [1] Catalysts are usually avoided as they are not needed to start or end esterification. They do, however, increase the rate of polycondensation and the degree of polymerisation, but the catalysts contaminate the product. [31a] Catalysts that are used for the PET production include Zinc acetate with a reaction time of two hours, while with manganese acetate the reaction is completed within twenty minutes. [31a] The equilibrium constant for the polycondensation reaction is very low (about 0.5), and the rate of ethylene glycol consumption is used as the rate-controlling factor. [32] If the rate at which temperature is increased is too high, this may lead to the flooding of the distillation column because EG and DMT volatalise and escape with the produced methanol. [32]

2.4.2 Polypropylene terephthalate (PPT)

The monomers used are 1,3-propanediol (trimethyleneglycol) and TPA or DMT.[31b, 35]

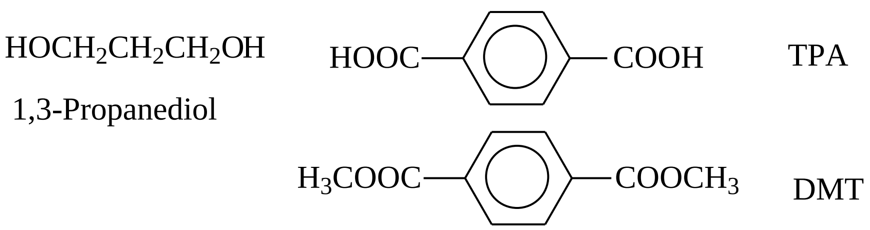


Figure 2.4 Monomers for the synthesis of PPT

The synthesis of PPT is similar to PET synthesis, because the reacting groups are the same. There may be very small differences caused by the length of chain of an alcohol.

Karayannidis et al. [36] used $Mg(OCOCH_3)_2.2H_2O$, $Mn(OCOCH_3)_2.4H_2O$, a zinc catalyst, a tin catalyst and titanium as catalysts for esterification. However, they prefer to use Sb_2O_3 as the catalyst for the production of PPT.

2.4.3 Polypentamethylene terephthalate (PPMT)

The monomers are 1,5-pentanediol (pentamethyleneglycol) and TPA or DMT.

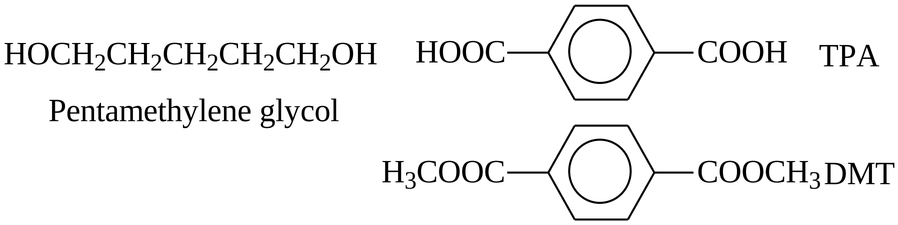


Figure 2.5 Monomers for the synthesis of poly(pentamethylene terephthale)

The synthesis of poly(pentamethylene terephthale) is similar to the PET synthesis because of the similar reacting groups; there may be very small differences caused by the length of chain of an alcohol.

2.5 Properties of polyesters and applications

The properties of polyesters depend on their structures, symmetries, and conformational features.[1] The copolymer of hydroquinone and terephthalate has great strength and a high melting point. [37] Looking at its structure, one notices that it has two phenyl rings. The terephthalate polymers are tough, colourless, semi-crystalline solids. The glass transition temperatures T_g fall steadily with increasing alkylene group length. [1] The flexibility of the polymer chains increase with the number of methylene groups, for instance polyethylene (PE) which does not contain any aromatic group, but is only made up of methylene groups and is very flexible because of the infinite value of methylene groups. Polybutelene terephthalate and polyhexelene terephthalate show double melting point behaviour at atmospheric pressure, and this is indicated by two peaks in the melting curve of differential scanning calorimetry (DSC).

Properties are also changed when making composites; for instance, PPT and PET, to study the properties of polyesters. [38] PPT and PET composite is also used to study mechanical properties. [38b, 39] The monomers are very important in changing properties as well, for instance the use of glycerol produces a highly branched polymer. [40] The tensile strength of polyester is very important as it will determine where the polyester will be applied. [41] Some polymers actually become stronger when a composite is made. [42]

PET is produced in different grades for different applications, and it is the raw material for the production of many products like synthetic fibres, films, filament and plastic objects. [32] It has been stated that some by-products that are formed have an important influence of the fibre properties. In the production of PET, diethylene glycol (DEG) is also formed. Small amounts present in PET (after purification) have a pronounced effect on the physical properties of PET. The melting point of PET, for instance, decreases by 5°C for each weight per cent of DEG present in PET. [32] The presence of small amounts of DEG also has a considerable influence on dyeing. PET is important in fibres that are used for industrial production because of its high performance, low cost, and recyclability. Today PET is mainly used in containers. By 1995, 1.2 million tons of containers were recycled, but this number is smaller than the market demand of 1.8 million tons. [43] The properties of a polymer changes after the treatment with heat, for example if PET is treated with heat the oxygen-barrier properties are changed. [44]

At least 50% of containers go to landfills or they are incinerated. The major post-consumption of PET is used for the production of fibres for ropes, needlework (monofilament) and brushes for domestic cleaning. [43] Other uses include the moulding of automobile parts, plates for vacuum thermo-forming detergents bottles, or for mantles, carpets, and pillows. The recycling of plastics except for the elimination of waste is important, as it only uses 30% of the energy necessary for the production of new resin. [43]

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Chapter 3 Experimental

3.1 Materials

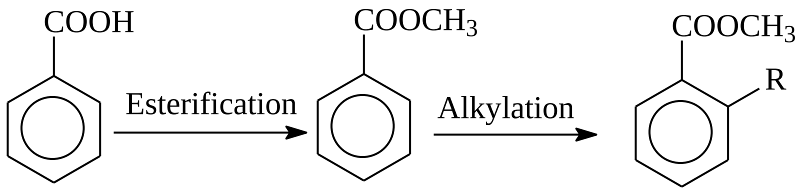
Chemicals and reagents were supplied by Sigma-Aldrich, they were used as they were without further purification.

A Parr 4842 batch reactor was used for high-pressure and high-temperature reactions.

3.2 Envisaged synthetic procedures

These were the envisaged synthetic procedures for the whole experimental work.

Method 1



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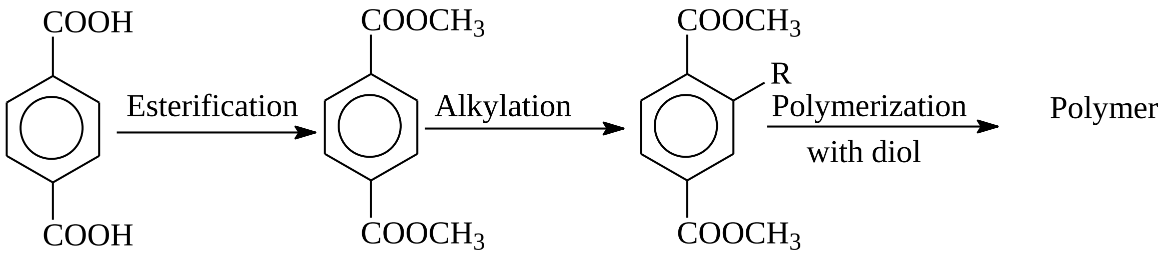

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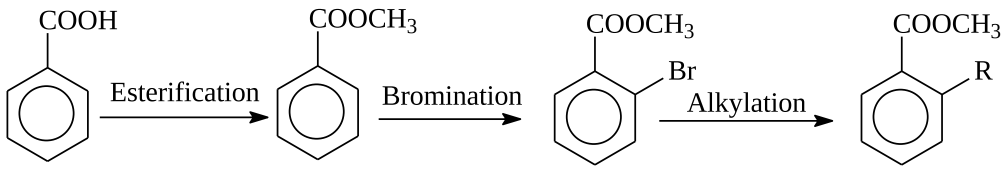
Method 2



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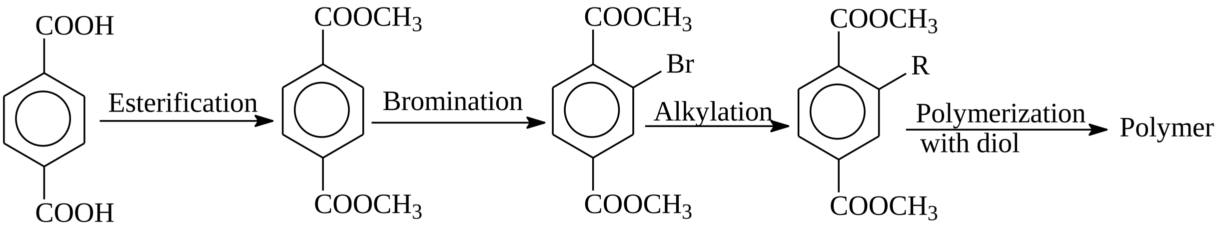

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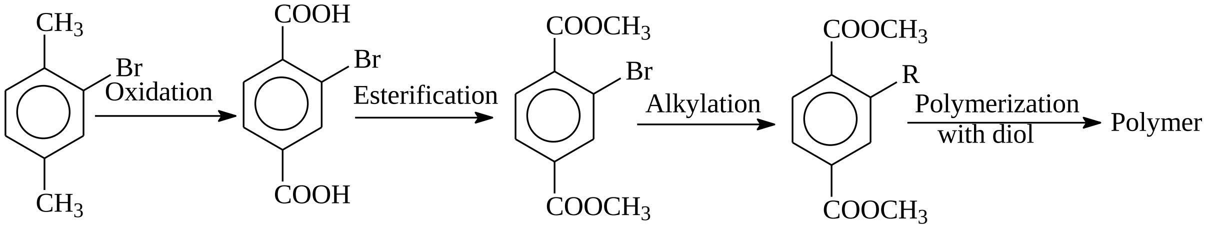
Method 3



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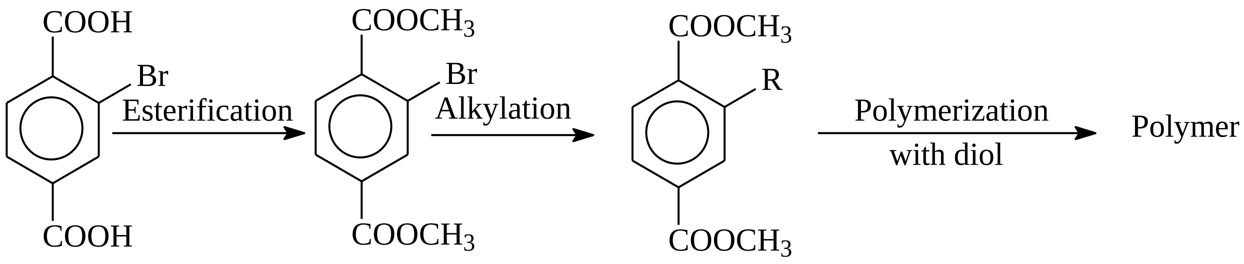
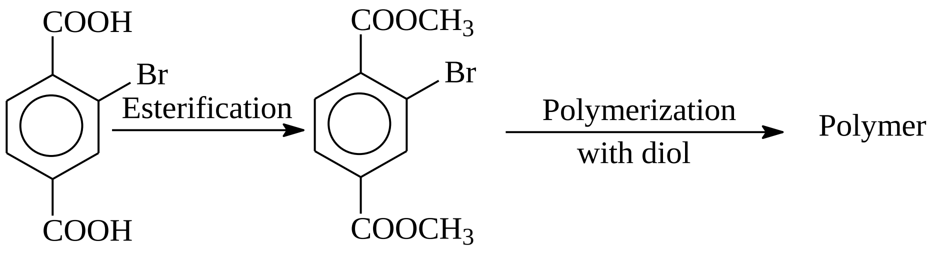
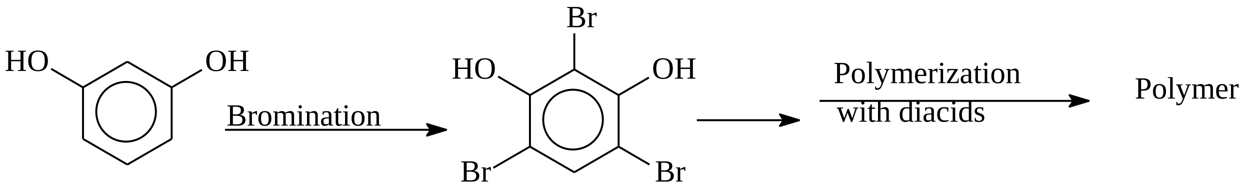


Method 5



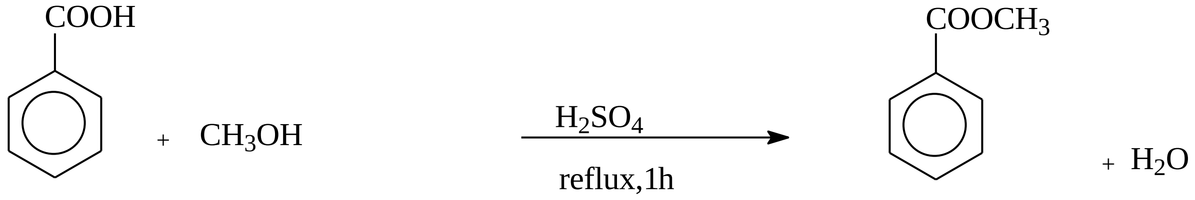
Method 6



Scheme 3.1 Methods 1 to 6 synthetic methodology

3.2.1 Esterification

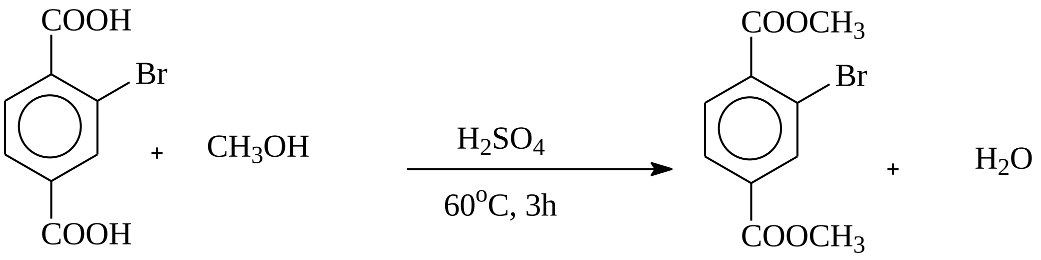
The first reaction that was undertaken was the preparation of methyl benzoate that would be used in the alkylation and bromination reactions to prepare monomers with alkyl substitutions, as shown in methods 1 and 2 in reaction schemes 3.1. The second esterification reaction entailed the preparation of DMT. The carboxylic acid, methanol and sulphuric acid were heated in a reaction flask. For reactions performed in the reactor, copper sulphate pentahydrate was also added. The copper sulphate pentahydrate was added to inhibit corrosion of the reactor. The reaction temperature in this reaction was 110°C for half an hour. [1]



Scheme 3.2 Preparation of methylbenzoate

Procedure

Benzoic acid (15.0809 g, 0.1235 mol) and methanol (25.0 mL, 0.6164 mol) were added into a 100 mL round bottom flask and cooled down in the ice bath. Sulphuric acid concentrated (1.5 mL) was added slowly down the walls of the flask while swirling. After the addition of acid, the reaction mixture was refluxed for 1 hour. The solution was cooled to room temperature, and decanted into the separating funnel containing 25 mL of water. The flask was rinsed with 25 mL diethyl ether, which was poured into the funnel, and mixed thoroughly. The aqueous layer containing the unreacted acid and excess methanol was drained. The organic layer was washed with 25 mL water, and then with 25 mL of 10% sodium bicarbonate. The organic layer was also washed with brine and dried with anhydrous sodium sulphate. The ether was evaporated in the fume cupboard to give the product (9.0047 g, 53.56%). The product was characterised using IR.

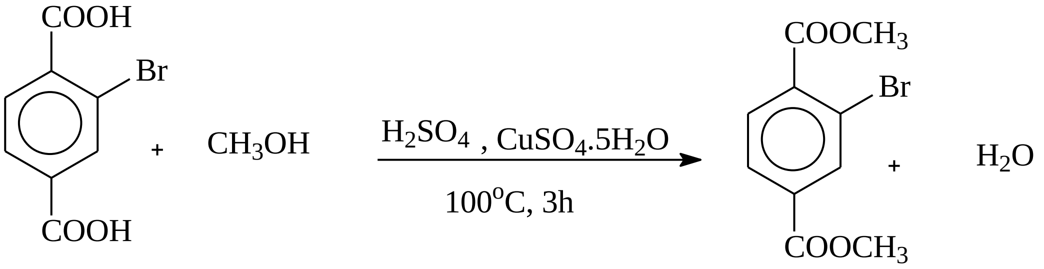


Scheme 3.3 Preparation of 2-bromodimethylterephthalate

The procedure for this experiment is similar to the procedure for experiment in Scheme 3.2 but different temperature and reaction time.

White powder (4.6667 g, 99.65%) was obtained and characterised using IR, NMR and MS.

A similar reaction was also done at 100°C in the batch reactor with copper sulphate pentahydrate as the corrosion inhibitor.



Scheme 3.4 Preparation of 2-bromodimethylterephthalate

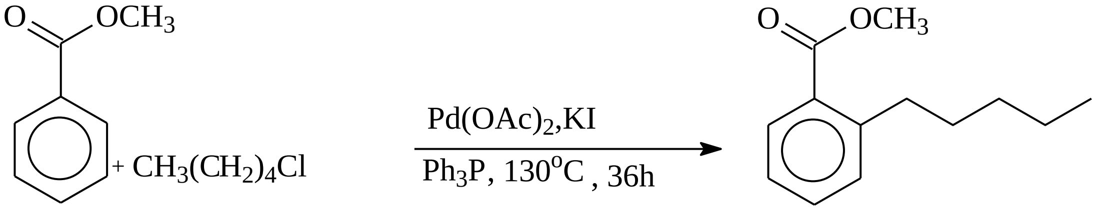
The procedure for this experiment is similar to the procedure for experiment in Scheme 3.2 but different temperature, reaction time and the use coppersulphate.

The product (2.7396 g, 92.70%) obtained was characterised using IR, NMR and MS.

3.2.2 Alkylation

One of the objectives was to achieve alkylated products that could be polymerised. It was decided to perform alkylation reactions on benzoic acid and methyl benzoate to test the method that would be used to alkylate DMT or TPA.

3.2.2.1 Alkylation H substitution on benzene ring

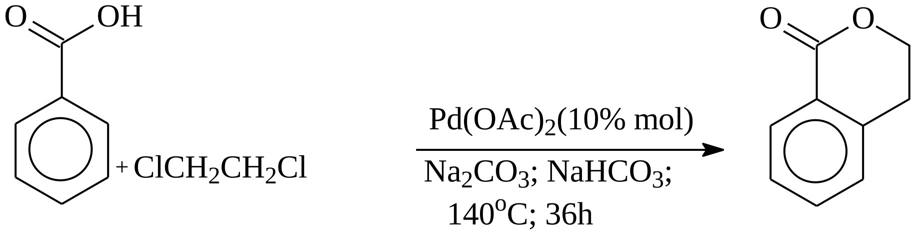


Scheme 3.5 Palladium (II) – catalysed *ortho*-alkylation of methyl benzoate with chloropentane.[2]

Procedure (with KI)

Into the 50mL reactor tube the following reagents were added, 15.5991g (0.1146mol) methyl benzoate, 14.5487g (0.1365mol) chloropentane, 18.6555g (0.1124mol) KI, 3.8999g (0.01487mol) Ph_3P, and 0.8020g (3.5723×10^{-3}mol) $Pd(OAc)_2$ catalyst were added. The reaction mixture was stirred at 130°C for 36 hours. The reaction was cooled to room temperature, poured into 100mL of 10% $CaCO_3$. It was tried to separate the reaction mixture but it was very difficult to do it. Then the reaction mixture was acidified with 10% HCl, and then separation was done. The aqueous layer was extracted with ethyl acetate 5 times with 25mL. The extracts were combined then concentrated under vacuum.

The product was purified using column chromatography, and also using the ethyl acetate and n-hexane mobile phase 1:9 ratio. White crystals (0.8164 g, 3.44%) were obtained and characterised using IR and GCMS.



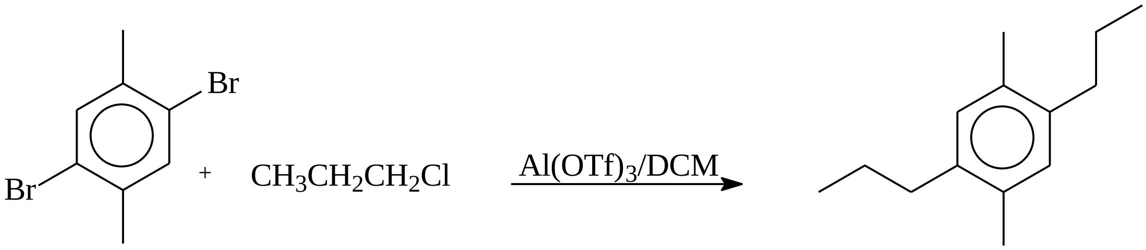
Scheme 3.6 Palladium (II) – catalysed *ortho*-alkylation of benzoic acid with dichloroethane.[3]

The procedure used was similar to the one for reaction Scheme 3.5 with different reaction conditions and reagents.

Cream white crystals (0.0888 g, 2.92%) were obtained and characterised using IR and MS.

3.2.2.2 Alkylation of substituted bromoparaxylene using aluminium triflate as the catalyst

This reaction was performed in order to establish whether it would be possible to achieve the alkylation of the disubstituted terephthalic acid derivatives when preparing the monomers. In this reaction, aluminium triflate (Al(OTf)$_3$) was used as the Friedel-Crafts catalyst. [4]

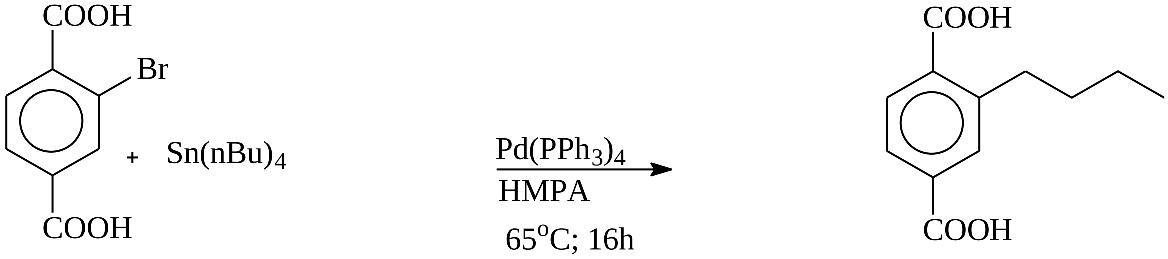


Scheme 3.7 Alkylation of dibromoparaxylene using aluminium triflate as the catalyst.

Procedure

2,5-dibromo*para*xylene (1.5128 g, 5.7312x10^{-3} mol), chloropropane (10.0512 g, 0.1280 mol) and a saturated solution of aluminium triflate in dichloromethane (DCM) (20.0 mL) were mixed in a round bottom flask. This reaction mixture was stirred for three hours at room temperature after which the reaction was quenched with 10% sodium carbonate in ice water. The reaction mixture was extracted with DCM (3 x 25 ml), the extractions were then combined and dried with anhydrous sodium sulphate (Na$_2$SO$_4$). DCM was evaporated in the fume hood, and the product (1.2636 g which was higher than 1.0908 g theoretical yield) was characterised using IR, MS and NMR.

A similar experiment was conducted with the mono-substituted *para*-xylene, dimethyl terephthalate, and 2-bromoterephthhalic acid (BrTPA).



Scheme 3.8 Alkylation of 2-bromotererephthalic acid using Sn(Bu)$_4$ as an alkylating agent. [5]

Procedure

2- bromoterephthalic acid (2-BrTPA) (0.4912 g, 2.0047x10^{-3}mol), tetrabutyl tin [Sn(Bu)$_4$] (1.0 mL, 3.0360x10^{-3}mol, 0.01214mol butyl), Pd(PPh$_3$)$_4$ (0.0281 g, 2.4317x10^{-5}mol), and hexamethylene phosphoramide (HMPA) (2.0 mL) were added into a glass tubular (50 mL).

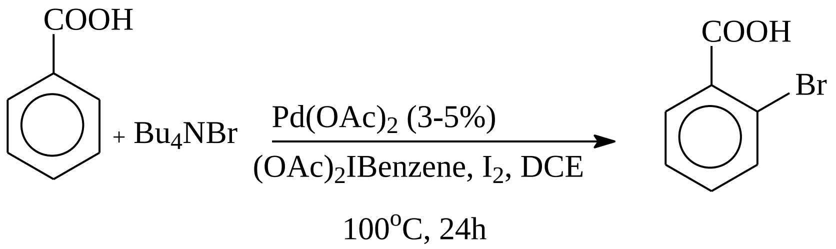
The glass tubular was placed in the reactor, purged with N_2, and sealed. The reaction mixture was heated to 65°C for 16 hours. The reaction mixture was then cooled to room temperature, after which it was partitioned with water and ether to give a white product. The product was filtered, washed with ether and later with water, and dried in an oven at 70°C overnight. The product (0.5132 g, which was higher than theoretical yield of 0.4455 g) was characterised using IR, MS and NMR. A similar reaction was done with 2-bromodimethylterephthalate.

3.2.3 Bromination

This is the process of adding the bromide onto the compound. According to reaction Scheme 3.1 method 2, bromination would be done, followed by alkylation reaction to substitute the bromide on the benzene ring.

3.2.3.1 Bromination using Palladium acetate as catalyst

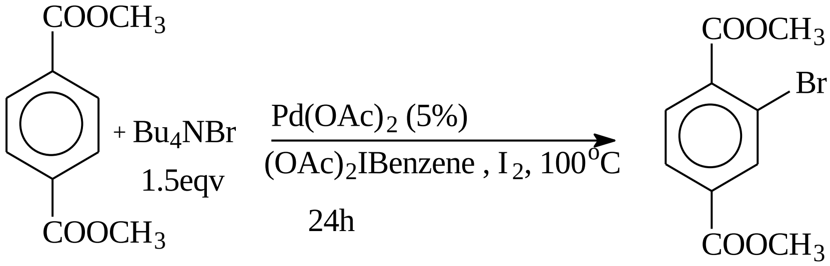
Before bromination of TPA and DMT was attempted, model reactions were done using benzoic acid as substrate. $Pd(OAc)_2$ was chosen as catalyst for this method of selective *othor*-halogenating is used for the synthesis of 1,2,3 substituted arene compounds which are important for the pharmaceutical industries. [6]



Scheme 3.9 Bromination of benzoic acid using Palladium acetate as catalyst.

Procedure

Iodobenzene diacetate (2.6726 g, 0.008324 mol), Iodine (2.5144 g, 0.009907 mol), and DCE (15.0 mL) were added into the reactor. The reaction mixture was stirred at room temperature for 1 hour; benzoic acid (2.5011 g, 0.02048 mol), palladium acetate (0.1081 g, 6.5333×10^{-4} mol) (3.2% of benzoic acid) and tetrabutyl ammonium bromide (4.5810 g, 0.01421 mol) (limiting reagent) were added, the reaction mixture was heated to 100°C for 24 hours. The reaction was stopped, cooled to room temperature and Na_2CO_3 (100 mL of 10%) was added. Then the reaction mixture was placed in a separating funnel. The organic layer was separated and the aqueous layer was washed with diethyl ether (2 x 50 mL). The aqueous layer was acidified with HCl (10%), and again extracted with ethyl acetate (4 x 50 mL). The ethyl acetate extract was dried with anhydrous Na_2SO_4 and evaporated. Column chromatography (with silica gel stationary phase n-hexane: diethyl ether: ethyl acetate (8:1:1) mobile phase) gave a white crystals (0.6952 g, 24.34% yield) after the evaporation of the solvent. The product was analysed using MS and NMR.



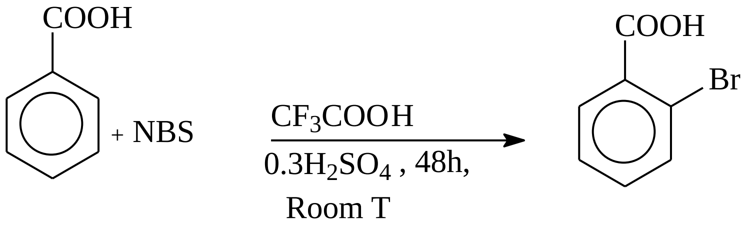
Scheme 3.10 Bromination of DMT using Palladium acetate as catalyst.

The experimental procedure used was similar to the one for reaction Scheme 3.9.

Cream white crystals (0.0556 g, 0.52% yield) were analysed using IR and NMR.

3.2.3.2 Bromination using NBS

Duan, Zhang and Dolbier [7] used N-bromosuccinimide (NBS) as the brominating reagent.



Scheme 3.11 Bromination of benzoic acid. [8]

Procedure

Benzoic acid (12.2031 g), trifluoro acetic acid (TFA) (50 mL), H_2SO_4 (15 mL) and NBS (26.7800 g) (added slowly over eight hours) was added into a round bottom flask. The reaction mixture was stirred at room temperature for 48 hours. The reaction mixture was poured into 200 mL ice water. The aqueous layer was separated by filtration. The aqueous layer was then extracted (4 x 50 mL) DCM. The organic layers were combined and washed with brine and then dried with $CaCl_2$. The DCM was evaporated in the fume hood.

Cream white crystals (2.6162 g, 12.95% yield) were obtained and characterised using MS, IR and NMR.

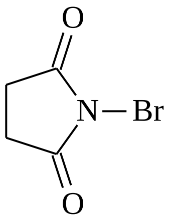
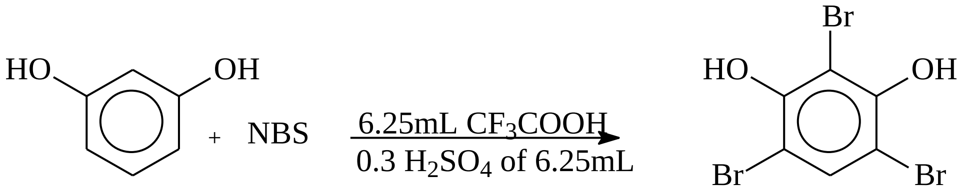


Figure 3.1 NBS structure

3.2.3.3 Bromination of resorcinol

Mono- or dibromination of resorcinol could not be done selectively. For this reason, it was decided to use 3 moles of NBS to 1 mol of resorcinol to produce the tri-brominated product. The same procedure as described from the previous paragraph was followed to give white crystals (13.8231 g, 87.74%) which were characterised by IR, MS and NMR.

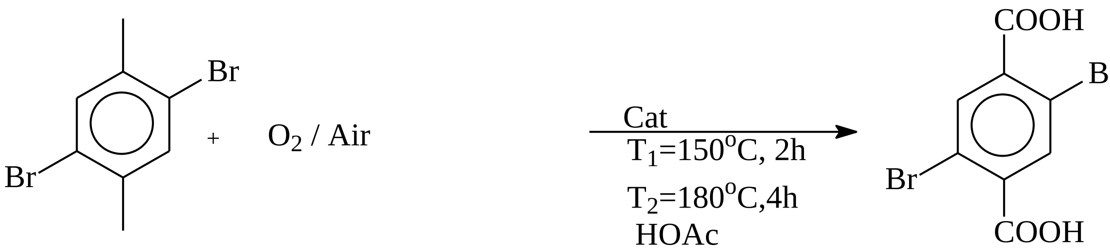


Scheme 3.12 Bromination of resorcinol using NBS. [7-8]

3.2.4 Oxidation of paraxylene

Another method (Method 3, reaction Scheme 3.1) of achieving the objectives was to do oxidation of the already brominated *para*xylene.

The synthesis of halogenated aromatic diacids was achieved by means of the oxidation of the halogenated dimethyl benzenes. A four-component catalyst combination was used in a two-stage temperature process. [9]

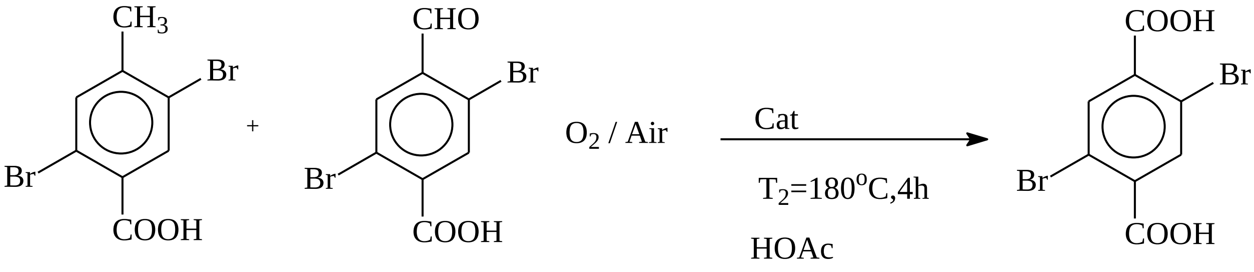


Scheme 3.13 Synthesis of 2,5-dibromotherephthalic acid from 2,5 dibromo-1,4-dimethylbenzene. [9-10]

Procedure

2,5-dibromo*para*xylene (9.9214 g, 0.03759mol) and acetic acid 35 mL were added in the reactor. The catalysts cobalt acetate tetrahydrate (0.0618 g, 2.481×10^{-4}mol), manganese acetate tetra hydrate (0.0619 g, 2.526×10^{-4}mol), zirconium acetate solution in acetic acid (0.01 mL, 7.6×10^{-6} mol Zr^{4+}), and sodium bromide (0.0519 g, 5.044×10^{-4}mol) were also added into the reactor.

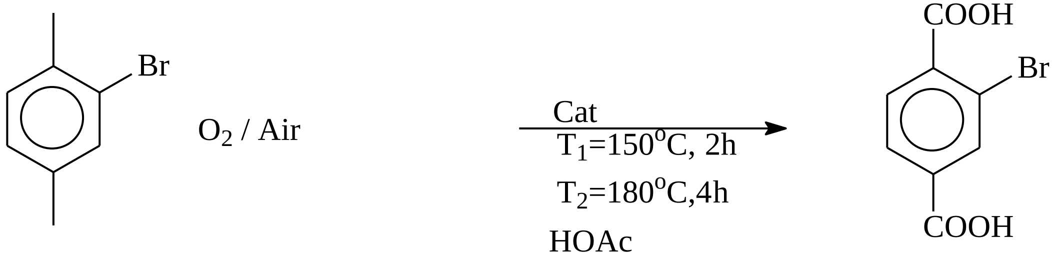
The reactor was pressurised with O_2 (8.2 bar) and then air (to 11.7 bar), after which the temperature was raised to 150°C. As the oxidation proceeded, the pressure of the reactor dropped. When the pressure reached 5.5 bar, the reactor was cooled to 40°C (this was done for ease of handling and safety) and the above procedure of pressurising with O_2 and air was repeated. The temperature was increased to 180°C (the reactor was kept under pressure using the above procedure again). This was done until no pressure drop could be noticed. The reaction was cooled to 40°C; and then the reaction mixture was transferred into a beaker. The reactor was washed with acetic acid (50 mL) and this was poured into the beaker. The solvent was evaporated and left to cool down, and then the product formed. Cream white powder (8.5671 g, 70.3% yield) was obtained and characterised using IR, MS and NMR. After analysis of the product (reaction Scheme 3.13), it was discovered that the reaction did not proceed all the way to completion because both the desired product, the aldehyde and unreacted starting material, were present in the mixture.



Scheme 3.14 Completion of the oxidation reaction. [11]

The same experimental procedure as in reaction Scheme 3.13 was then used, but the temperature was immediately elevated to 180°C for four hours.

Cream white powder (0.7994 g, 48.29% yield) was obtained and characterised using IR and MS.



Scheme 3.15 Oxidation of 2-bromoparaxylene. [12]

The same procedure of oxidation as in reaction Scheme 3.13 was used for the oxidation of 2-bromo*para*xylene.

The product (3.9967 g, 43.48% yield) was analysed using IR, MS and NMR.

3.2.5 Polymerization

Polymerization experiments were performed in a batch reactor to which a vacuum pump was connected.

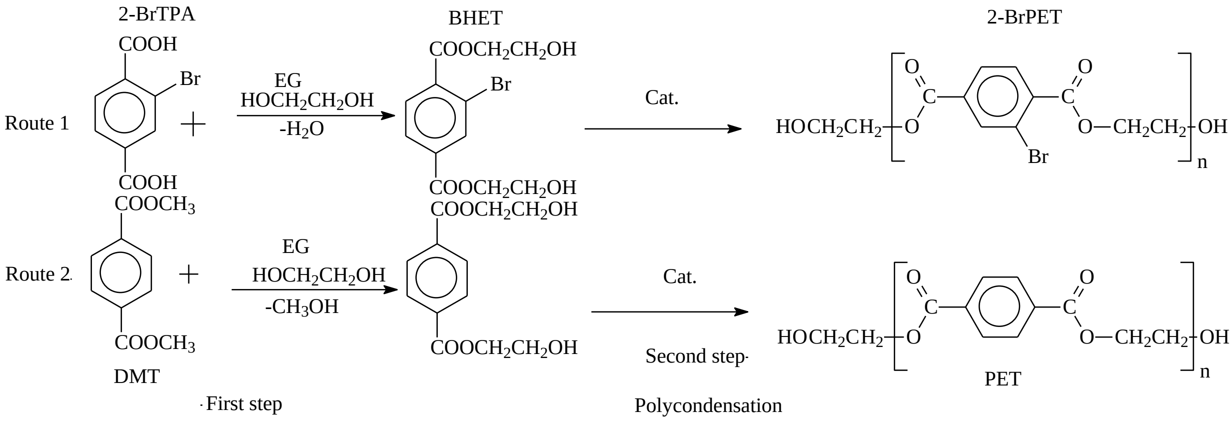
3.2.5.1 Synthesis of PET

The raw materials for PET were terephthalic acid (TPA) or dimethylterephthalate (DMT) and ethylene glycol (EG). [13]

Two synthetic routes were followed:

1) Direct esterification of 2-bromoterephthalic acid (2-BrTPA) with ethylene glycol (EG), to form an intermediate diester and oligomers, followed by polycondensation to form brominated PET.
2) Transesterification of dimethylterephthalate ester (DMT) with ethylene glycol (EG) to form an intermediate diester and oligomers, followed by polycondensation to form PET.

After the formation of diester (bis-hydroxy ethylene terephthalate (BHET)) and oligomers, the two routes are similar.



Scheme 3.16 Process for polymerization of PET [14] [15] [16]

First step

The monomers shown in reaction Scheme 3.16 reacted in a molar ratio of 1:2.1-2.3 TPA/DMT: EG while a steady stream of nitrogen was purged into the reactor under atmospheric pressure at 150–170°C to form BHET and methanol.

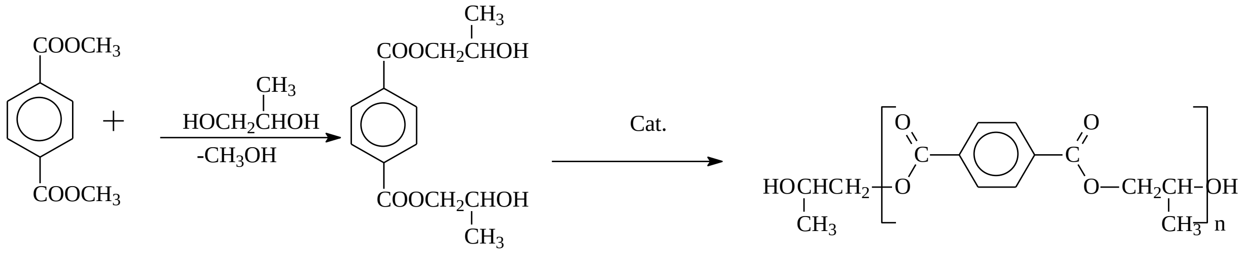
Second step

BHET was gradually heated to 200°C, while reducing the pressure to less than 1mmHg. The reaction time for both esterification and polycondensation was 5 to 10 hours. Water (for route 1) and methanol (for route 2) were by-products during the PET synthesis. Manganese acetate and sodium acetate in a 1:1 ratio were used as catalysts.

Procedure

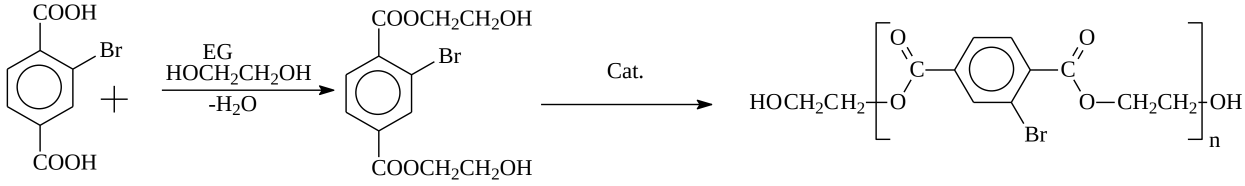
DMT (7.4031 g, 0.03833mol), EG (15.0 mL) (excess) were mixed and melted in the reactor at 110°C and $Mn(OAc)_2$/Na(OAc) (0.1227 g) catalyst, was added. After this, the temperature was raised to 150 - 180°C. As the reaction continued, methanol formed (condensed in a cold trap). Once methanol stopped forming, the temperature was increased by 30°C up to 210°C, and the vacuum was applied. The by-product methanol and excess EG were evaporated into the cold trap. The reactor was allowed to cool down after six hours, and the product was recovered.

The product was analysed using IR, DSC, DTG and SEM (no NMR and GPC analyses were done due to sample insolubility in TCB).



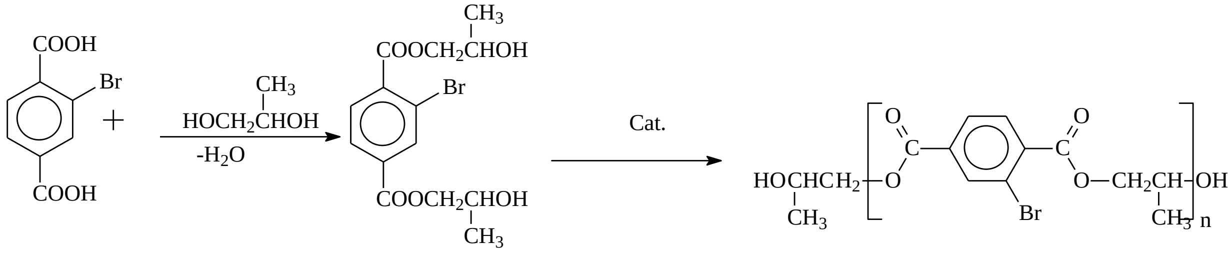
Scheme 3.17 Process for preparation of poly(1,2-propanediol) terephthalate [P(1,2-P)T].

The product was analysed using IR, NMR (TCB80%:$C_6D_6$20%), DSC, DTG, GPC and SEM.



Scheme 3.18 Process for polymerization of polyethylene 2-bromoterephthalate (PE2-BrT) (similar to Route 1, Scheme 3.16)

The product was analysed using IR, NMR (TCB80%:$C_6D_6$20%), DSC, DTG, GPC and SEM.

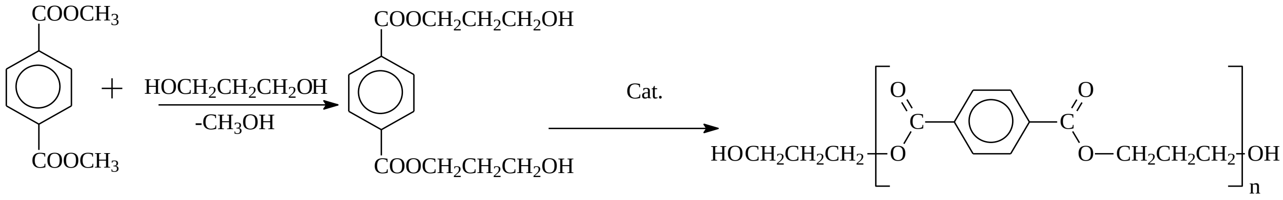


Scheme 3.19 Process for polymerisation of poly(1,2-propanediol) 2-bromoterephthalate [P(1,2-P)2BrT]

The product was analysed using IR, NMR (TCB80%:$C_6D_6$20%), DSC, DTG, GPC and SEM.

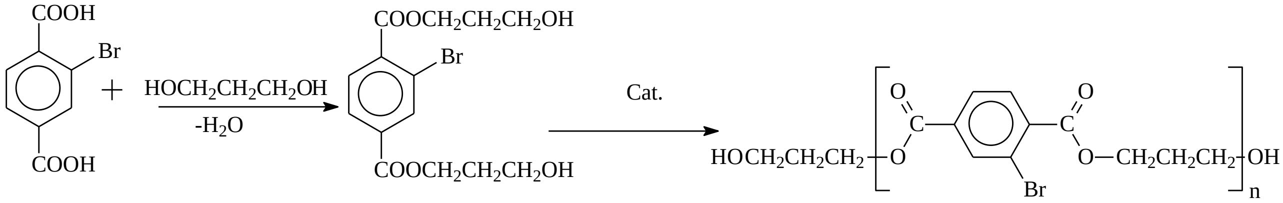
3.2.5.2 Synthesis of polypropylene terephthalate (PPT)

The synthesis of PPT was similar to PET synthesis because the reacting groups are the same but different number of methylene units.



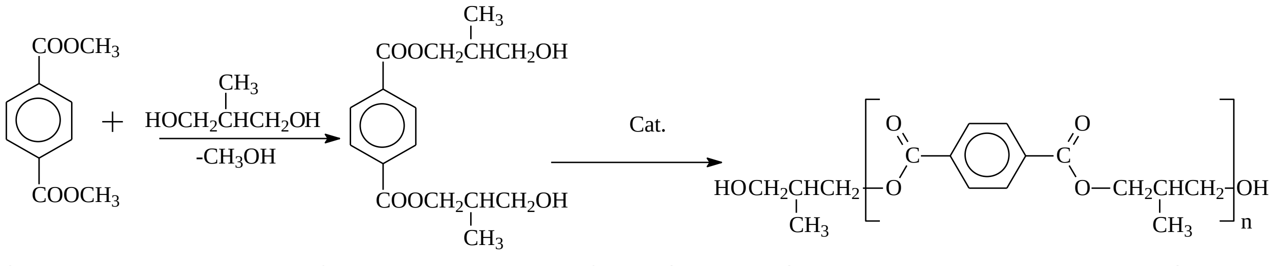
Scheme 3.20 Process for polymerisation of PPT.[17] [18]

The product was analysed using IR (no NMR due to sample insolubility in TCB), DSC, GPC and DTG.



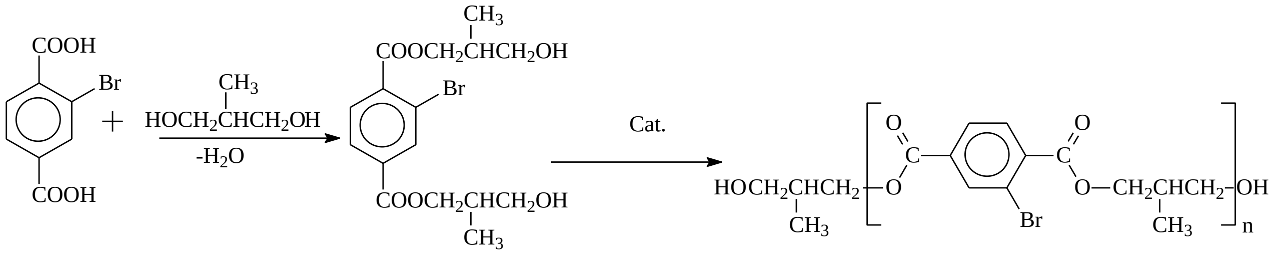
Scheme 3.21 Process for polymerisation of polypropylene 2-bromoterephthalate (PP2-BrT)

The product was analysed using IR, NMR (TCB80%:$C_6D_6$20%), DSC and DTG.



Scheme 3.22 Process for polymerisation of poly(2-methyl) propylene terephthalate [P(2-M)PT]

The product was analysed using IR, NMR (TCB80%:$C_6D_6$20%), DSC and DTG.

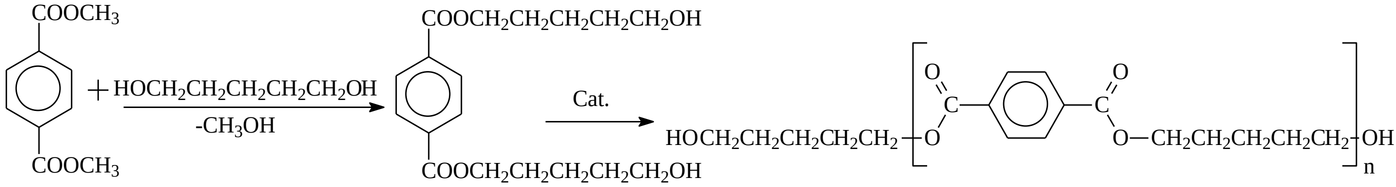


Scheme 3.23 Process for polymerisation of Poly(2-methyl)propylene 2-bromoterephthalate [P(2-M)P2-BrT

The product was analysed using IR, NMR (TCB80%:$C_6D_6$20%), DSC and DTG.

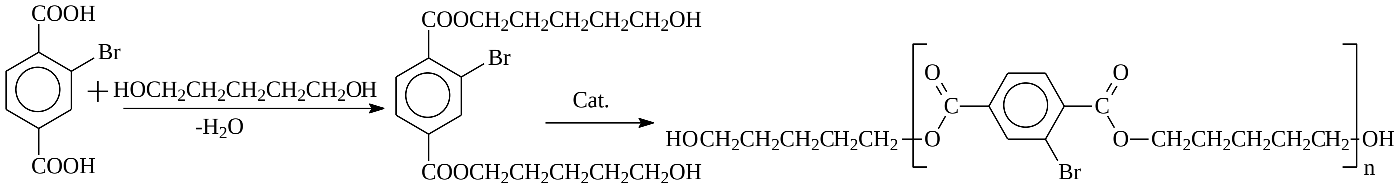
3.2.5.3 Synthesis of poly pentamethylene terephthate (PPMT)

The synthesis of PPMT was similar to PET synthesis because the reacting groups are the same but different number of methylene units.



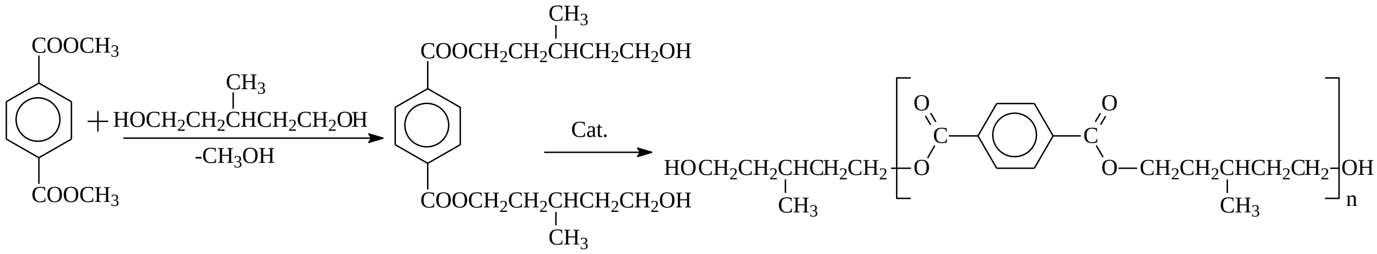
Scheme 3.24 Process for polymerisation of polypentamethylene terephthalate (PPMT)

The product was analysed using IR, NMR (TCB80%:$C_6D_6$20%), DSC and DTG.



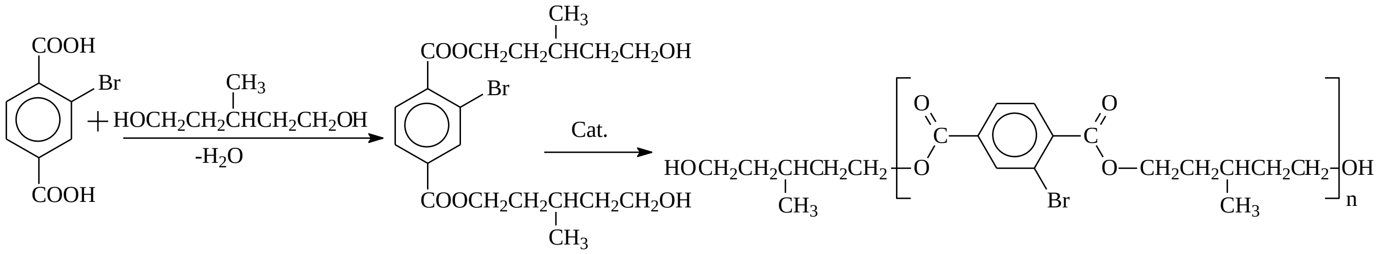
Scheme 3.25 Process for polymerisation of polypentamethylene 2-bromoterethalate (PPM2-BrT)

The product was analysed using IR, NMR (TCB80%:$C_6D_6$20%), DSC and DTG.



Scheme 3.26 Process for polymerization of Poly(3-methyl)pentamethylene terephthalate [P(3-M)PMT]

The product was analysed using IR, NMR (TCB80%:$C_6D_6$20%), DSC and DTG).



Scheme 3.27 Process for polymerization of Poly(3-methyl)pentamethylene 2-bromoterephthalate [P(3-M)PM2-BrT]

The product was analysed using IR, NMR (TCB80%:$C_6D_6$20%), DSC and DTG.

3.3 Analytical methods

3.3.1 Infrared Spectroscopy (IR)

IR spectra were recorded using the FTIR Bruker Tensor 27 equipped with a diamond ATR. OPUS software was used for the data analysis. The samples were analysed as they were no sample preparation was required.

3.3.2 Gas Chromatography-Mass Spectrometry (GC-MS)

GC-MS analysis were performed on an HP 6890 GC-MS equipped with a PE-001 capillary column (60m x 0.32mm x 1.00$_{\mu}$m, Elite Methyl Siloxane) connected to an Autospec Micromass Time-of-Flight (TOF) mass spectrometer. The NIST database of the OPUS v 3.6 X software was used for characterization of the products. The samples were dissolved in methanol.

3.3.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

Bruker Advance III Ultra Shield 600 MHz Nuclear Magnetic Resonance spectrometer (NMR); Top spin 2.1 Version 2.1.1 was used for processing commands and parameters as well as data acquisition. 20 mg of the sample was dissolved in 0.8 mL of solvent in a vial filtered through the cotton wool into an NMR tube.

3.3.4 Mass Spectrometry (MS)

A micrOTOF-Q II instrument from Bruker was used with atmospheric pressure chemical ionization (APCI) source, dry sample in a glass capillary, positive ion mode detection and dry heater at 200°C in normal MS mode.

3.3.5 Thermogravimetric Analysis (TGA)

An SDTQ 600 Thermal instrument which carries out parallel recording of thermogravimetry (TG) and differential scanning calorimetry (DSC) curves. 10-12 mg samples were contained within alumina crucibles and heated at a rate of 10°C/min from room temperature to 500°C under flowing nitrogen.

3.3.6 Differential Scanning Calorimetry (DSC)

A DSC 2010 from TA instruments was used, initial heating from 30°C, heating ramp 10°C/min to 250°C, isothermal for 5 min cooling ramp 10°C/min to 30°C. The analysis were performed under N_2 atmosphere.

3.3.7 Gel Permeation Chromatography (GPC)

An HP 1100 series liquid chromatograph was utilized for relative molecular mass determinations. The chromatograph was equipped with a refractive index detector. GPC was performed using 1,2,4-trichlorobenzene as both sample solvent and mobile phase. Two PLgel columns (type B, 10 μm) were connected in series and maintained by a thermostat compartment at 55 °C and the optical cell of the refractive index detector was regulated at 40°C. Elution of samples (~ 5 mg/mL) was performed at 1 mL/min with sample volumes of 100 μL Polystyrene GPC standards were used to calibrate the columns in the range of 1 050 – 2 400 000 g/mol and therefore the molecular masses reported here are relative to polystyrene standards.

3.3.9 Scanning Electron Microscopy (SEM)

A Quanta Feg 250 environmental scanning electron microscope was used, for micro analysis: Oxford X Map detector using INCA software was used. The sample was ground into small particles and attached to the double sided tape and analysed.

3.4 References

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Chapter 4 Results and Discussions

4.1 Chemical characterisation of products

4.1.1 Esterification

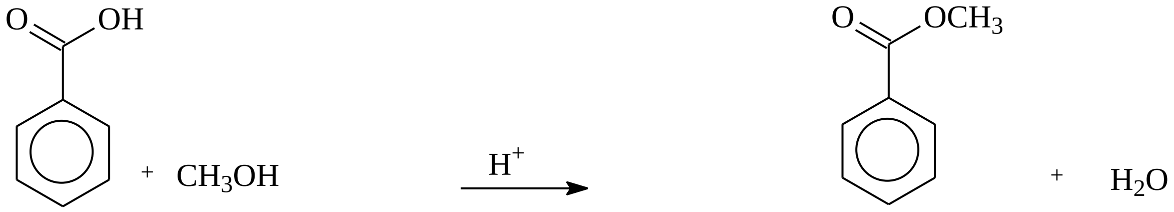
4.1.1.1 Esterification of benzoic acid

Benzoic acid was analysed so that it could be compared to the product obtained during esterification.

(IR Figure C.1, Appendix C)

IR spectrum :v_{max}(cm^{-1}) 3300 – 2500 (O-H stretching vibrations), 3070 and 2985 (C-H superimposed on OH band), 1715 (C=O stretch), 1408 (C-O-H in-plane bend), 1280 (C-O stretch), 930 (O-H out-of-plane bend).

Benzoic acid was analysed with IR, the results were compared with the product produced in reaction Scheme 4.1 methylbenzoate.



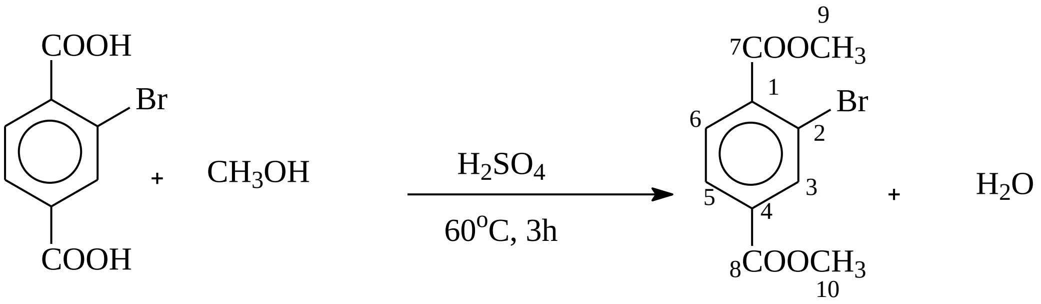
Scheme 4.1 Preparation of methylbenzoate

The product (9.0047g, 53.56% yield) was analysed with IR (Figure C.2 Appendix C) confirming it was the desired product.

IR spectrum :v_{max} (cm^{-1})3070 (C-H stretch aromatic), 2985 (w) (C-H stretch CH_3), 1719(s) (C=O stretch), 1431(m) [CH_3-O-C(=O)-R], 1245(s) [C-O (C-C(=O)-O) stretch], 1110(s) [C-O (O-C-C) aromatic esters of primary alcohols], 744(s) [C-H out-of-plane bending].

The results showed that the reaction took place. IR of the experiment did not have carboxylic acid OH stretch. This was also proof that the benzoic acid was esterified. The CH stretch peak at 2959 cm^{-1} for the CH_3 was observed. The peak at 1110 cm^{-1} for primary alcohol esters was observed. The carbonyl C=O stretch peak at 1719 cm^{-1} and the CH_3-O-C(=O)-R bend were observed. The C-O stretch at 1245 cm^{-1} (C-C(=O)-O), C-O (O-C-C) aromatic esters of primary alcohols. C-H out-of-plane bending vibration was also observed.

4.1.1.2 Esterification of 2-bromoterephthalic acid



Scheme 4.2 Preparation of 2-bromodimethyleterephthalate.

A white powder (4.6667 g, 99.65%) was obtained and characterised with IR (Figure C.3 Appendix C), NMR (Figure D.1 Appendix D) and MS (Figure B.1 Appendix B).

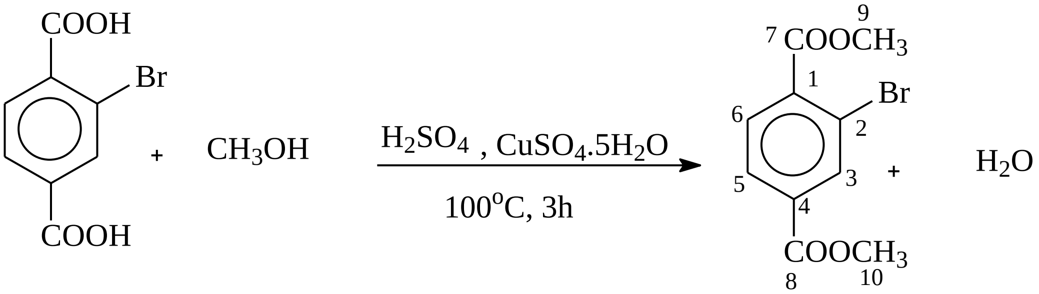
IR spectrum	:ν_{max} (cm^{-1}) 2959 (w) (C-H stretch CH_3), 1719(s) (C=O stretch), 1431(m), 1245(s) [C-O (C-C(=O)-O)], 1110(s) [C-O (O-C-C) aromatic esters of primary alcohols], 744(s)
^{1}H NMR spectrum	:(DMSO, 600 Hz) δ_H(ppm) 8.14(s) H-C_3, 7.98(d) H-C_6 , 7.85(d) H-C_5 3.87(s)(6H) H-$C_{9,10}$, 2.49(solvent)
^{13}C NMR spectrum	:(DMSO, 600 Hz) δ_C(ppm) 165.697 C_7, 164.285 C_8, 136.487 C_2, 134.050 , 133.886 C_3, 133.345 C_4, 128.285 C_6, 120.049 C_5, 52.915 C_9, 52.787 C_{10}, 39.6(solvent)
MS spectrum	:(m/z) M$^+$ 272.977

IR showed that the esterification was done successfully with 2959 cm^{-1} C-H stretch for CH_3, no OH stretch peak carboxylic acid was observed, 1110 cm^{-1} peak for primary alcohol esters was also observed.

^{1}H NMR results showed the C-H peaks for CH_3 of the ester group at 3.87 ppm, and C-H aromatic peaks were also observed. ^{13}C NMR also confirmed the esterified results, with C=O carbons at 165.697 ppm and 164.285 ppm, aromatic carbons at 136.487, 134.050, 133.886, 133.345, 128.285, 120.049 ppm and methyl carbons for the esters at 52.915 and 52.787 ppm.

MS results with molecular ion of 272.977 m/z confirmed the ester product.

A similar reaction was also done at 100°C for 3 hours in the batch reactor with copper sulphate pentahydrate as a corrosion inhibitor



Scheme 4.3 Esterification of terephthalic acid with $CuSO_4.5H_2O$ as an inhibitor.

The product was characterised using IR (Figure C.4 Appendix C), NMR (Figure D.2 Appendix D) and MS (Figure B.2 Appendix B)

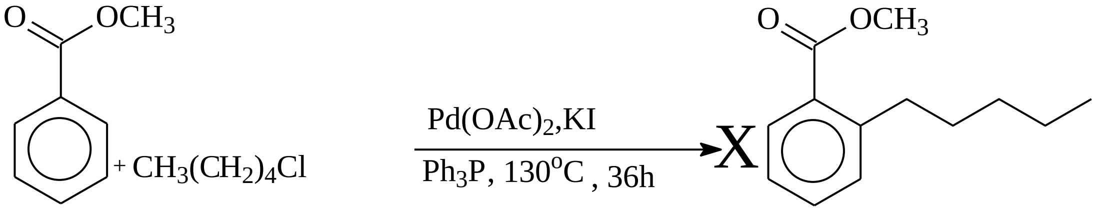
IR spectrum	:ν_{max} (cm^{-1}) 2959(w) (C-H stretch CH_3), 1720(s) (C=O stretch), 1482(m), 1247(s) [C-O (C-C(=O)-O)], 1112(s) (C-O (O-C-C) aromatic esters of primary alcohols), 745(s)
^{1}H NMR spectrum	:(DMSO, 600 Hz) δ_H (ppm) 8.17(s) (H-C_3), 8.01(d) (H-C_6), 7.87(d) (H-C_5), 3.88(s) (6H) (H-$C_{9,10}$), 2.49 (solvent).
^{13}C NMR spectrum	:(DMSO, 600 Hz) δ_C (ppm) 165.644 (C_7), 164.250 (C_8), 136.474 (C_2), 133.843 (C_1), 133.309 (C_3), 131.022 (C_4), 128.325 (C_6), 119.997 (C_5), 52.877 (C_9), 52.747 (C_{10}), 39.6(solvent)
MS spectrum	:(m/z) M^+ 272.976

The above results constitute confirmation of the product 2-bromodimethylterephthalate. More esterification products were produced and they were used in the other reactions.

4.1.2 Alkylation

The main objective of the experimental work was to produce alkylated products that could later be polymerised. After the literature study it was decided to perform alkylation reactions on benzoic acid and methylbenzoate ester with a view to test the method, which will later be used to alkylate dimethyl terephthalate (DMT).

4.1.2.1 Alkylation H substitution on benzene ring



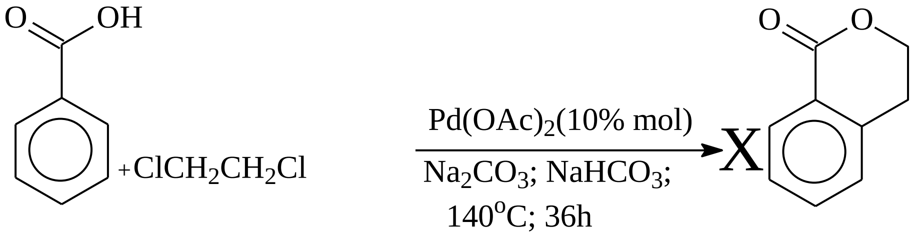
Scheme 4.4 Alkylation of methylbenzoate using palladium acetate as the catalyst and chloropentane as alkylating agent

The product was characterised using IR (Figure C.5 Appendix C) and GC-MS (Figure A.1 Appendix A)

IR spectrum :ν_{max} (cm^{-1}) 3070(w) (C-H aromatic), 2957(w) (C-H stretch), 2551(w), 1678(s) C=O (stretch), 1452(m), 1273(s), 704(s)

GC-MS :(m/z) M^+ 137 ($C_8H_8O_2$)

GC-MS showed that the compound contained chloropentane and methyl benzoate, indicating that no reaction took place.



Scheme 4.5 Alkylation of benzoic acid using 1,2-dichloroethane.

Cream white crystals (0.0888 g, 2.92% yield) were analysed using IR (Figure C.6 Appendix C) and MS (Figure B.3 Appendix B).

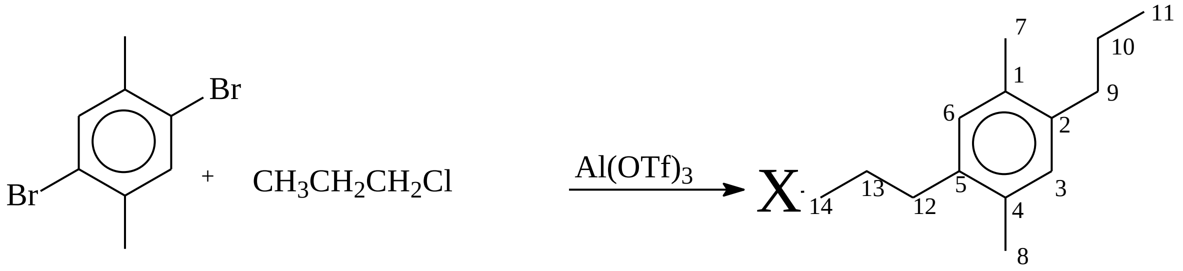
IR spectrum :ν_{max} (cm^{-1}) 3062(w) (C-H aromatic), 2959(w), 2910(w) (C-H stretch), 1709(s) (C=O stretch), 1601(w), 1451(m), 1265(s), 1112(s), 701(s)

MS spectrum :(m/z) M^+ 123.04 ($C_7H_6O_2$)

The results above showed that no reaction took place.

4.1.2.2 Alkylation of brominated aromatic compounds

In this reaction aluminium triflate ($Al(OTf)_3$) was used as the Friedel-Crafts catalyst.



Scheme 4.6 Alkylation of 2,5-dibromo *para*xylene.

This reaction was done in order to establish the possibility of doing alkylation reaction of the disubstituted terephthalic acid derivatives when preparing the monomers. The product was analysed using IR (Figure C.7 Appendix C), NMR (Figure D.3 Appendix D).

IR spectrum :ν_{max} (cm^{-1}) [2982(w), 2951(w), 2918(w)] C-H stretch, 1471(m), 1435(m), 1342(w), 1052(m), 749(m)

^1H NMR spectrum :(DMSO, 600 Hz) δ_H (ppm) 7.566(s)(2H) H-$C_{3,6}$, 3.349(s) (6H) H-$C_{7,8}$, 2.490(DMSO), 2.273(s), 2.071(s)

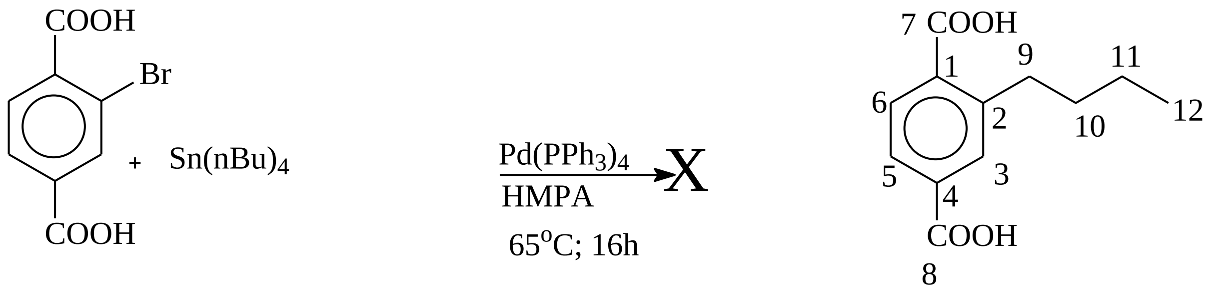
^{13}C NMR spectrum :(DMSO, 600 Hz) δ_C (ppm) 206.527 $C_{2,5}$, 136.907 C_1, 133.846 C_4, 123.037 $C_{3,6}$, 39.639(DMSO), 30.691 $C_{7,8}$, 21.488

IR showed the CH stretch vibration for the methyl groups at 2982 and 2951cm^{-1} and the CH aromatic stretch vibrations. There were other vibration peaks observed at different wavenumbers.

^1H NMR showed the aromatic C-H peak at 7.567 ppm. There were also CH peak for methyl groups observed at 3.349 ppm.

^{13}C NMR showed CBr carbon at 206.527 ppm, aromatic carbons were observed as shown above, and the two methyl groups carbons were also observed. However, the methylene carbons were not observed. It was concluded that the reaction did not take place. The reaction did not take place because of the methyls on the benzene ring are not electronwithdrawing to activate the ring, and the bromide is also not a good leaving group.

A similar experiment was also done with the mono-substituted *para*-xylene, dimethyl terephthalate, and 2-bromoterephthalic acid.



Scheme 4.7 Alkylation of 2-bromotererephthalic acid using tetrabutyl tin as an alkylating agent

The product was analysed using IR (Figure C.8 Appendix C), NMR (Figure D.4 Appendix D).

IR spectrum :ν_{max} (cm^{-1}) 3000 – 2800 (O-H stretch carboxylic acid), 1684 (s) (C=O stretch), 1554(m), 1484(m), 1408(s), 1251(s), 746(s)

^{1}H NMR spectrum :(DMSO, 600 Hz) δ_H (ppm) 13.655 O-H carboxylic acid, 8.124(s) H-C_3, 7.970(d) H-C_6, 7.810(d) H-C_5, 3.491?, 2.493 (DMSO), 2.070, 1.284

^{13}C NMR spectrum :(DMSO, 600 Hz) δ_C (ppm) 167.072 C_7=O, 165.432 C_8=O, 137.855 C_2, 134.128 C_1, 133.961 C_3, 130.529 C_4, 128.419 C_6, 119.639C_5, 39.639(DMSO)

IR showed the OH stretch vibration for the carboxylic acid at 3000-2800 cm^{-1} and the C=O stretch vibration for the carboxylic acid was observed at 1684 cm^{-1}. There were other vibration peaks observed at different wavenumbers.

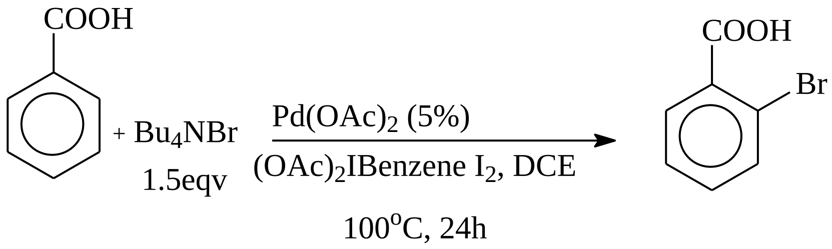
^{1}H NMR showed the OH peak at 13.655 ppm, the aromatic C-H peaks from 8.124 to 7.810 ppm. There were also some CH alkane peaks observed at 2.070 and 1.284 ppm.

^{13}C NMR C=O carbon at 167.072 ppm (C_7) and 165.432 ppm (C_8), this meant that there were two different types of C=O bonds in the product. The aromatic carbons were observed as shown above, but the methylene carbons were not observed.

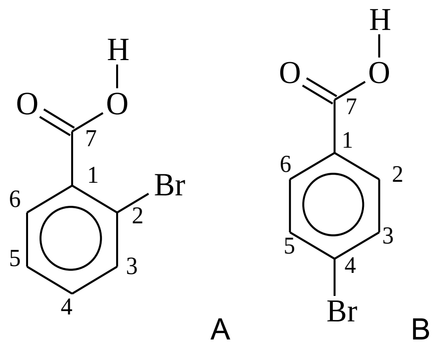
It was concluded that the reaction did not take place. Looking at the results from all the results it showed that the bromide was not substituted. The benzene ring was unable to be activated.

4.1.3 Bromination

Bromination was done by means of the reaction of IOAc with Bu_4NBr to form the brominating agent IBr that would brominate aryl palladium complex.



Scheme 4.8 Bromination of benzoic acid using Bu_4NBr



A B + C an aldehyde

Figure 4.1 Products formed in reaction Scheme 4.8 2-bromobenzoic acid (A), 4-bromobenzoic acid (B) and unknown aldehyde C. These compounds would be to separate as they yields were low and would end-up losing all the product during separation.

The product white crystals (0.6952 g 16.80% yield) were analysed using IR (Figure C.9 Appendix C) NMR (Figure D.5 Appendix D) and MS (Figure B.4 Appendix B).

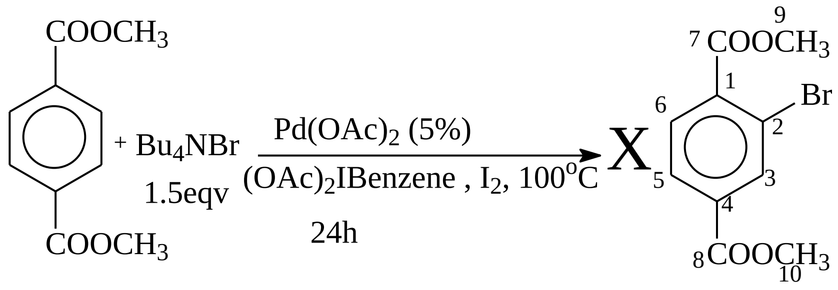
IR spectrum :v_{max} (cm^{-1}) 3300-2500 (O-H stretch carboxylic acid with C-H aromatic superimposed), 1680(s) C=O stretch conjugation reduced the frequency of absorption, 1601(m), 1582(m), 1453(m), 1419(m) O-H bend , 1289(s) C-O stretch (C-O-H) , 1026(w), 931(m) out-of-plane bend O-H, 705(s)

^{1}H NMR spectrum :(CDCCl_3, 600 Hz) δ_H (ppm) 10.472 (H-C aldehyde), 8.124(d) H-C_2 (B), 8.111(d) C_3 (B), 8.014(d) C_5 (B), 7.994(d) C_6 (B), 7.704(d) H-C_3 (A), 7.692(d) H-C_6 (A), 7.607(t) H-C_4 (A), 7.443(t) H-C_5 (A), 7.24(s) solvent , 2.167(s)

^{13}C NMR spectrum :(CDCCl_3, 600 Hz) δ_C (ppm) 207.554?, 172.384, 171.441 C=O acid/ aldehyde, 134.819, 133.835 , 133.448, 132.384, 130.582, 130.204, 129.254, 128.482, 127.250, 122.501 (C aromatic), 77.000(solvent), 30.928

MS spectrum : (m/z) M^+ 200.96 ($C_7H_5BrO_2$)

^{1}H NMR results show that an aldehyde that was formed with a peak at 10.472 ppm. CH aromatic peaks were also observed. ^{13}C NMR showed CBr at 207.554, C=O carbons at 172.384 and 171.441ppm. Aromatic carbons appeared at 134.819 to 122.501. From these results it was clear that the *ortho* brominated product was not the only product formed, but rather that a mixture of *ortho* and *para* brominated products was formed. The MS results confirmed that the molecular ion peak was of the desired product.



Scheme 4.9 Bromination of DMT

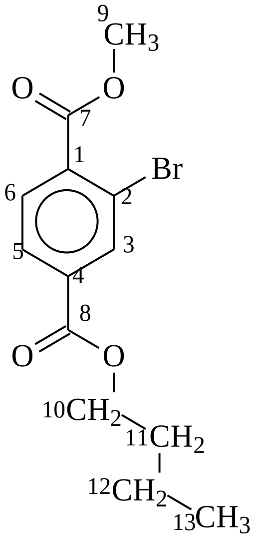
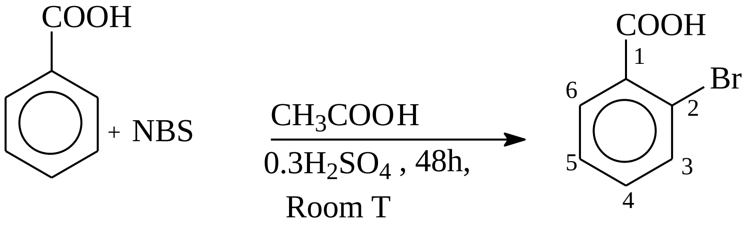


Figure 4.2 Product obtained for the reaction in Scheme 4.9.

The product cream white crystals (0.0556 g, 0.52% yield) was analysed using IR (Figure C.10 Appendix C), NMR (Figure D.6 Appendix D)

IR spectrum	:v_{max} (cm^{-1}) 3015(w) (C-H aromatic), 2958(w) (C-H CH_3), 2537(w), 1964(w), 1719(m) (C=O stretch), 1683(m), 1507(w), 1429(m), 1409(m), 1273(s) [C-O (C-C(=O)-O)], 1103(s) (C-O (O-C-C) aromatic esters of primary alcohols), 727(s)
^1H NMR spectrum	:($CDCCl_3$, 600 Hz) δ_H (ppm) 8.961(s) H-C_3, 8.274(s), 8.063(s), 7.964(d) H-C_6, 7.785(d) H-C_5, 7.24(s) (solvent) 3.921(s), 2.727(s) H-C_9, 2.139(s) H-C_{10}
^{13}C NMR spectrum	:($CDCl_3$, 600 Hz) δ_C (ppm) 178.082, 166.303, 164.996 C=O ester, [136.033, 135.116, 133.824, 133.620, 131.171, 129.504, 128.054 (C aromatic)], 77.000(Solvent), 52.757H-C_{10}, 52.681 H-C_{11}, 52.431 H-C_{12}, [30.889, 29.518 CH_3]

The results for the above experiment showed that the methyl from dimethylterephthalate was substituted. ^1H NMR showed the peaks for the methylene groups of the butyl. It was concluded that the bromination reaction did not take place. The only reaction that occurred was that of methyl substitution by the butyl group from the tetrabutylammoniumbromide the brominating agent. The inactive benzene ring could not be activated, and nosubstituion took place in the ring. The structure in Figure 4.2 was confirmed by NMR.

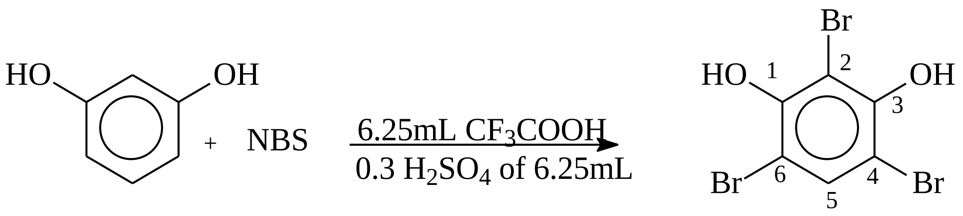


Scheme 4.10 Bromination of benzoic acid using NBS

Cream white crystals (2.6162 g, 12.95% yield) were analysed using IR (FigureC.11 Appendix C), NMR (Figure D.7 Appendix D) and MS (Figure B.5 Appendix B).

IR spectrum	:ν_{max} (cm^{-1}) 3200-2500 O-H stretch carboxylic acid, 1678 (s) C=O stretch, 1582(m), 1452(m), 1419(m) O-H bend, 1322(m), 1287(s) C-O stretch (C-O-H), 1178(s), 929(s) out-of-plane O-H, 704(s), 665(s)
^{1}H NMR spectrum	:($CDCCl_3$, 600 Hz) δ_H (ppm) 8.097(d) H-C_3, 8.082(d) C_6 , 7.695(t) C_4, 7.598(t) C_5, 7.24(s) Solvent , 2.937(s), 2.895(s), 2.753(s), 2.157(s), 2.107(s), 1.226(s)
^{13}C NMR spectrum	:($CDCCl_3$, 600 Hz) δ_C (ppm) : 207.616 (C-Br), 178.404, 173.256, 171.835 (C=O acid/ aldehyde), 136.557. 134.667, 133.715 , 132.253, 132.191, 131.817, 129.323, 122.288 (C aromatic), 77.000(solvent), 30.905, 29.671
MS spectrum	:(m/z) M^+ Many Molecular ions observed 157.01 $C_{13}H$; 199.95 $C_7H_5BrO_2$; 200.96 $C_7H_6/_5BrO_2$; 234.92 $C_{13}Br$; 278.86 $C_7H_5Br_2O_2$

The ^{1}H NMR results showed CH aromatic peaks at 8.097 to 7.598 ppm, and some alkyl carbons at 2.937 to 2.107 ppm. ^{13}C NMR showed a peak at 207.616 for C-Br, C=O at 173.256, and 171.835. From the information given here, it was concluded that there was more than one type of C=O carbons. The aromatic carbons were observed at 136.557 to 122.288. Alkyl carbons were also observed, but it was not clear from what source they came, or the impurities from solvent. The conclusion was that the desired product was not obtained.



Scheme 4.11 Bromination of resorcinol

White crystals (13.8231 g, 87.74 % yield) were analysed using IR (Figure C.12 Appendix C), NMR (Figure D.8 Appendix D) and MS (Figure B.6 Appendix B).

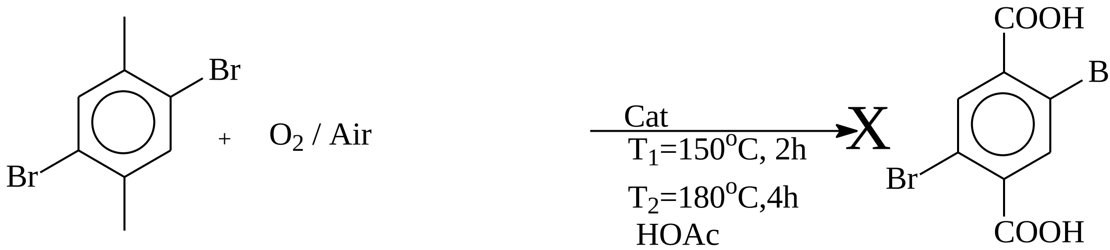
IR spectrum	:v_{max} (cm^{-1}) 3465 (wide, strong) (O-H stretch), 3073 C-H aromatic, 1573 (s), 1455(s), 1424(s), 1328(m), 1295 (s), 1183(s), 1025(s), 864(m), 710(w), 687(m), 657(m), 604(w)
^{1}H NMR spectrum	:(DMSO, 600 Hz) δ_H (ppm) 9.969(s) H-O (2H), 7.677(s) H-C_5, 2.49 Solvent
^{13}C NMR spectrum	:(DMSO, 600 Hz) δ_C (ppm) M151.242 $C_{2,4,6}$, 133.124 $C_{1,3}$, 103.415, 101.786 C_5, 39.500 (solvent)
MS spectrum	: (m/z) M^+ 345.77 ($C_6H_3Br_3O_2$)

IR showed the OH stretch vibration peak at 3465 cm^{-1} for the alcohol and the CH aromatic at 3073 cm^{-1}.

The ^{1}H NMR showed O-H peak at 9.969 ppm, and the C-H aromatic peak at 7.677 ppm. ^{13}C NMR confirmed the C-Br carbons at 151.242, C-OH carbons at 133.124, and C-H carbon.

The MS results with the molecular ion of 345.77 m/z also confirmed that the product was indeed the desired one.

4.1.4 Oxidation experiments

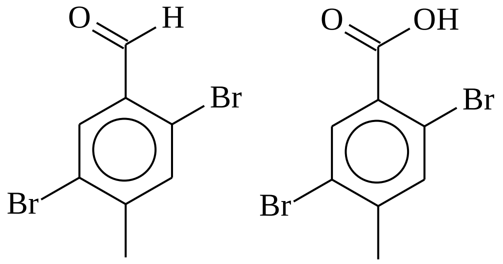


Scheme 4.12 Synthesis of 2,5-dibromotherephthalic acid from 2,5 dibromo-1,4-dimethylbenzene

The product (8.5671 g, 70.3% yield) was analysed using IR (Figure C.13 Appendix C), NMR (Figure D.9 Appendix D) and MS (Figure B.7 Appendix B).

IR spectrum	:v_{max} (cm^{-1}) 3300-2700 (O-H stretch carboxylic acid with C-H aromatic superimposed), 2526(w), 1673(s) (C=O stretch conjugation reduced frequency), 1583(m) (C=C aromatic), 1475(w), 1255(m) (C-O stretch (C-O-H)), 1055(s), 777(m) (C-H out-of-plane)
^{1}H NMR spectrum	:(DMSO, 600 Hz) δ_H (ppm) 13.575(s) O-H carboxylic acid, [10.148, 10.110, 10.102]10.070(s) C-H aldehyde, [8.069, 8.042, 7.992] 7.915, 7.839, 7.803, 7.741, 7.569 C-H aromatic, 5.037, 3.339 water from solvent, 2.49 DMSO, 2.092 C-H (CH_3)
^{13}C NMR spectrum	:(DMSO, 600 Hz) δ_C (ppm) 206.495, 165.700 (C aldehyde), 146.220, 142.705, 136.902, 135.905, 134.497, 133.354, 123.027, 122.988, 119.299 (C aromatic), 39.50 Solvent DMSO, 21.96 C (CH_3)
MS spectrum	:(m/z) M^+ 292.88 ($C_8H_7Br_2O_2$)

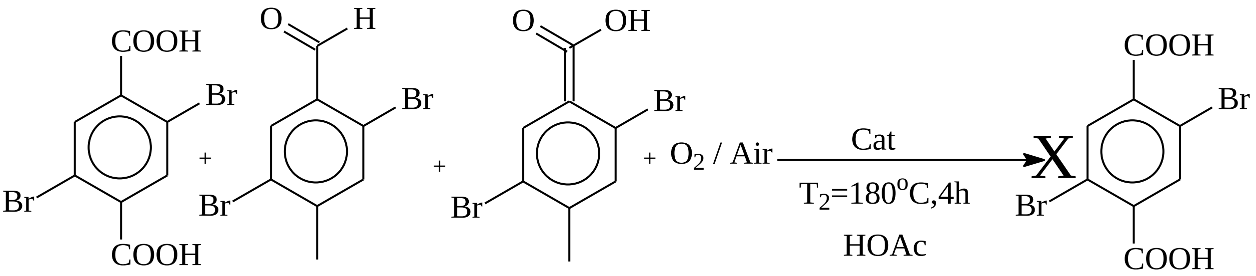
The IR results showed the OH stretch band for the carboxylic acid at 3300 – 2700 cm^{-1} as well as the C=O stretch band at 1673 cm^{-1} and the C-O stretch band at 1055 cm^{-1}. ^{1}H NMR results show the OH peak at 13.575 ppm for the carboxylic acid. There were peaks observed at 10.1 ppm for CH aldehyde, indicating that oxidation was not complete. A peak observed at 2.09 for CH alkane (CH_3) showed that not only the aldehyde was formed, but that some of the methyl group did not react at all. ^{13}C NMR results also confirmed what was observed in the ^{1}H NMR results. The aldehyde at 165.700 ppm the methyl carbon at 21.96 ppm was also observed on ^{13}C NMR. It was concluded that the desired product was not obtained, but that instead a mixture of products in Figure 4.3 was obtained, although it was the reaction time and oxygen was increased.



A B

Figure 4.3 Oxidation products obtained in reaction Scheme 4.12.

After the analysis of the product from above experiment, a decision was made that the above mixture of products should be reacted further in order to complete the reaction. The reaction was attempted again, using the above-mentioned products as the starting material.

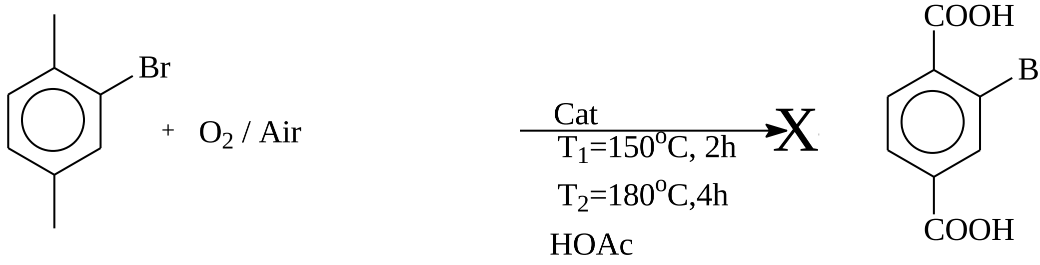


Scheme 4.13 Completion of oxidation of 2,5 dibromo-1,4-dimethylbenzene

The product (0.7994 g, 48.29% yield) was analysed using IR (Figure C.14 Appendix C) and MS (Figure B.8 Appendix B). It was clear from the MS that the second methyl group was not oxidised at all.

IR spectrum	:v_{max} (cm^{-1}) 3300-2700 (O-H stretch carboxylic acid with C-H aromatic superimposed), 2526(w), 1673(s) (C=O stretch conjugation reduced frequency), 1583(m) (C=C aromatic), 1475(w), 1255(m) (C-O stretch (C-O-H)), 1055(s), 777(m) (C-H out-of-plane)
MS spectrum	:(m/z) M^+ 292.88 ($C_8H_7Br_2O_2$)

From IR, the OH stretch peak for carboxylic acid at 3300-2700cm^{-1} was observed, and the C=O stretch peak for the carbonyl at 1673cm^{-1} was observed. CO stretch peak at 1255 ppm.



Scheme 4.14 Synthesis of 2-bromotherephthalic acid from 2-bromo-1,4-dimethylbenzene.

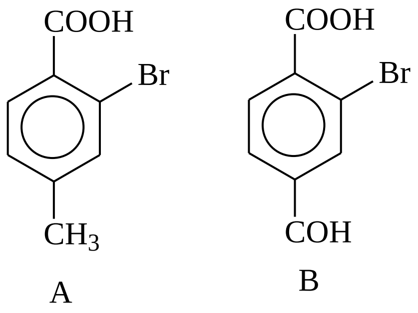


Figure 4.4 Products obtained during oxidation.

The product (3.9967 g, 43.48% yield) was analysed using IR (Figure C.15 Appendix C), NMR (Figure D.10 Appendix D) and MS (Figure B.9 Appendix B)

IR spectrum :v_{max} (cm^{-1}) 3100-2800 (O-H stretch carboxylic acid), 1674(s) (C=O), 1601(m), 1423(m), 1304(m), 1264(m), 1037(m), 836(m), 765(s), 679(m)

^1H NMR spectrum :(DMSO, 600 Hz) δ_H (ppm) 13.193 O-H (carboxylic acid), 10.243, 10.152, 10.093, 10.003 (C-H aldehyde), 8.188(d), 7.825(d), 7.668(d), 7.545(s), 7480(d), 7.290(d), 7.249(d) (C-H aromatic), 3.590 (water from solvent), 2.394(s) (solvent), 2.318(s) (C-H from CH_3)

^{13}C NMR spectrum :(DMSO, 600 Hz) δ_C (ppm) 167.314, 167.089, 165.979 (C aldehyde), 143.214, 142.604, 134.233, 132.614, 130.882, 130.236, 128.307, 124.082, 120.292 (C aromatic), 39.500 solvent, 22.600, 21.139, 20.418 C (CH_3)

MS spectrum :(m/z) M^+ 213.96 ($C_8H_7BrO_2$), 214.97 ($C_8H_8BrO_2$)

IR results showed the OH stretch vibration for carboxylic acid at 3100-2800 cm^{-1}, and the C=O stretch vibration peak was also observed at 1674 cm^{-1}. ^{1}H NMR showed the OH peak for the carboxylic acid at 13.193 ppm. There were also the CH aldehyde peaks observed at 10.2, 10.1 and 10.0 ppm, and the CH methyl peak was also observed at 2.318 ppm. From ^{13}C NMR C=O carbon was observed at 167.314, 167.089 and 165.979 ppm. The aromatic carbons were also observed from 143.214 to 120 ppm. Some peaks for CH from the methyl group were observed from 22.600 to 20.418 ppm. From the above results it can be concluded that the oxidation reaction did not go to completion, and instead a mixture of products was obtained - as was the case with the previous experiments.

4.2 Polyesters characterisation and the study of the properties

IR and NMR was used for the characterisation of polyesters. ^{1}H NMR, ^{13}C NMR, DEPT 90 and DEPT 135 NMR were employed. The solvent used was 1,2,4-trichlorobenzene (TCB), with benzene at ratios: TCB80%:$C_6D_6$20%.

SEM, TGA, DSC, XRD were used to study the properties of the polyesters.

SEM was used in the surface, composition and morphology studies. TGA was used for thermal, physical and chemical analyses. DSC was used thermal analysis of polyesters, melting points and crystallisation points. XRD was used for atomic and molecular structures of the polyesters.

4.2.1 Characterisation of polyesters

4.2.1.1 Type 1 Polyesters with 1,2-gylcol as diol component.

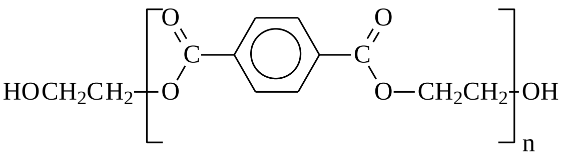


Figure 4.5 Polyethylene terephthalate.

The product was analysed using IR (Figure C.16 Appendix C), DTG (Figure E.1 Appendix E), DSC (Figure F.1 Appendix F), XRD (Figure G.1 Appendix G) and SEM (Figure H.1 Appendix H)

IR spectrum :v_{max} (cm^{-1}) 3600-3400(vw) O-H stretch alcohol endgroup, 2968(w) (CH stretch alkyl), 1712(s) (C=O carbonyl), 1409(w), 1341(m), 1245(s), 1101(m), 1019(m), 721(s)

NMR: Sample was insoluble in TCB and the NMR was not done.

The results for IR showed the expected peaks O-H stretch; this peak was very weak compared to the O-H peak of the unpolymerised dialcohol. C-H stretch was also observed at 2968 cm^{-1}as well as the C=O peak at 1712 cm^{-1}.

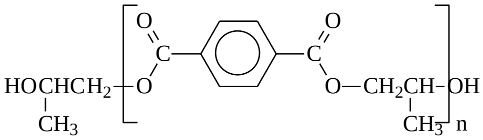


Figure 4.6 Poly(1,2-propanediol) terephthalate.

The product was analysed using IR (Figure C.17 Appendix C), NMR (Figure D.11 Appendix D), DTG (Figure E.2 Appendix E), DSC (Figure F.2 Appendix F), XRD (Figure G.2 Appendix G), SEM (Figure H.2 Appendix H) and GPC

IR spectrum :v_{max} (cm^{-1}) 3600-3400(vw) O-H stretch alcohol endgroup, 2984(w) C-H stretch alkyl, 1714(s) C=O stretch, 1407(m), 1240(s), 1097(s), 1016(s), 725(s)

Table 4.1 NMR for poly(1,2-propanediol) terephthalate

	$C_{Ar/CHar}$	**C=O**	**CH_2**	**CH**	**OH**	**CH_3**
^{1}H NMR	7.93-6.625		4.225	1.301	4.497	0.833
			4.154	1.169	4.384	0.822
			3.703	1.107	4.354	0.802
			3.694	1.063		0.772
			3.603			
^{13}C NMR	138.29-120.81	165		69.59		16.74
				67.08		
				30.50		
				30.34		
DEPT135	138-120		67.15	69.59		16.76
	114.99		30.39	67.07		16.72
				30.50		
				30.33		
DEPT90	138-120			69.59		
	114.99			67.07		
				30.32		

From FTIR the weak peak for OH stretch at 3600-3400 cm^{-1}, and a weak peak CH (alkyl) stretch at 2984 cm^{-1}, 1714 cm^{-1} C=O peak carbonyl were observed.

From the proton NMR it was difficult to identify the exact CH aromatic peaks as there were three different types of those CH peaks from TCB, C_6D_6 and the sample. The TCB peaks could be identified because of their high intensity, since the sample solution contained 80% TCB, 20% C_6D_6, as well as the dissolved polyester product. ^{1}H NMR showed the CH aromatic peaks between 7.930 and 6.625 ppm, OH 4.497 to 4.354 ppm, CH (CH_2) 4.225 to 3.603 ppm, CH (CH) 1.301 to 1.063 ppm and CH (CH_3) 0.833 to 0.772 ppm. The ^{13}C NMR spectrum showed the C=O at 165 ppm, and the other peaks were also observed on DEPT90 and DEPT 135. The compound had all the peaks as they were expected, but at very low intensity due to the low concentration of the compound in the solution.

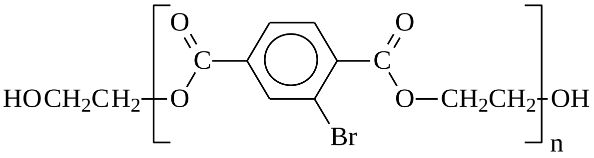


Figure 4.7 Polyethylene 2-bromoterephthalate

The product was analysed using IR (Figure C.18 Appendix C), NMR (Figure D.12 Appendix D), TGA (Figure E.3 Appendix E), DSC (Figure F.3 Appendix F), XRD (Figure G.3 Appendix G), SEM (Figure H.3 Appendix H) and GPC.

IR spectrum :ν_{max} (cm^{-1}) 3600-3400(vw) O-H stretch, 2957(w) C-H stretch, 1715(s) C=O strech, 1380(w), 1229(s), 1098(s), 1036(m), 746(m)

Table 4.2 NMR for polyethylene 2-bromoterephthalate

	$C_{Ar/CHar}$	C=O	CH_2	CH	OH	CH_3
^{1}H NMR	7.261-6.299		3.743	1.157 1.125 1.074 1.061 (con)	4.509 4.294 4.287	0.825 0.806 0.794 0.782 (con)
^{13}C NMR	134-120	nv	63.45			
DEPT135	139-120 114.98		63.45			
DEPT90	135-120 114.98					

A weak OH stretch peak was observed at 3600-3400 cm^{-1}, CH (alkyl) at 2957 cm^{-1}, C=O at 1715 cm^{-1}.

^{1}H NMR CH aromatic peaks were observed between 7.261 and 6.299 ppm. OH peaks were also observed at between 4.509 and 4.287 ppm, CH (CH_2) at 3.743 ppm, CH (CH) at 1.157 to 1.061 ppm and CH (CH_3) from 0.825 to 0.782 ppm. The CH and CH_3 peaks observed suggested some kind of contamination from the solvents used (TCB and C_6D_6). The peaks due to contamination were not observed in ^{13}C NMR, DEPT90 and DEPT135 spectra. From the ^{13}C NMR, the C=O peak was not observed, but the CH_2 peaks were observed in Carbon 13 as well as in DEPT135.

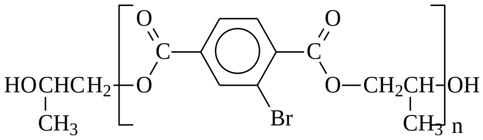


Figure 4.8 Poly(1,2-propanediol) 2-bromoterephthalate.

The product was analysed using IR (Figure C.19 Appendix C), NMR (Figure D.13 Appendix D), DTG (Figure E.4 Appendix E), DSC (Figure F.4 Appendix F), XRD (Figure G.4 Appendix G), SEM (Figure H.4 Appendix H) and GPC

IR spectrum	:ν_{max} (cm^{-1}) 3600-3400(vw) O-H stretch, 2983(w) C-H stretch, 1718(s) C=O stretch, 1379(w), 1230(s), 1103(m), 1036(m), 747(m)

Table 4.3 NMR for poly(1,2-propanediol) 2-bromoterephthalate

	$C_{Ar/CHar}$	**C=O**	**CH_2**	**CH**	**OH**	**CH_3**
^{1}H NMR	7.190-6.299		5.433 5.395	1.307 1.299 1.157 1.124 1.074 1.061 1.049	4.413 4.331	0.824 0.805 0.794 0.782
^{13}C NMR	135.43-120.68	nv	67.29	30.52		30.34
DEPT135	145.50-119.39 114.98		67.29	30.52		30.38 30.31
DEPT90	135.44-120.68 114.98			30.32		

A weak OH stretch peak was observed at 3600-3400 cm^{-1}, CH (alkyl) at 2983 cm^{-1}, C=O at 1718 cm^{-1} were observed

^{1}H NMR 7.190 to 6.299 ppm CH aromatic, CH (CH_2) at 5.433 and 5.395 ppm, OH at 4.413 and 4.331 ppm, CH (CH) between 1.307 and 1.049 ppm and CH (CH_3) between 0.824 and 0.782 ppm. These peaks were confirmed in DEPT90 CH at 30.32 ppm and DEPT135 CH_2 at 67.29 ppm. The C=O peak was not observed in the ^{13}C NMR spectrum.

4.2.1.2 Type 2 Polyesters with 1,3-propylene diol as a diol component

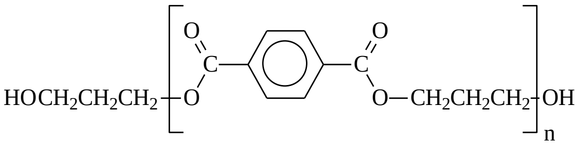


Figure 4.9 Polypropylene terephthalate (PPT)

The product was analysed using IR (Figure C.20 Appendix C), DTG (Figure E.5 Appendix E), DSC (Figure F.5 Appendix F), XRD (Figure G.5 Appendix G) and GPC

IR spectrum :ν_{max} (cm^{-1}) 3600-3400(vw) O-H stretch, 2963(w) C-H stretch, 1708(s) C=O stretch, 1463(w), 1408(m), 1245(s), 1099(s), 1017(m), 935(m), 871(m), 724(s)

NMR: Sample was insoluble in TCB and the NMR was not done.

IR data was used to confirm the product PPT, with the weak OH bond for the end group of the polyesters at 3600-3400 cm^{-1}, the weak CH alkyl stretch peaks were observed at 2963 cm^{-1}, and C=O carbonyl at 1708 cm^{-1}.

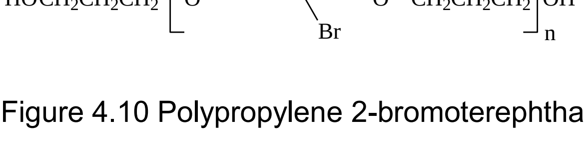


Figure 4.10 Polypropylene 2-bromoterephthalate

The product was analysed using IR (Figure C.21 Appendix C), NMR (Figure D.14 Appendix D), DTG (Figure E.6 Appendix E), DSC (Figure F.6 Appendix F), XRD (Figure G.6 Appendix G), SEM (Figure H.5 Appendix H) and GPC.

IR spectrum :v_{max} (cm^{-1}) 3600-3400(vw) O-H stretch, 2961(w) C-H stretch, 1714(s) C=O stretch, 1557(w), 1377(m), 1273(s), 1233(s), 1102(s), 1036(s), 746(s), 660(m)

Table 4.4 NMR for polytrimethylene 2-bromoterephthalate

	$C_{Ar/CHar}$	**C=O**	**CH_2**	**CH**	**OH**	**CH_3**
^1H NMR	7.186-6.606		4.399 4.390 4.364		4.354	
^{13}C NMR	135.28-120.68 114.99	165	62.67			
DEPT135	135.44-119.44 113.13/116.33		62.73 62.25 55.77			
DEPT90	135.44-123.59 114.99					

The functional groups were identified from the IR. ^1H NMR CH aromatic peaks were observed between 7.186 and 6.606 ppm, CH (CH_2) at 4.399, 4.390, 4.364 ppm and OH at 4.354 ppm. From the ^{13}C NMR spectrum, C=O peak was observed at 165 ppm, and aromatic carbons as well as the CH_2 carbons were observed at 62.67 ppm. The CH_2 was confirmed in the DEPT135.

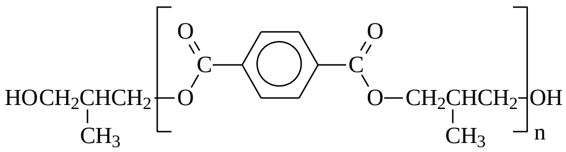


Figure 4.11 Poly(2-methyl)propylene terephthalate.

The product was analysed using IR (Figure C.22 Appendix C), NMR (Figure D.15 Appendix D), DTG (Figure E.7 Appendix E), DSC (Figure F.7 Appendix F) and XRD (Figure G.7 Appendix G)

IR spectrum :ν_{max} (cm^{-1}) 3600-3400(vw)O-H stretch, 2965(w)C-H stretch, 1713(s) C=O stretch, 1467(m), 1408(m), 1243(s), 1097(s), 1017(s), 979(m), 873(m), 725(s)

Table 4.5 NMR for poly(2-methyl)trimethylene terephthalate

	$C_{Ar/CHar}$	C=O	CH_2	CH	OH	CH_3
^{1}H NMR	7.944-6.587		4.254	1.663		1.006
			3.442	1.181		0.995
				1.064		0.980
				1.051		0.886
						0.788
						0.777
^{13}C NMR	134.49-120.68	165	67.08	33.16		30.46
	118.50		66.91	14.20		14.15
						13.89
DEPT135	138.25-122.26		69.80	66.91		33.16
	114.99		67.08	14.20		30.47
						14.15
						13.89
DEPT90	135.44-120.68			66.90		
	115.00			33.13		
				33.11		
				14.19		

The functional groups were identified from the IR. From ^{1}H NMR, CH aromatic peaks were observed at 7.944 to 6.587 ppm, CH (CH_2) at 4.254 and 3.442 ppm, CH (CH) at 1.663 to 1.051 ppm and CH (CH_3) at 1.006 to 0.777 ppm. These peaks were confirmed by DEPT. From DEPT90, the CH at 66.90, 33.13, 33.11 ppm another peak at 14.19 CH was observed. From DEPT135 the CH_2 peaks at 69.80 and 67.08 ppm, the CH_3 peaks were observed at 14.15 and 13.89 ppm. There were other CH_3 peaks observed that might have resulted from solvent contamination at 33.16 and 30.47 ppm. The C=O carbonyl peak was observed from ^{13}C NMR at 165 ppm.

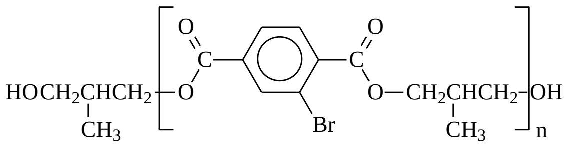


Figure 4.12 Poly(2-methyl)propylene 2-bromoterephthalate

The product was analysed using IR (Figure C.8 Appendix C), NMR (Figure D.16 Appendix D), DTG (Figure E.8 Appendix E), DSC (Figure F.8 Appendix F), XRD (Figure G.8 Appendix G), SEM (Figure H.6 Appendix H) and GPC.

IR spectrum :ν_{max} (cm^{-1}) 3600-3400(vw) O-H stretch, 2965(w) C-H stretch, 1716(s) C=O stretch, 1465(m), 1378(m), 1273(s), 1231(s), 1104(s), 1036(s), 977(m), 746(s)

Table 4.6 NMR for poly(2-methyl)trimethylene 2-bromoterephthalate

	$C_{Ar/CHar}$	C=O	CH_2	CH	OH	CH_3
^{1}H NMR	8.1 7.191-6.300		4.279 4.251	1.157		1.048 1.013 1.003 0.824 0.805 0.793 0.781
^{13}C NMR	135.35-120.68 107.77	nv	67.27	33.02		14.27
DEPT135	144.06-122.25 114.98		69.80 67.08			14.20
DEPT90	135.44-120.68 114.98					

The functional groups were identified from the IR. From ^{1}H NMR, the CH aromatic peaks were observed at 8.1 ppm and at 7.191 to 6.300 ppm, CH (CH_2) at 4.279 and 4.251 ppm, CH (CH) at 1.157, and CH (CH_3) at 1.048 to 0.781 ppm. From DEPT135 the CH_2 peaks at 69.27 and 67.08 ppm were confirmed and the CH_3 peak at 14.20 ppm was also confirmed. The CH peak was not observed from DEPT 90. The C=O peak was also not observed from the ^{13}C NMR spectrum.

4.2.1.3 Type 3 polyesters with 1,5-pentyl diol as diol component

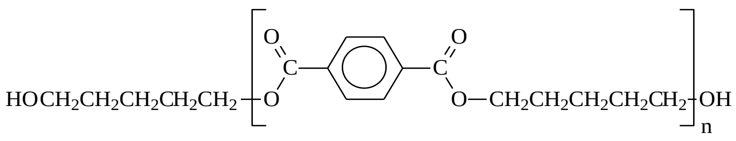


Figure 4.13 Polypentamethylene terephthalate.

The product was analysed using IR (Figure C.24 Appendix C), NMR (Figure D.17 Appendix D), DTG (Figure E.9 Appendix E), DSC (Figure F.9 Appendix F), XRD (Figure G.9 Appendix G) and GPC.

IR spectrum :ν_{max} (cm^{-1}) 3600-3400(vw) O-H stretch, 2954(w) C-H stretch, 1709(s) C=O stretch, 1408(m), 1247(s), 1098(s), 1017(s), 871(m), 724(s)

Table 4.7 NMR for polypentamethylene terephthalate

	$C_{Ar/CHar}$	**C=O**	**CH_2**	**CH**	**OH**	**CH_3**
^{1}H NMR	7.931 7.030-6.729		5.696 5.686 5.428 5.193 5.141 5.107		4.915 4.744 4.693 4.192	1.629- 0.098 (con)
^{13}C NMR	133.57-125.91	165	65.10			30.45 28.73 (con)
DEPT135	133.57-127.70		65.14			30.46 28.71 22.93 (con)
DEPT90	134.64-125.89					

The functional groups were observed from the IR. From ^{1}H NMR, CH aromatic peaks were observed at 7.931 ppm, 7.030 to 6.729 ppm, CH (CH_2) at 5.696 to 5.107 ppm OH peaks at 4.915 to 4.192 ppm and CH (CH_3) at 1.629 to 0.098 ppm that resulted from contamination. From ^{13}C NMR spectrum, C=O peak was observed at 165 ppm, the CH_2 were confirmed in DEPT135 spectrum at 65.14 ppm.

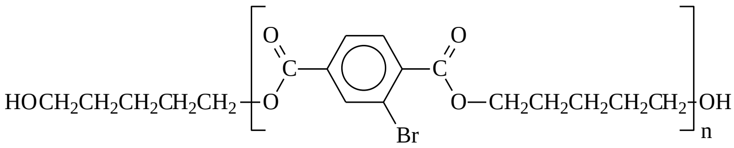


Figure 4.14 Polypentamethylene 2-bromoterephthalate

The product was analysed using IR (Figure C.25 Appendix C), NMR (Figure D.18 Appendix D), DTG (Figure E.10 Appendix E), DSC (Figure F.10 Appendix F), XRD (Figure G.10 Appendix G) and GPC.

IR spectrum :v_{max} (cm^{-1}) 3600-3400(vw) O-H stretch, 2952(w) C-H stretch, 1715(s) C=O stretch, 1377(m), 1273(s), 1235(s), 1104(s), 1037(s), 748(s), 660(m)

Table 4.8 NMR for polypentamethylene 2-bromoterephthalate

	$C_{Ar/CHar}$	**C=O**	**CH_2**	**CH**	**OH**	**CH_3**
^{1}H NMR	8.136 7.777-6.613		4.217 4.207		4.191	1.640-0.797 (con)
^{13}C NMR	135.28-120.68	nv	65.71 65.53			28.67 28.61 23.00 (con)
DEPT135	135.28-126.50 114		65.71			28.71 28.66 28.61
DEPT90	135.43-120.68 114					

The functional groups were observed from the IR. From the ^{1}H NMR spectrum, CH aromatic peaks were observed at 8.136 ppm, 7.777 to 6.613 ppm, CH (CH_2) peaks at 4.217 and 4.207 ppm, OH peak at 4.191 ppm, and CH (CH_3) at 1.640 to 0.797 ppm that resulted from contamination. From the DEPT 135 spectrum, the CH_2 peaks at 65.71 ppm were confirmed.

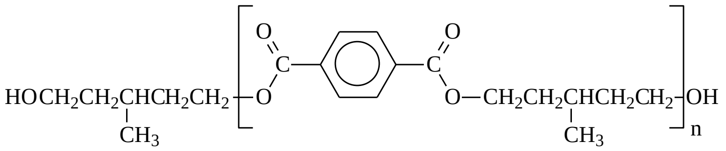


Figure 4.15 Poly(3-methyl)pentamethylene terephthalate.

The product was analysed using IR (Figure C.26 Appendix C), NMR (Figure D.19 Appendix D), DTG (Figure E.11 Appendix E), DSC (Figure F.11 Appendix F), XRD (Figure G.11 Appendix G) and GPC.

IR spectrum :v_{max} (cm^{-1}) 3600-3400(vw) O-H stretch, 2959(w) C-H stretch, 1713(s) C=O stretch, 1408(m), 1383(w), 1263(s), 1099(s), 1017(s), 948(m), 874(m), 726(s)

Table 4.9 NMR for poly(3-methyl)pentamethylene terephthalate

	$C_{Ar/CHar}$	C=O	CH_2	CH	OH	CH_3
^{1}H NMR	7.905-6.272		4.283	1.175 1.141 1.076	4.268	0.795 0.757
^{13}C NMR	134.61-120.68	165	63.79	63.51 35.75 27.56		
DEPT135	146.83-120.68		63.80 62.32	63.51 35.54 27.57 27.43 19.67		19.74
DEPT90	135.44-123.59			63.51 35.75 27.56 27.43 19.67		

The functional groups were observed from the IR. From the ^{1}H NMR, CH aromatic peaks were observed at 7.905 to 6.272 ppm, CH (CH_2) at 4.283 ppm, OH peaks at 4.268 ppm, CH (CH) at 1.175 to 1.076 ppm and CH (CH_3) at 0.795 and 0.757 ppm. From ^{13}C NMR spectrum C=O peak was observed at 165 ppm, the CH_2 peaks were confirmed in DEPT 135 spectrum at 63.80 and 62.32 ppm and CH_3 at 19.74 ppm. The CH peaks were confirmed in DEPT 90 at 63.51 ppm and more peaks were observed there, but these were from an unknown source.

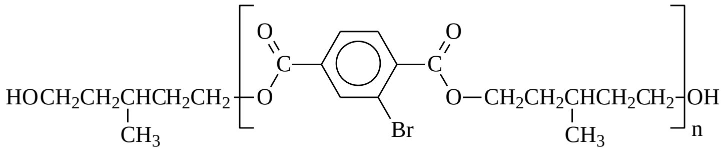


Figure 4.16 Poly(3-methyl)pentamethylene 2-bromoterephthalate.

The product was analysed using IR (Figure C.27 Appendix C), NMR (Figure D.20 Appendix D), DTG (Figure E.12 Appendix E), DSC (Figure F.12 Appendix F), XRD (Figure G.12 Appendix G) and GPC.

IR spectrum :ν_{max} (cm^{-1}) 3600-3400(vw) O-H stretch, 2959(m) C-H stretch, 1715(s) C=O stretch, 1377(m), 1274(s), 1234(s), 1105(s), 1037(s), 945(m), 747(s), 730(m), 660(m)

Table 4.10 NMR for Poly(3-methyl)pentamethylene 2-bromoterephthalate

	$C_{Ar/CHar}$	**C=O**	**CH_2**	**CH**	**OH**	**CH_3**
^1H NMR	8.571-6.730		4.245	1.177		0.864
^{13}C NMR	135.32-125.89	nv	63.90			35.67
DEPT135	135.32-125.89		64.02 63.89			35.79 35.64 27.61
DEPT90	135.32-125.88					

The functional groups were observed from the IR. From the ^1H NMR, CH aromatic peaks were observed at 8.571 to 6.730 ppm, CH (CH_2) at 4.245 ppm, CH (CH) at 1.177 ppm and CH (CH_3) at 0.864 ppm. The CH_2 were confirmed in DEPT 135 spectrum at 64.02 and 63.89 ppm and CH_3 at 35.79, 35.64 and 27.61 ppm. The CH peaks were not observed in DEPT 90.

The IR for all the samples showed the C=O carbonyl peak, and although it was not observed in some ^{13}C NMR spectra, this was the confirmation that the polymers were synthesised successfully. The contaminations observed in the NMR spectra might have resulted from the catalysts manganese and sodium acetate (CH_3COO) and the solvents TCB and C_6D_6 that may have contained the contamination.

4.2.2 The properties of polyesters

The results of properties of polyesters done were listed in Table 4.11.

Tables 4.11 Table of DTG; DSC; Melting points; GPC results

Polymer	DTG (T_{max}/°C)	DSC (°C)		GPC		
		T_c	T_m	<M_w> (g/mol)	D	n
Ethyl diol						
PET	427.56	190	225			
P(1,2-P)T	368.74	Nv	48	3866.6	1.85	17.2
				4437.6	1.71	19.8
				1468.1	1.00	6.5
PE2-BrT	393.50	Nv	51	5206.6	1.74	18.0
				5244.4	1.75	18.1
				4984.4	1.71	17.2
				4967.9	1.70	17.2
P(1,2P)2-BrT	348.55	Nv	49_a	47759	1.00	157.6
				2822.1	1.53	9.3
Propyl diol						
PPT	392.89	140	192	48068	72.1	214.4
				98919	1.00	441.2
PP2-BrT	381.52	Nv	76	9309.4	2.22	30.7
				10033	2.35	33.1
				1624.2	1.01	5.4
P(2M)PT	364.67	Nv	107_a			
P(2-M)P2-BrT	384.43	Nv	65	4371.1	4.58	13.8
				5427.9	1.66	17.1
				1572.1	1.01	5.0
				5553.2	1.66	17.5
				1619.5	1.01	5.1
Pentyl diol						
PPMT	399.72	Nv	116	4033.3	8.83	16.0
				4583.8	2.07	18.2
PPM2-BrT	349.38	Nv	80	1423.3	1.00	4.3
				4692.3	1.64	14.2
P(3-M)PMT	401.92	Nv	63	126210.0	1.03	474.0
				1912.3	1.17	7.2
P(3-M)PM2-BrT	359.85	Nv	65_a	209780	2.93	607.7
				59897	1.35	173.5
				3228.4	1.00	9.4
				59645	1.35	172.8
				3254.6	1.00	9.4

Not visible = Nv

The properties of the polyesters were studied using different techniques that are shown in the table above.

The following three families of polyesters were synthesised and compared:

1. Type 1, in which the diol component had two carbon atoms.
2. Type 2, in which the diol component had three carbon atoms.
3. Type 3, in which the diol component had five carbon atoms.

4.2.2.1 Type 1 Polyesters with 1,2-dialcohol as diol component.

The reference polyester was PET. It had the highest melting point of 225°C, and the highest crystallisation point of 190°C. The polymer also had the highest decomposition temperature of 428.56°C. The polymer was insoluble in TCB, and as a result GPC was not done. These high temperatures are due to the fact that it had the smallest number of methylene units; hence it was very difficult to dissolve.

Poly (1,2-propanediol) terephthalate had the lowest melting point of 48°C, the crystallisation point was not observed and it had a decomposition temperature of 368.74°C, which was lower than PET. GPC molecular weight distribution (with dispersity in brackets) was 3866.6 (1.9), 4437 (1.7) and 1468 (1.0). This was the first polymer with alkyl substitution on the diol chain, and the melting point and decomposition temperatures dropped.

Polyethylene 2-bromoterephthalate had a melting point of 51°C, a crystalisation point not observed, and a decomposition temperature of 393.5°C which was lower than that of PET. GPC showed four molecular weight distributions of 5206.6, 5244.4, 4984.4 and 4967.9, all with a dispersity of 1.7, which showed good molecular weight distribution but with many different chain lengths.

This first synthetic polymer with substitution on the benzene ring showed significant changes compared to PET.

Poly (1,2-propanediol) (2-bromo) terephthalate had a melting point of 49°C, the crystallisation point was not observed, and it had a decomposition temperature of 348.6°C. GPC showed two molecular weight distributions (with dispersity in brackets) of 47759 (1.0) and 2822.1 (1.5). The bromine substitution on the ring thus lowered both the crystallisation and decomposition temperatures.

XRD results showed that the reference polyester PET (Figure G.1 Appendix G) was crystalline; brominated PET (Figure G.3 Appendix G) was amorphous with crystalline structures. Poly (1,2-propanediol) terephthalate (Figure G.2 Appendix G) was mainly amorphous with very small crystalline structures; the brominated Poly (1,2-propanediol) terephthalate (Figure G.4 Appendix G) was amorphous, also with crystalline structures.

4.2.2.2 Type 2 Polyesters with 1,3-propylene diol as diol component

The reference polyester was polypropylene terephthalate. The melting point for the reference polymer was 192°C, the crystallisation point was 140°C and the decomposition temperature was 392.9°C. GPC results of 48068 (72.1) and 98919 (1.0) molecular weight distribution (with dispersity in brackets) were observed. Polytrimethylene (2-bromo) terephthalate had a melting point of 76°C, the crystallisation point was not observed, and the decomposition temperature was 381.5°C. The melting point decreased drastically in the presence of bromide on benzene ring, while the decomposition temperature decreased by 11.4°C. GPC molecular weights (with dispersity in brackets) of 9309.4 (2.2), 10033 (2.4), 1624.2 (1.0) were observed.

Poly (2-methyl) trimethylene terephthalate had a melting point of 107°C, the crystallisation temperature was not observed, and it had a decomposition temperature of 364.67°C. Due to insolubility, the sample could not be GPC analysed.

Poly (2-methyl) trimethylene 2-bromoterephthalate had a melting point of 65°C, the crystallisation point was not observed, with a decomposition temperature of 384.4°C. The melting point showed a large decrease with the substitution on both monomers, namely 2-bromo terephthalic acid and 2-methyl-1,3 propanediol, bromide on benzene ring and 2-methyl on dialcohol, with a difference of 127°C recorded. GPC molecular weight distributions (with dispersity in brackets) of 4371.1 (4.6), 5427.9 (1.7), 1572.1 (1.0), 5553.2 (1.7) and 1619.5 (1.0) were observed.

XRD results showed that the reference polyester PTMT (Figure G.5 Appendix G) was crystalline, the brominated PTMT (Figure G.6 Appendix G) was amorphous with very small crystalline structures. P(2-M)TMT (Figure G.7 Appendix G) was amorphous, the brominated P(2-M)TMT (Figure G.8 Appendix G) was amorphous but also crystalline.

4.2.2.3 Type 3 Polyesters with 1,5-pentyl diol as diol component

The reference polymer was PPMT. The melting point was 116°C, the crystallisation temperature was not observed, and the decomposition temperature was 399.7°C. GPC molecular weight distributions (with dispersity in brackets) were as follows: 4033.3 (8.8), and 4583.8 (2.1).

PPM2-BrT had a melting point of 80°C, the recrystallisation was not observed, and it had a decomposition temperature of 349.4°C. GPC molecular weight distributions were 1423.3 (1.0) and 4692.3 (1.6).

P(3-M)PMT had a melting point of 63°C, the recrystallisation temperature was not observed and it had a decomposition temperature of 401.9°C. The GPC molecular weight distributions (with dispersity in brackets) were as follows: 126210 (1.0) and 191230 (1.6).

For P(3-M)PM2-BrT the melting point was 65°C, the recrystallisation temperature was not observed, and the decomposition temperature was 359.9°C. This was the polymer with the largest number of methylene units with a 3-methyl substituent on the diol. It also had a bromide substituent on the benzene ring. GPC results were as follows: 209780 (2.9), 59897 (1.4), 3228.4 (1.0), 59645 (1.3) and 3254.6 (1.0)

XRD results showed that the reference polyester PPMT (Figure G.9 Appendix G) was crystalline; but the brominated PPMT (Figure G.10 Appendix G) was amorphous. P(3-M)PMT (Figure G.11 Appendix G) was amorphous and had a lot of crystalline structures, while the brominated P(3-M)PMT (Figure G.12 Appendix G) was not crystalline but amorphous.

The methylene units added to flexibility in the polymers, but reduced the melting points and crystallisation points. Decomposition temperatures were also slightly affected. The synthetic polymers had different chain lengths that for the most part had a dispersity of 1 to 2, except for few namely polytrimethylene terephthalate (72), poly (2-methyl) trimethylene 2-bromoterephthalate (4.5), and polypentamethylene terephthalate (8.8).

SEM analyses were done for the following polyesters, namely PET (Figure H.1 Appendix H), brominated PET (Figure H.3 Appendix H), poly (1,2-propanediol) terepthalate (Figure H.2 Appendix H), brominated poly (1,2-propanediol) terepthalate (Figure H.4 Appendix H), polytrimethylene 2-bromoterephthalate (Figure H.5 Appendix H) and poly(2-methyl)trimethylene 2-bromoterephthalate (Figure H.6 Appendix H). These analyses showed that the polyesters became softer as the number of methylene units increased.

For tensile strength to be done, the polymers were dissolved in TCB; they were then poured into a mould and the solvent was removed under vacuum at temperature. Due to the long temperature exposure, the polymer structures degraded and became brittle and broke when removed from the mould. For this reason, no tensile strength test could be done.

Note: Reasons for results and/or reactions that were not successful are discussed in detail in the following chapter.

Chapter 5 Conclusions and future work recommendations

5.1 Conclusions

From the aims and objectives of this study, working towards monomer preparation alkylation was found not to be successful. Other methods had to be attempted before alkylation, namely halogenation and oxidation of the halogenated *para* xylene. However, these also proved to be unsuccessful. The polymers were then synthesised with branched diols and brominated TPA.

The above-mentioned attempts suggest that alkylation reactions are difficult to achieve. The reason for the difficulty in alkylation reactions is lodged in by the fact that the substrate to be alkylated (DMT, 2-bromo DMT or 2-bromoTPA) was inactive. Methods aimed at improving reactivity were attempted, such as using a base (K_2HPO_3) with palladium acetate catalyst. Tryphenyl phosphine was also tried as a means to activate the substrate. It can be argued that these substrates are so stable that they do not require any reaction that may make them unstable. Alkylation of 2-bromo *para* xylene was also attempted, but again without success. The reaction taking place on the benzene ring depends on what is bonded to it, because this affects the reactivity of the unsubstituted positions.

From the literature it was noted that benzoic acid has been alkylated, but when those reactions were used to alkylate aryl diacids, they were not successful.[1] This is an indication of significant effect that the second carbonyl group has on the chemical nature of the aromatic ring.

Oxidation reactions were not successful because a mixture of products was obtained which was difficult to separate as the required product TPA and 4CBA are similar. The oxidation reaction could, however, be improved by using a continuous feed of instead of adding oxygen after consumption, as was the case in this study.

From the analyses of three types of polyesters, the following observations were made:

1. All the unsubstituted aryl polyesters were crystalline.
2. Bromide substitution on the aromatic ring destroyed crystallinity, thus yielding amorphous products.
3. The polyesters showed a steady increase in T_{max} in DTG. This was due to the increase in the number of methylene units in the polymer.

4. The effect of side chains on the dialcohols was not sufficiently clearly observed to have a bearing effect on any changes on its own.
5. The polymers became softer as the number of methylene units increased, and they were also more flexible.
6. Bromination leads to soft polyesters.
7. The degree of polymerisation was not consistent. This could be due to the fact that vacuum applied was not strong enough to remove the by-products during polyester formation. [2]

It was concluded that:

1. The benzene ring did not become activated as number of methods were tried to activate it so that it can react either by alkylation reactions or bromination reactions.
2. The methyl branches on diols were not responsible for any changes in polyesters' properties.
3. Bromide lead to softer and amorphous polyesters

5.2 Future work recommendations

For future work another approach could be to oxidize trisubstituted alkyl aryl precursors to produce carboxylic acid derivatives. If two alkyl groups are oxidised, this would fulfil the role of alkyl-substituted diacids in the preparation of polyesters. If all three groups are however oxidised, hyperbranched polyesters could be produced.

5.3 References

[1] a) Y. H. Zhang, B. F. Shi and J. Q. Yu, *Angew Chem Int Ed Engl* **2009**, *48*, 6097-6100; b) C. Han and S. L. Buchwald, *J. A. C. S.* **2009**, *131*, 7532-7533; c) S. H. a. V. S. Sylvie Chamoin, *Tetrahedron* **1998**, *39*, 4175-4178.

[2] K. Pang, R. Kotek and A. Tonelli, *Progress in Polymer Science* **2006**, *31*, 1009-1037.

Appendices

Appendix A: GCMS

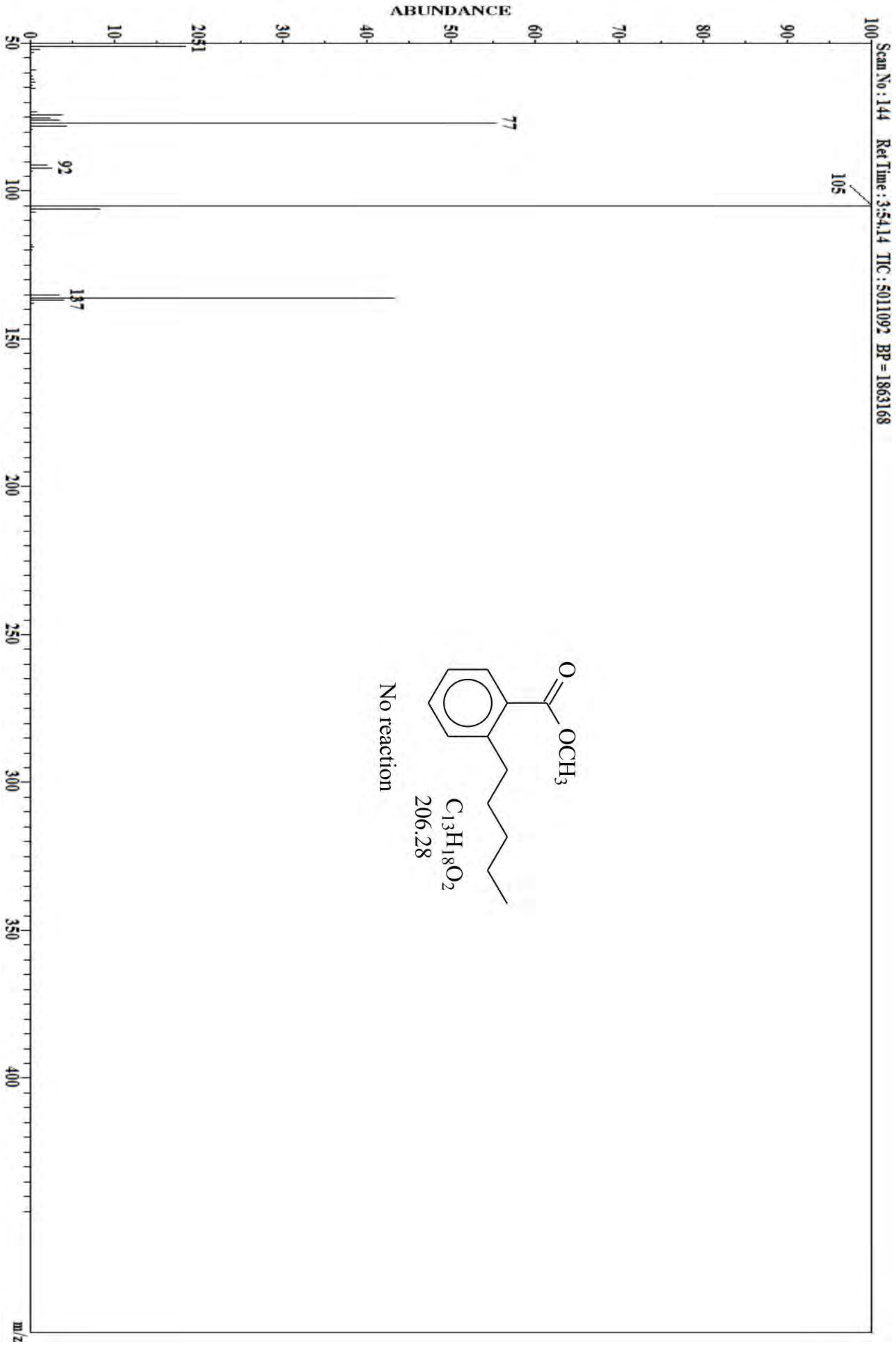
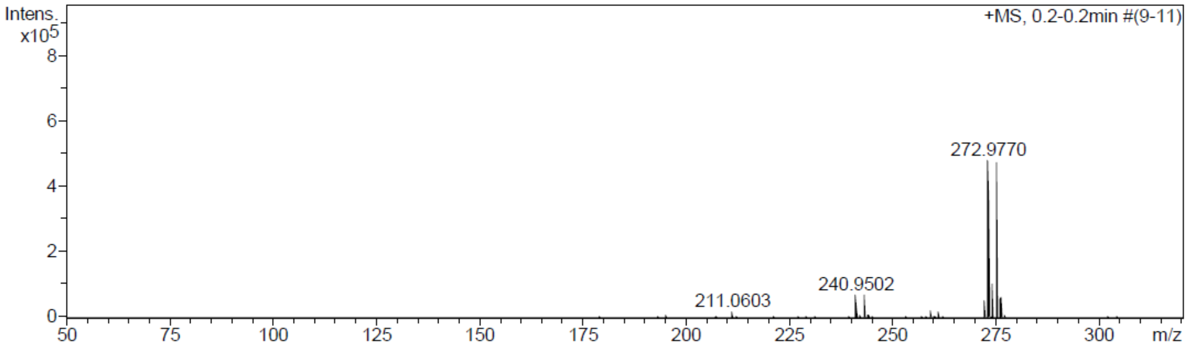


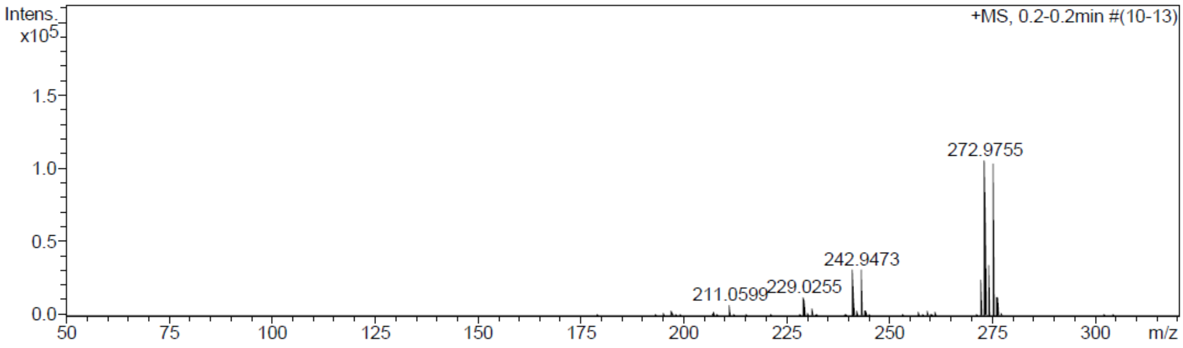
Figure A.1: GC-MS spectrum of reaction Scheme 4.4 alkylation of methyl benzoate

Appendix B: MS



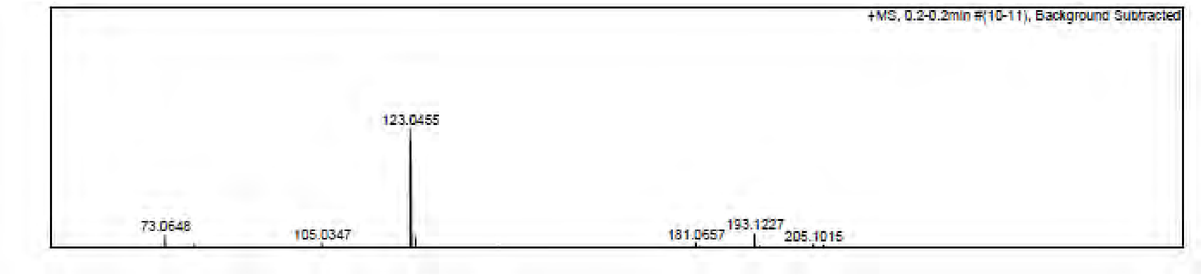
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e⁻ Conf
272.9770	1	C 10 H 10 Br O 4	100.00	272.9757	-1.4	-5.0	48.4	5.5	ok	even

Figure B.1: MS spectrum of reaction Scheme 4.2 preparation of methyl benzoate



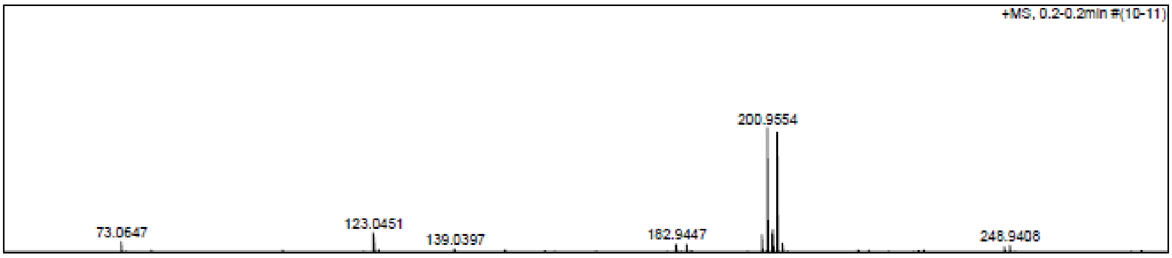
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e⁻ Conf
272.9755	1	C 10 H 10 Br O 4	100.00	272.9757	0.2	0.8	96.4	5.5	ok	even

Figure B.2: MS spectrum of reaction Scheme 4.3 esterification with coppersulphate as an inhibitor



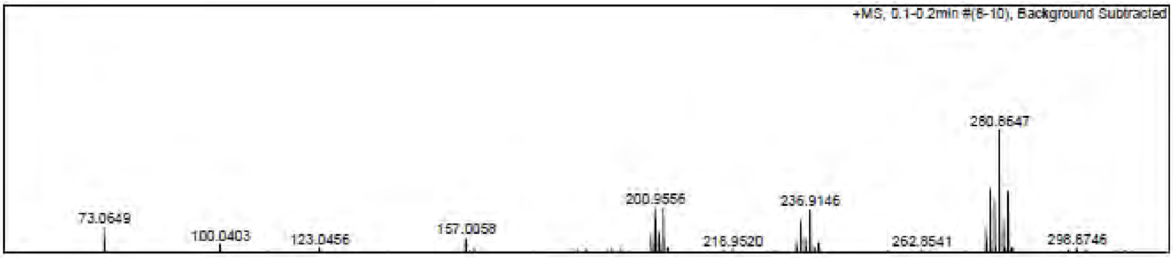
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e^- Conf
123.0455	1	C 7 H 7 O 2	100.00	123.0441	-1.4	-11.4	17.3	4.5	ok	even
	2	C 6 H 7 N 2 O	0.00	123.0553	9.8	79.9	19.1	4.5	ok	even
	3	C 5 H 5 N 3 O	30.98	123.0427	-2.7	-22.3	23.2	5.0	ok	odd
	4	C 4 H 5 N 5	0.00	123.0539	8.5	69.0	25.2	5.0	ok	odd
193.1227	1	C 12 H 17 O 2	100.00	193.1223	-0.4	-1.9	7.1	4.5	ok	even
	2	C 10 H 15 N 3 O	44.47	193.1210	-1.7	-8.9	8.9	5.0	ok	odd
	3	C 9 H 15 N 5	0.00	193.1322	9.5	49.3	10.6	5.0	ok	odd
	4	C 8 H 13 N 6	12.99	193.1196	-3.1	-15.8	14.1	5.5	ok	even
	5	C 8 H 19 N O 4	0.00	193.1309	8.2	42.4	25.3	0.0	ok	odd
	6	C 7 H 17 N 2 O 4	2.06	193.1183	-4.4	-22.8	29.3	0.5	ok	even
205.1015	1	C 4 H 11 N 7 O 3	0.00	205.0918	-9.8	-47.6	40.1	3.0	ok	odd
	2	C 5 H 13 N 6 O 3	100.00	205.1044	2.8	13.7	44.2	2.5	ok	even

Figure B.3: MS spectrum of reaction Scheme 4.5 alkylation of benzoic acid using 1,2-dichloroethane



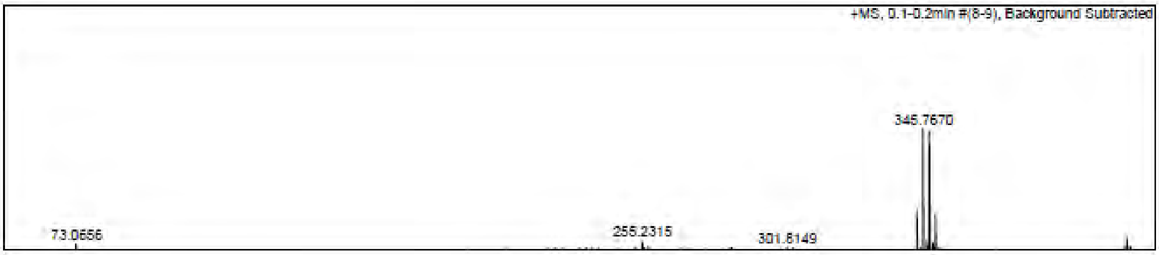
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e^- Conf
199.9473	1	C 2 O 11	100.00	199.9435	-3.8	-19.0	757.8	3.0	ok	odd
	2	C 7 H 5 Br O 2	1.31	199.9467	-0.6	-2.8	780.2	5.0	ok	odd
	3	C 5 H 3 Br N 3 O	0.00	199.9454	-1.9	-9.5	876.3	5.5	ok	even
	4	C 3 H Br N 6	0.00	199.9441	-3.3	-16.3	881.9	6.0	ok	odd
200.9554	1	C 7 H 6 Br O 2	100.00	200.9546	-0.9	-4.3	46.9	4.5	ok	even

Figure B.4: MS spectrum of reaction Scheme 4.8 bromination of benzoic acid



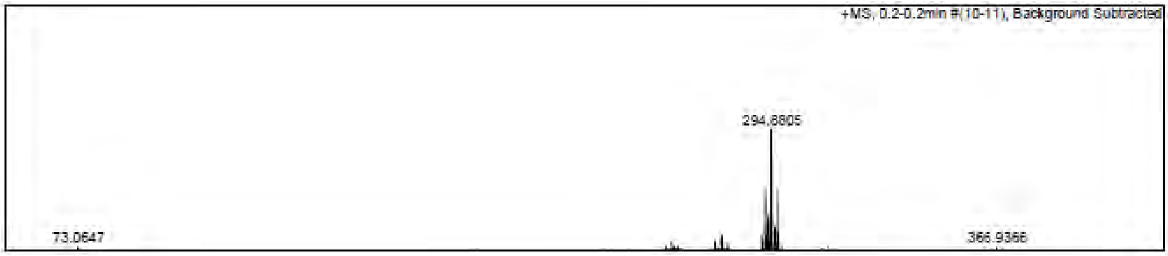
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e^- Conf
157.0058	1	C 7 H N 4 O	7.24	157.0145	8.7	55.5	16.7	9.5	ok	even
	2	C 13 H	100.00	157.0073	1.5	9.6	181.0	13.5	ok	even
	3	C 6 H 5 O 5	0.04	157.0131	7.4	47.0	182.6	4.5	ok	even
	4	C 5 H 3 N O 5	1.75	157.0006	-5.2	-33.1	183.3	5.0	ok	odd
	5	C 8 H N 2 O 2	37.55	157.0033	-2.5	-16.0	183.7	9.5	ok	even
199.9480	1	C 7 H 5 Br O 2	100.00	199.9467	-1.2	-6.1	680.0	5.0	ok	odd
	2	C 3 H 7 Br N O 4	0.00	199.9553	7.3	36.7	701.6	0.5	ok	even
	3	C 2 O 11	0.01	199.9435	-4.4	-22.2	704.2	3.0	ok	odd
	4	C 2 H 5 Br N 2 O 4	0.00	199.9427	-5.2	-26.2	705.5	1.0	ok	odd
	5	C N 2 O 10	0.00	199.9547	6.8	34.0	706.3	3.0	ok	odd
	6	C 5 H 3 Br N 3 O	0.00	199.9454	-2.6	-12.8	764.1	5.5	ok	even
	7	C 4 H 3 Br N 5	0.00	199.9566	8.7	43.4	766.2	5.5	ok	even
	8	C 3 H Br N 6	0.00	199.9441	-3.9	-19.5	770.4	6.0	ok	odd
200.9556	1	C 4 H 4 Br N 5	0.91	200.9645	8.8	44.0	40.7	5.0	ok	odd
	2	C 7 H 6 Br O 2	100.00	200.9546	-1.1	-5.2	168.3	4.5	ok	even
	3	C 3 H 8 Br N O 4	0.01	200.9631	7.5	37.3	188.3	0.0	ok	odd
	4	C 2 H 6 Br N 2 O 4	0.30	200.9505	-5.1	-25.3	192.0	0.5	ok	even
	5	C 5 H 4 Br N 3 O	5.28	200.9532	-2.4	-11.9	194.0	5.0	ok	odd
	6	C 3 H 2 Br N 6	0.86	200.9519	-3.7	-18.6	199.9	5.5	ok	even
	7	C 2 H O 11	0.00	200.9513	-4.3	-21.3	601.9	2.5	ok	even
	8	C H N 2 O 10	0.00	200.9626	6.9	34.6	603.9	2.5	ok	even
234.9169	1	C 9 H 2 Br N O 2	0.02	234.9263	9.5	40.3	129.0	9.0	ok	odd
	2	C 7 Br N 4 O	0.21	234.9250	8.1	34.6	143.4	9.5	ok	even
	3	C 13 Br	100.00	234.9178	0.9	3.9	189.6	13.5	ok	even
	4	C 8 Br N 2 O 2	5.65	234.9138	-3.1	-13.2	204.0	9.5	ok	even
	5	C 6 H 4 Br O 5	0.02	234.9237	6.8	28.9	212.6	4.5	ok	even
	6	C 5 H 2 Br N O 5	0.07	234.9111	-5.8	-24.6	215.1	5.0	ok	odd
	7	C 4 H 2 Br N 3 O 4	0.10	234.9223	5.5	23.2	216.8	5.0	ok	odd
	8	C 3 Br N 4 O 4	0.00	234.9097	-7.1	-30.3	219.5	5.5	ok	even
	9	C 2 Br N 6 O 3	0.40	234.9210	4.1	17.5	221.3	5.5	ok	even
	10	C 2 H 4 Br O 8	0.00	234.9084	-8.5	-36.0	228.0	0.5	ok	even
278.8666	1	C 7 H 5 Br 2 O 2	100.00	278.8651	-1.5	-5.5	175.2	4.5	ok	even

Figure B.5: MS spectrum of reaction Scheme 4.10 bromination of benzoic acid



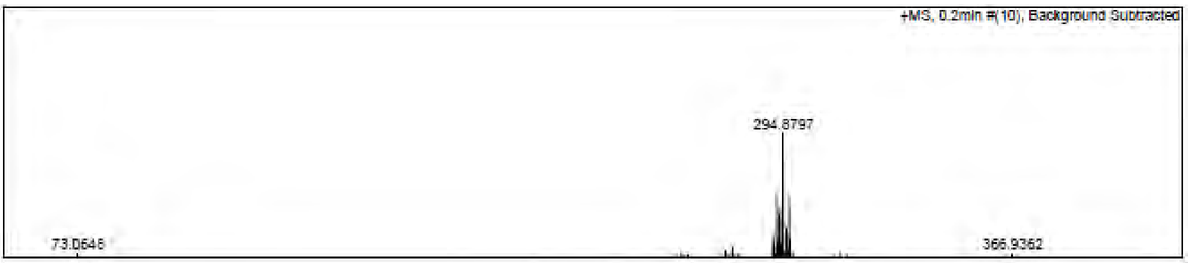
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e^- Conf
343.7684	1	C 6 H 3 Br 3 O 2	100.00	343.7678	-0.6	-1.9	11.1	4.0	ok	odd
	2	C 4 H Br 3 N 3 O	40.37	343.7664	-2.0	-5.8	14.2	4.5	ok	even
	3	C 3 H Br 3 N 5	0.00	343.7777	9.2	26.9	15.6	4.5	ok	even
	4	C 2 H 5 Br 3 N O 4	0.01	343.7763	7.9	23.0	27.8	-0.5	ok	even
	5	C H 3 Br 3 N 2 O 4	1.63	343.7637	-4.7	-13.6	32.6	0.0	ok	odd
345.7670	1	C 3 H Br 3 N 4 O	100.00	345.7695	2.5	7.3	352.2	4.0	ok	odd
	2	C 5 H 3 Br 3 N O 2	22.12	345.7708	3.9	11.2	353.2	3.5	ok	even
	3	C 4 H Br 3 N 2 O 2	0.01	345.7583	-8.7	-25.2	353.3	4.0	ok	odd
	4	C 9 H Br 3	7.07	345.7623	-4.7	-13.6	353.9	8.0	ok	odd

Figure B.6: MS spectrum of reaction Scheme 4.11 bromination of resorcinol



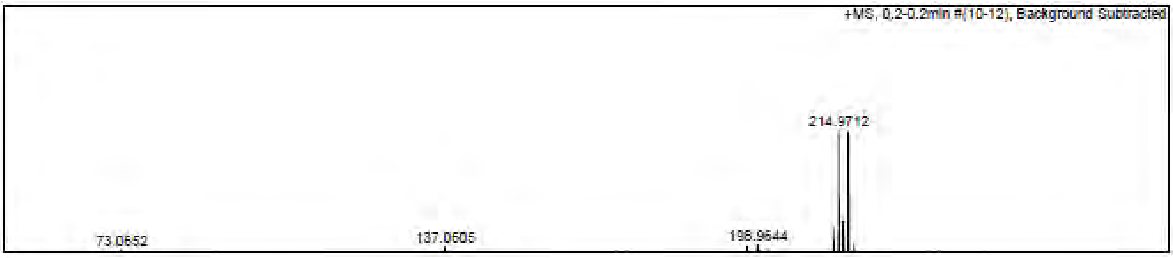
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e^- Conf
292.8821	1	$C_8H_7Br_2O_2$	100.00	292.8807	-1.3	-4.6	117.6	4.5	ok	even
364.9388	1	$C_8H_{11}Br_2N_6O$	100.00	364.9356	-3.3	-9.0	55.4	5.5	ok	even
	2	$C_9H_2BrN_8O_4$	0.00	364.9377	-1.2	-3.2	315.3	12.5	ok	even

Figure B.7: MS spectrum of reaction Scheme 4.12 synthesis of 2,5-dibromoterephthalic acid



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e^- Conf
292.8809	1	$C_8H_7Br_2O_2$	100.00	292.8807	-0.2	-0.6	158.0	4.5	ok	even

Figure B.8: MS spectrum of reaction Scheme 4.13 completion of oxidation of 2,5-dibromo-1,4-dimethylbenzene



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e^- Conf
213.9635	1	C_6NO_8	100.00	213.9618	-1.6	-7.6	719.9	7.5	ok	even
	2	$C_8H_7BrO_2$	0.02	213.9624	-1.1	-5.0	750.0	5.0	ok	odd
	3	$C_6H_5BrN_3O$	0.00	213.9611	-2.4	-11.3	842.7	5.5	ok	even
	4	$C_4H_3BrN_6$	0.00	213.9597	-3.8	-17.6	848.5	6.0	ok	odd
214.9712	1	$C_8H_8BrO_2$	100.00	214.9702	-1.0	-4.6	74.0	4.5	ok	even
	2	$C_6H_6BrN_3O$	22.03	214.9689	-2.3	-10.9	88.1	5.0	ok	odd
	3	$C_4H_4BrN_6$	4.67	214.9675	-3.7	-17.1	93.7	5.5	ok	even
	4	C_6HNO_8	0.00	214.9697	-1.5	-7.2	570.1	7.0	ok	odd

Figure B.9: MS spectrum of reaction Scheme 4.14 synthesis of 2-dibromoterephthalic acid

Appendix C: IR

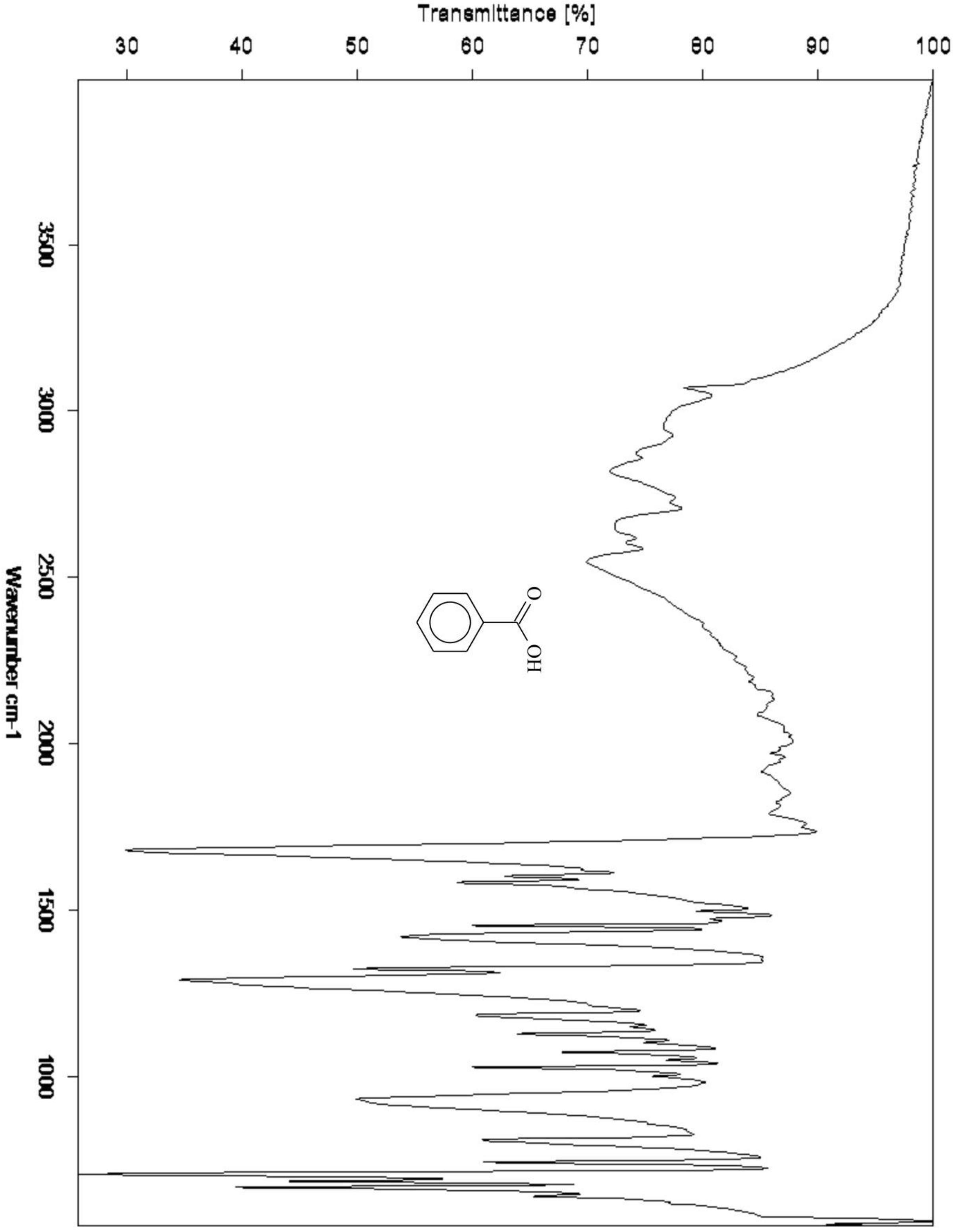


Figure C.1: IR spectrum of benzoic acid

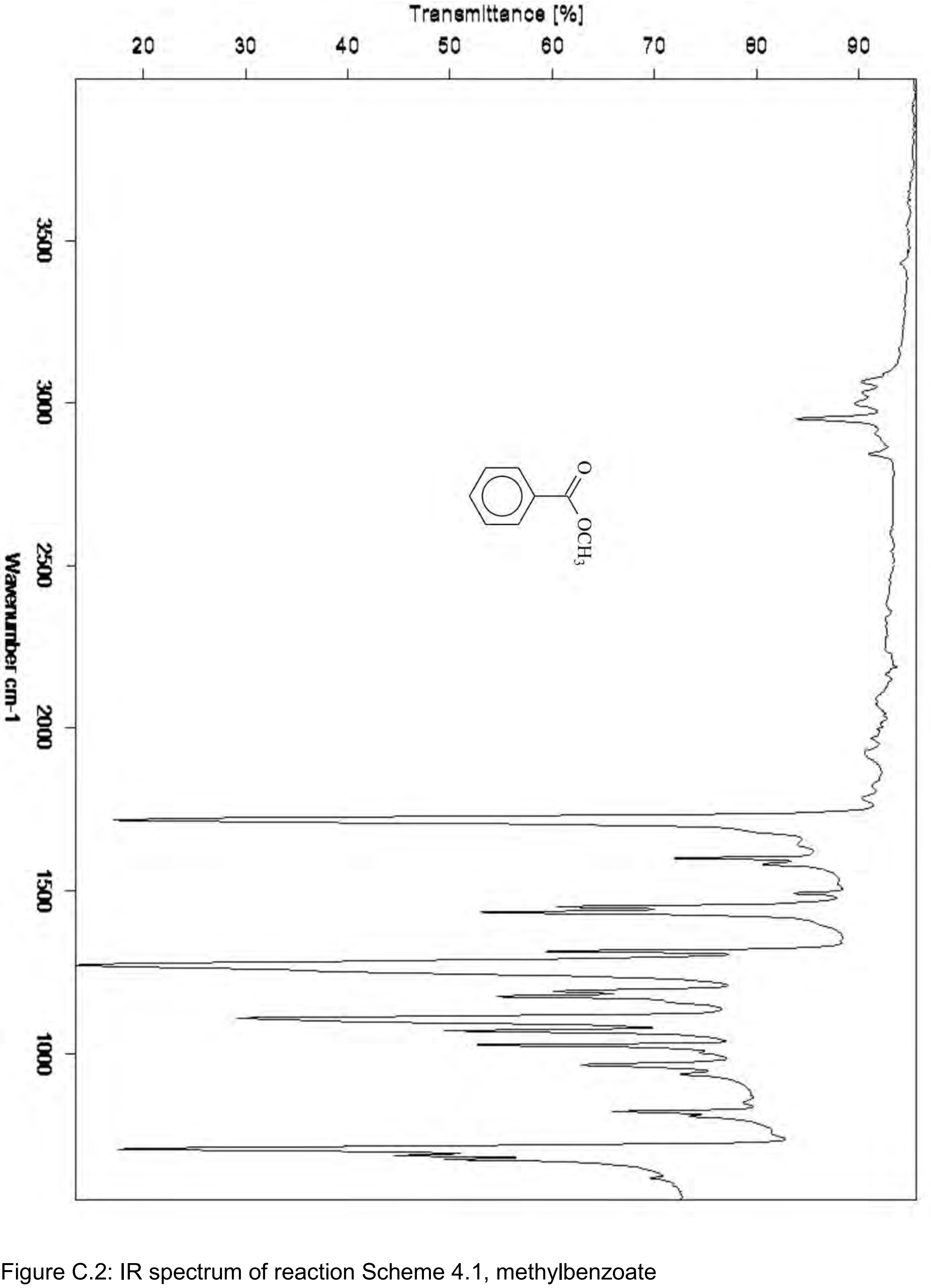


Figure C.2: IR spectrum of reaction Scheme 4.1, methylbenzoate

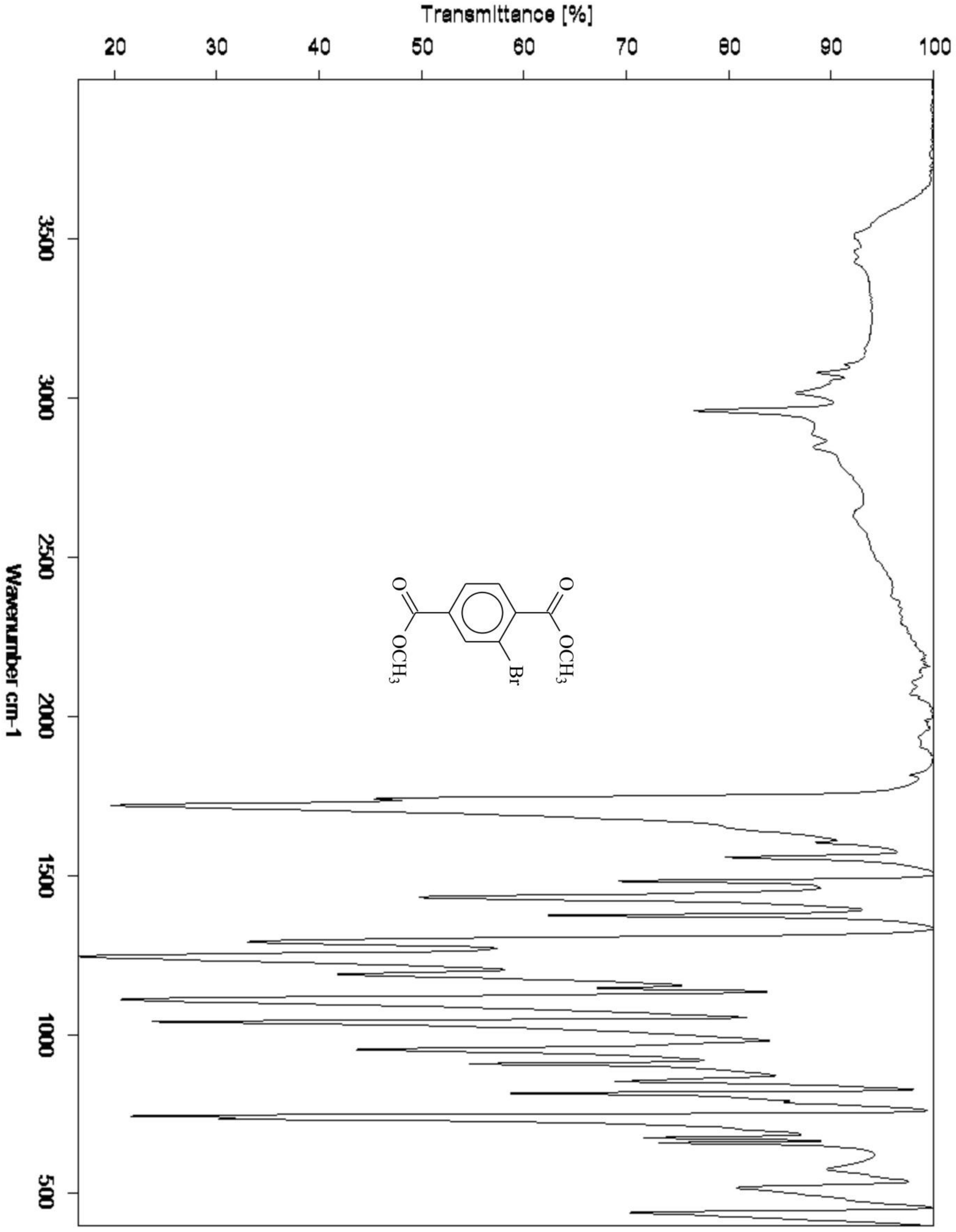


Figure C.3: IR spectrum of reaction Scheme 4.2, 2-bromodimetyhylterephthalate

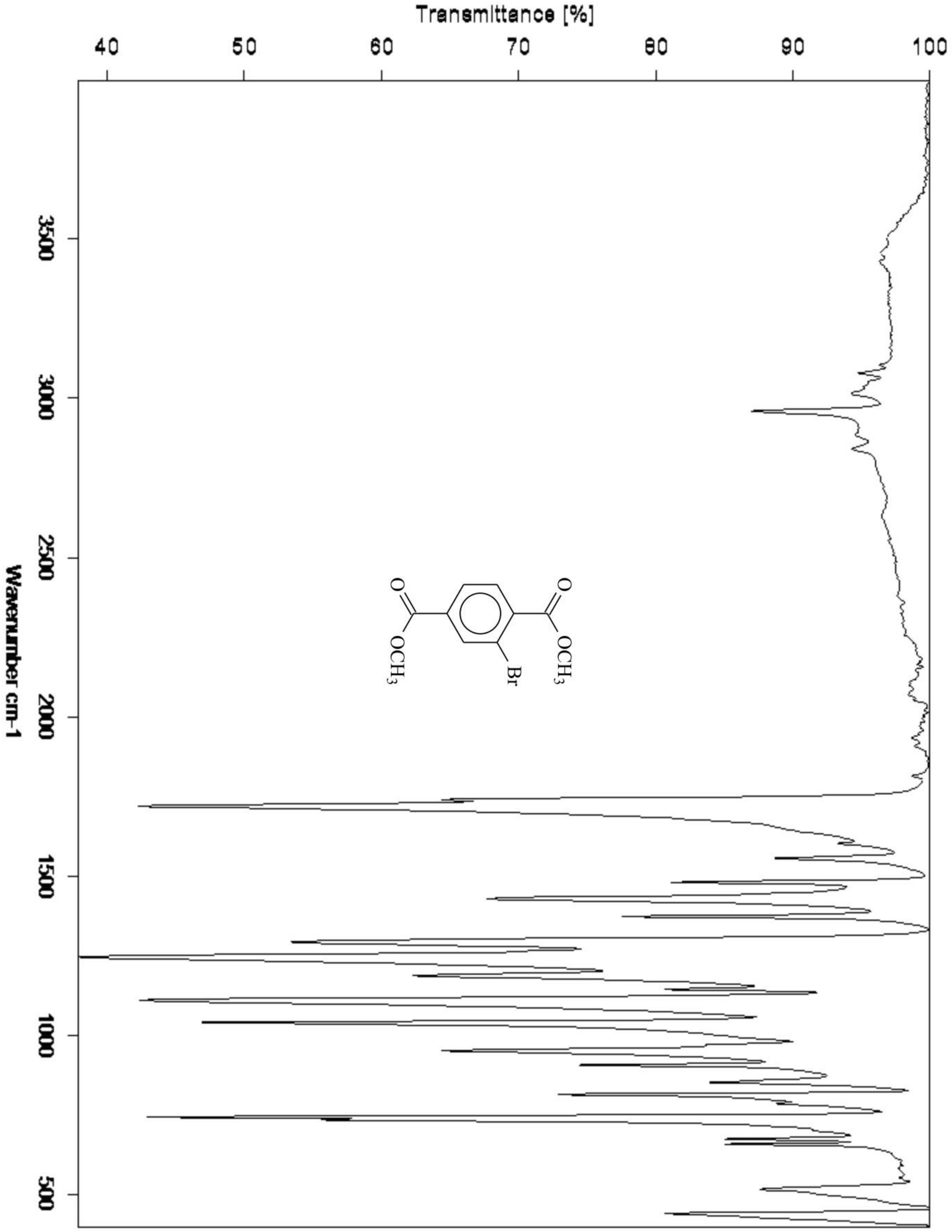


Figure C.4: IR spectrum of reaction Scheme 4.3, 2-bromodimethylterephthalate

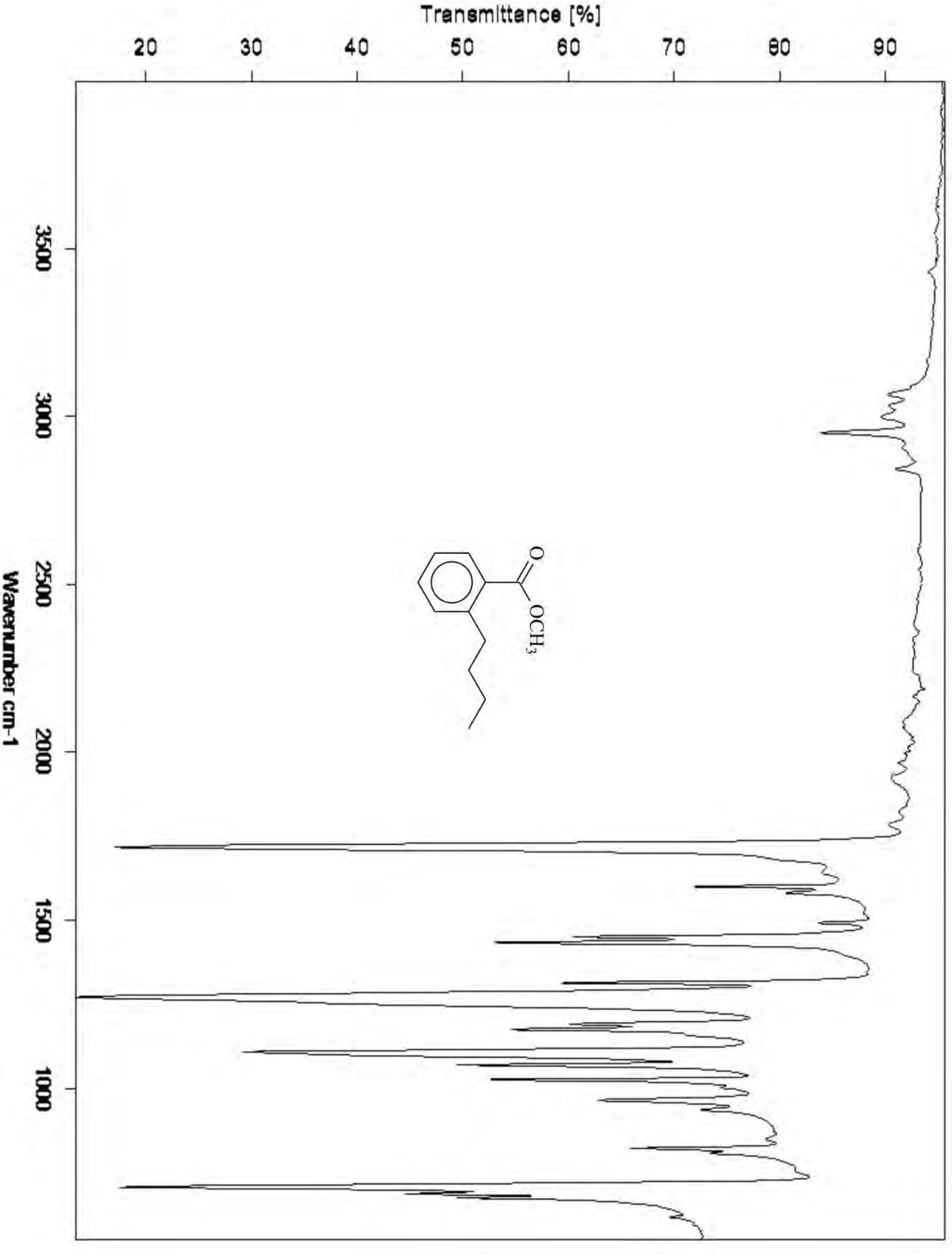


Figure C.5: IR spectrum of reaction Scheme 4.4, alkylation product of methylbenzoate (no reaction)

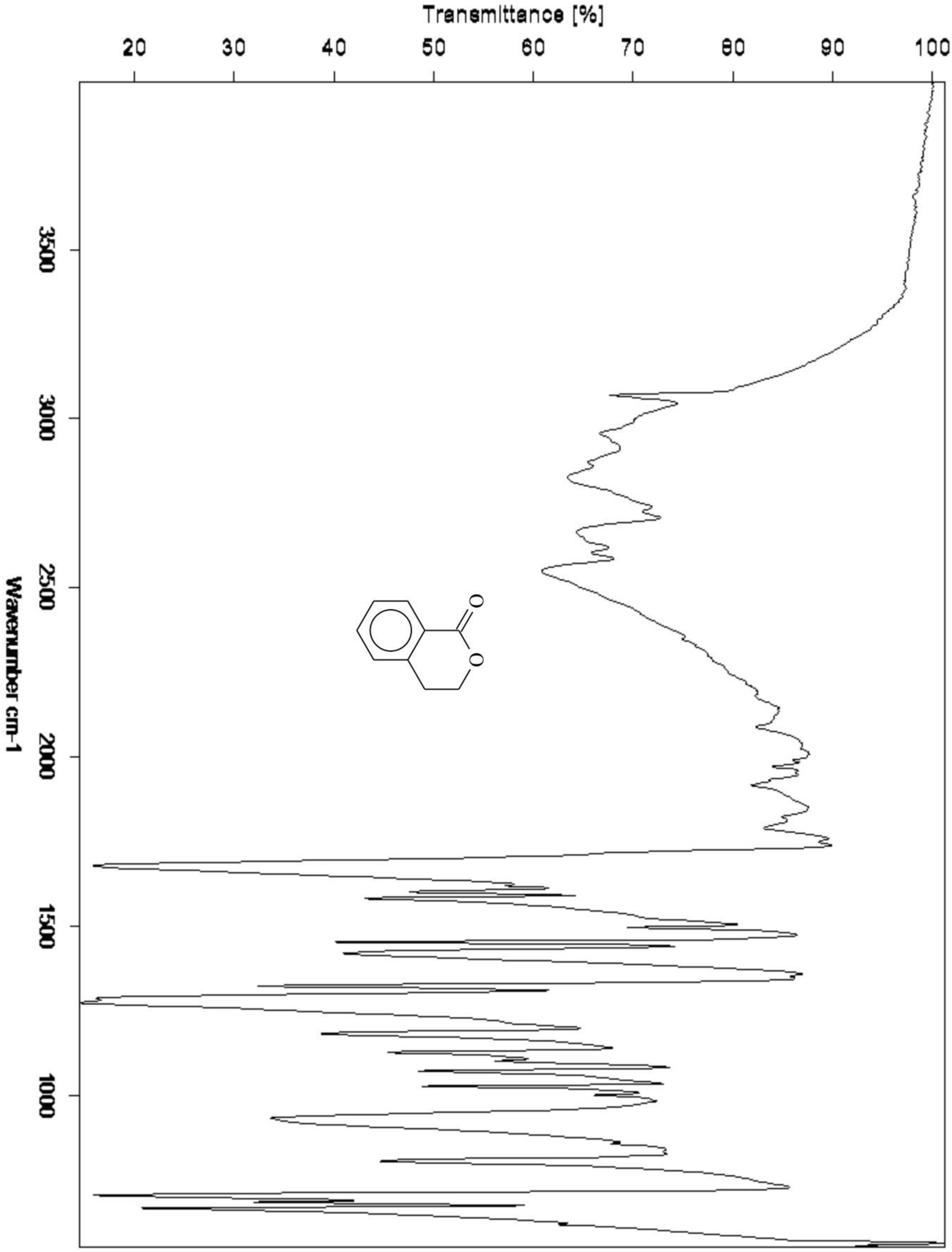


Figure C.6: IR spectrum of reaction Scheme 4.5, alkylation product of benzoic acid (no reaction)

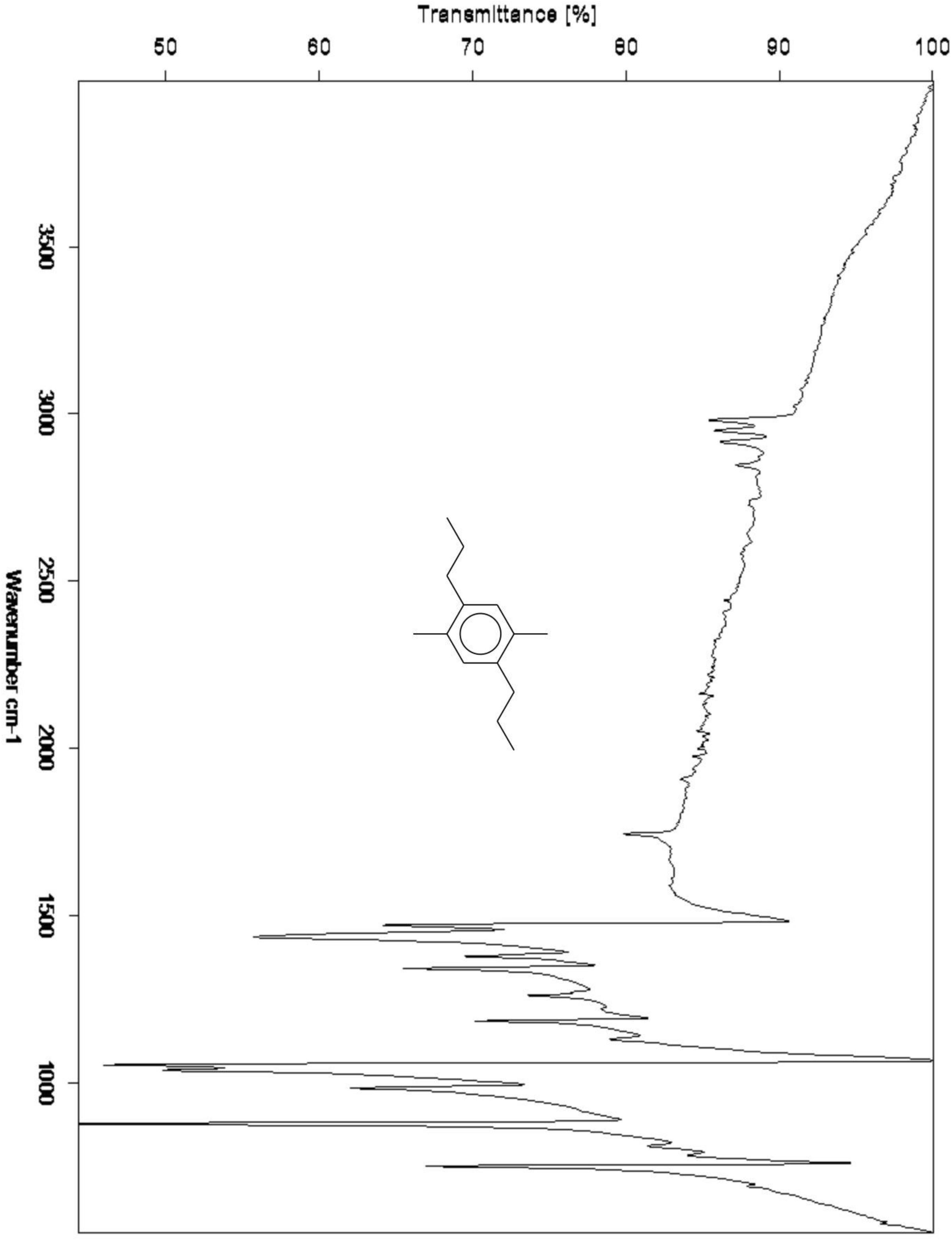


Figure C.7: IR spectrum of reaction Scheme 4.6, alkylation product of 2,5-dibrom*para*xylene (no reaction)

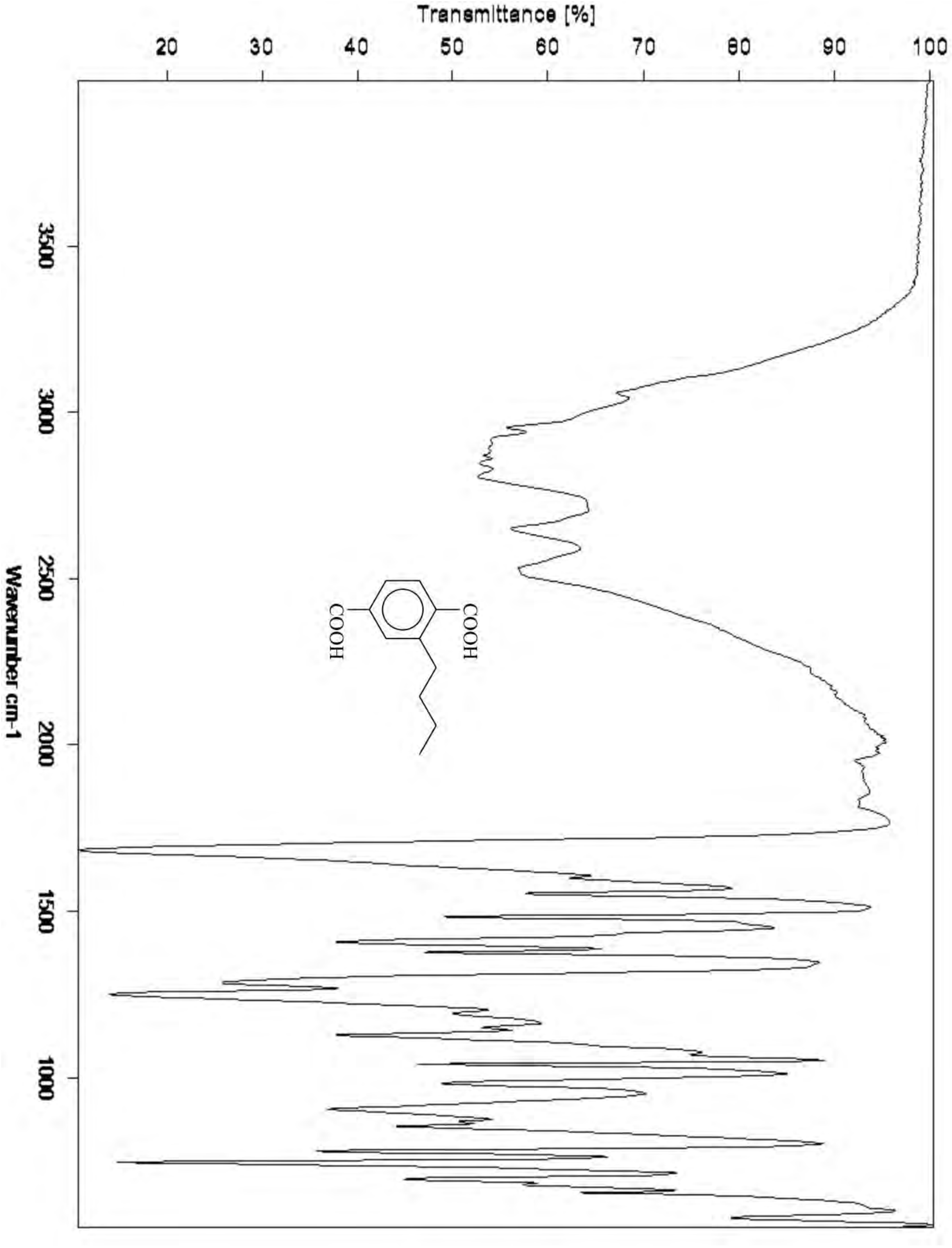


Figure C.8: IR spectrum of reaction Scheme 4.7, alkylation product of 2-bromoterephthalic acid (no reaction)

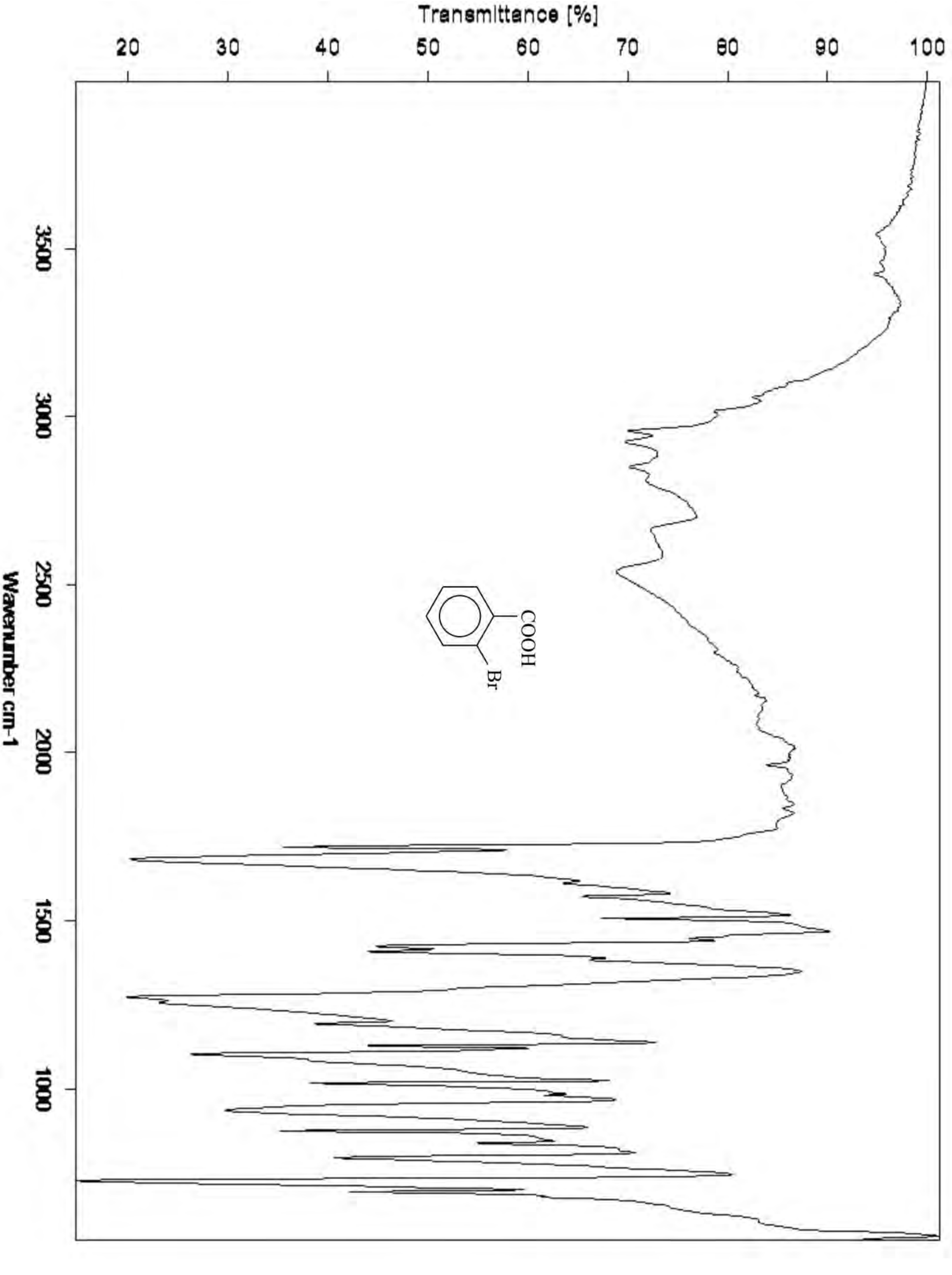


Figure C.9: IR spectrum of reaction Scheme 4.8, 2-bromobenzoic acid (and 4-bromobenzoic acid)

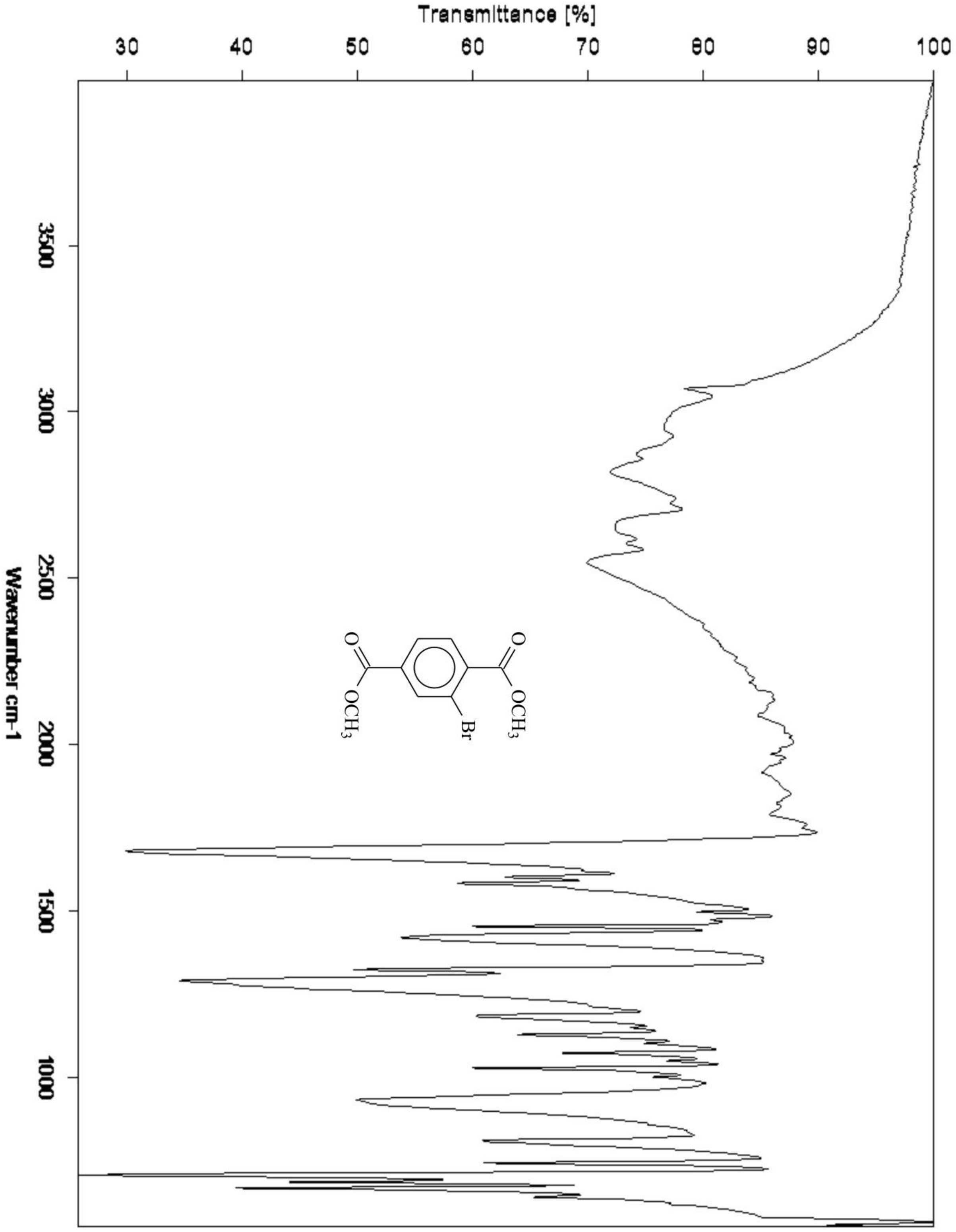


Figure C.10: IR spectrum of reaction Scheme 4.9, bromination product of dimethyl terephthalate (no reaction)

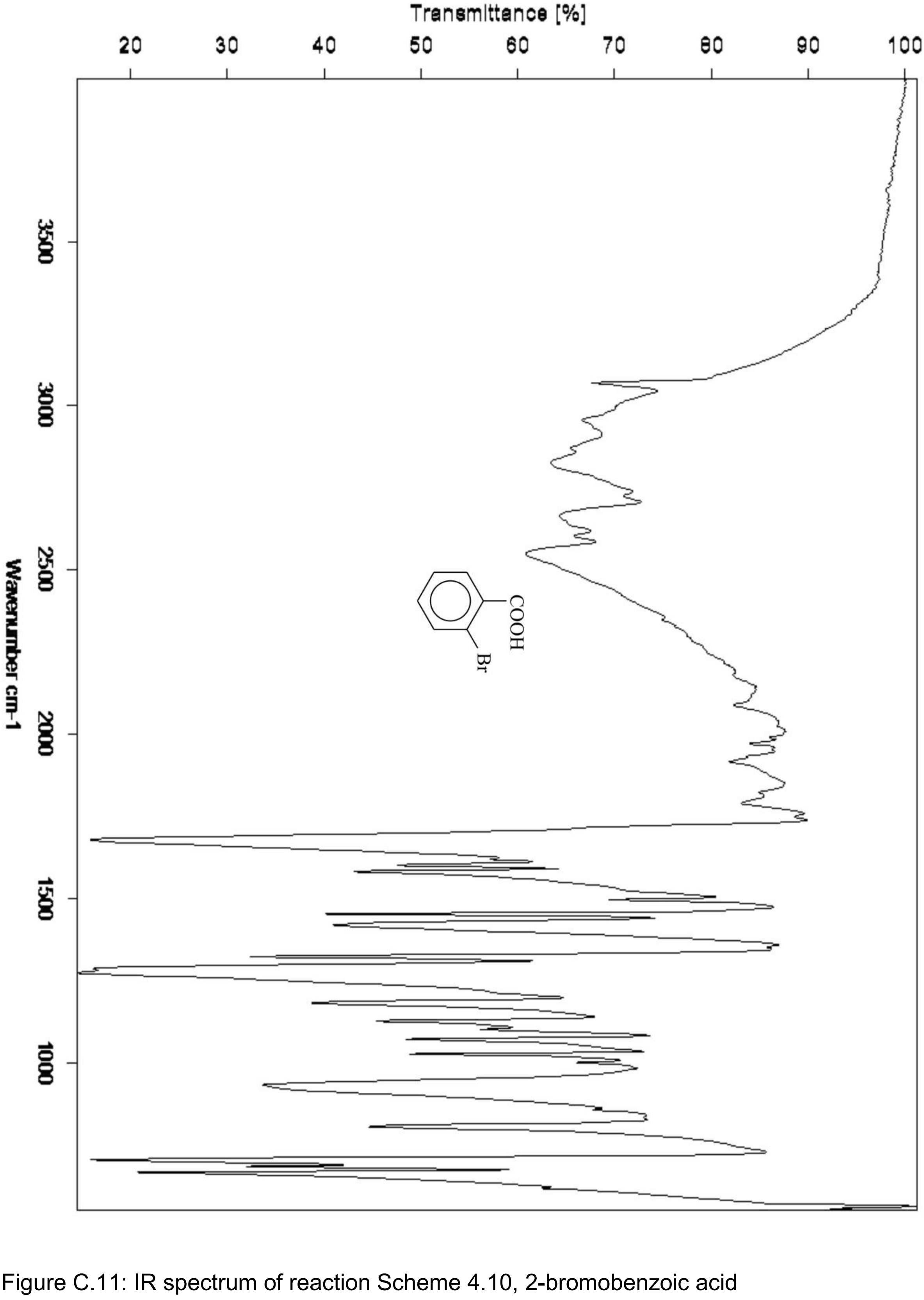


Figure C.11: IR spectrum of reaction Scheme 4.10, 2-bromobenzoic acid

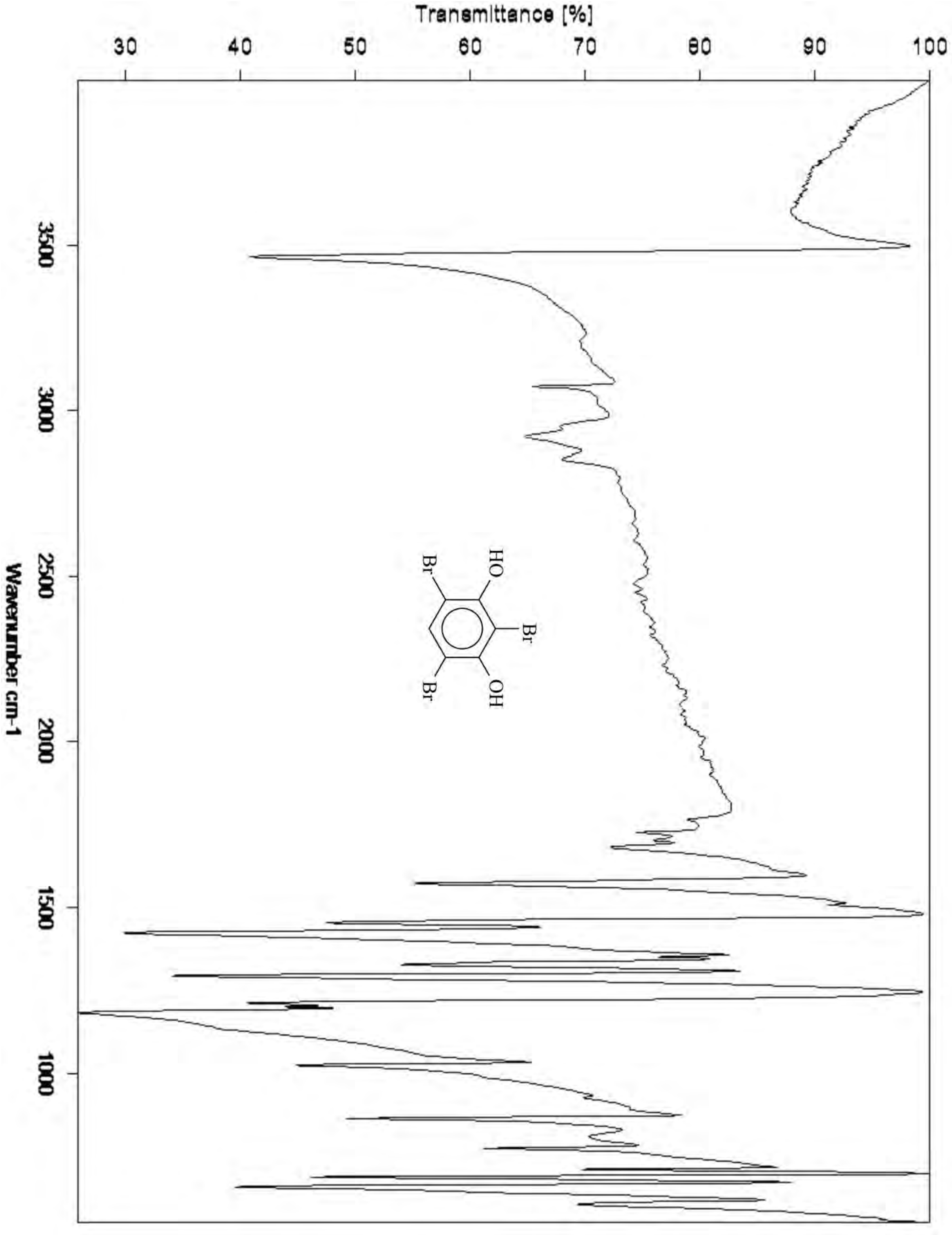


Figure C.12: IR spectrum of reaction Scheme 4.11, 2,4,6-tribromo-1,3-benzenediol (2,4,6-tribromoresorcinol)

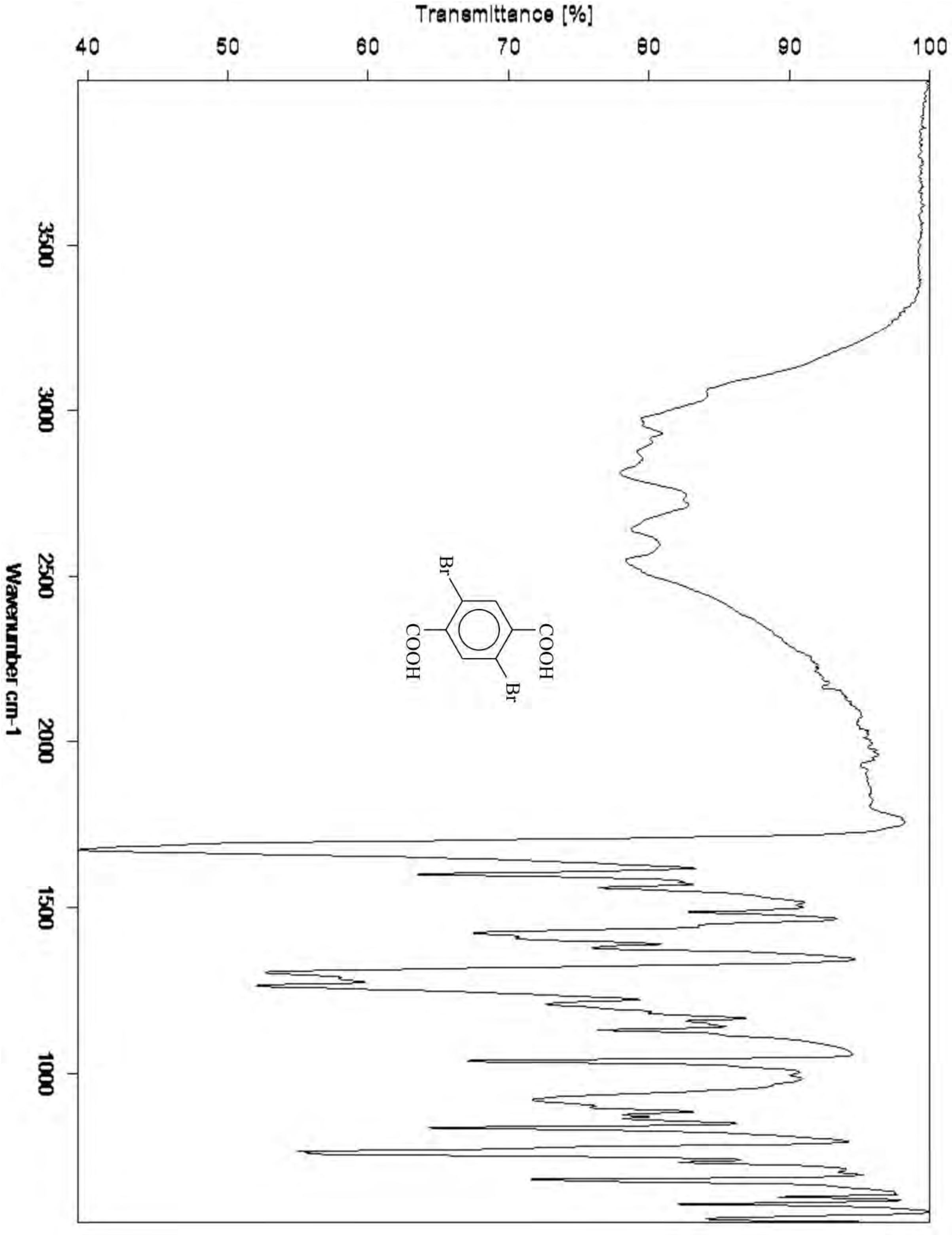


Figure C.13: IR spectrum of reaction Scheme 4.12, oxidation product of 2,5-dibromo*para*xylene

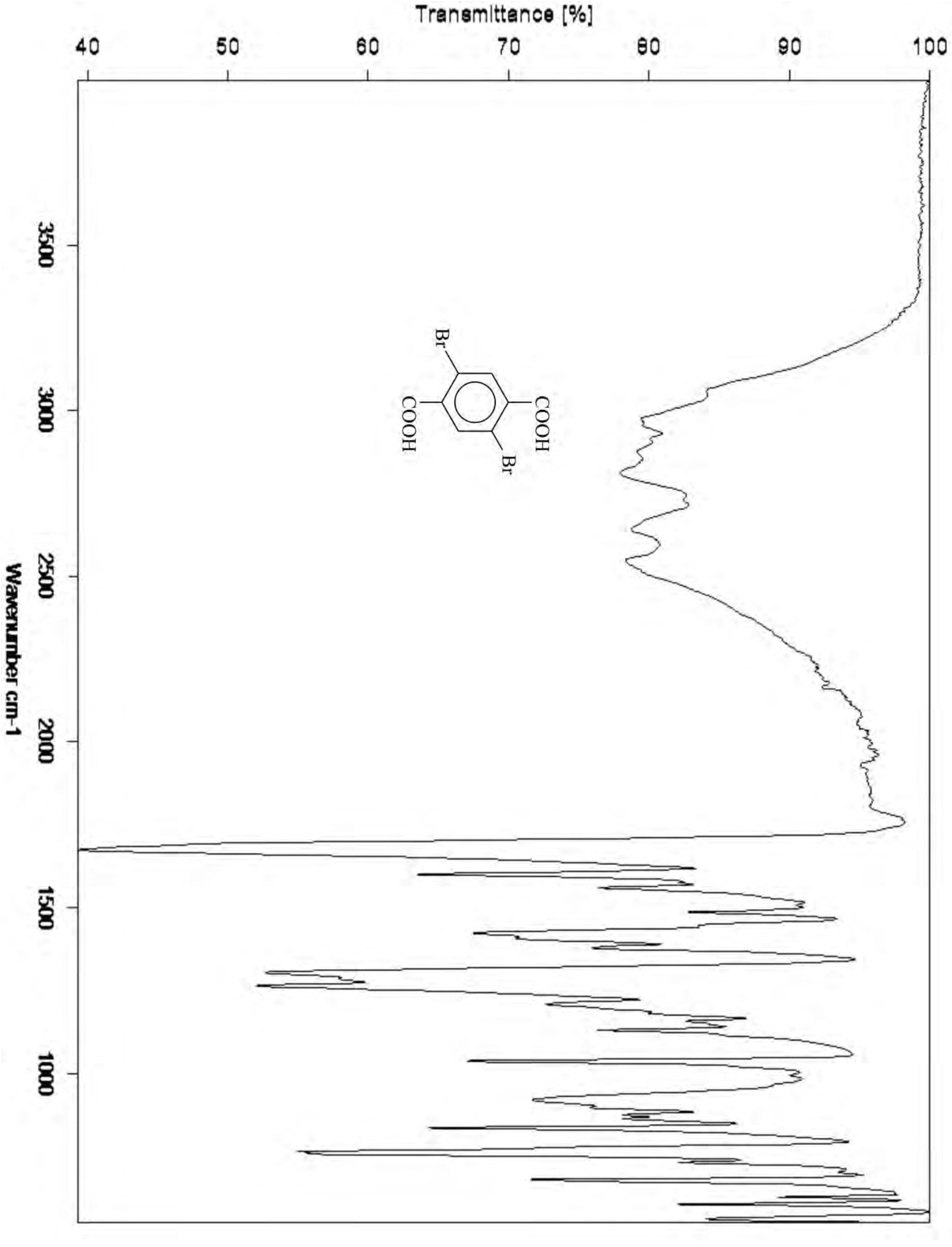


Figure C.14: IR spectrum of reaction Scheme 4.13, oxidation product of product in Figure C.13

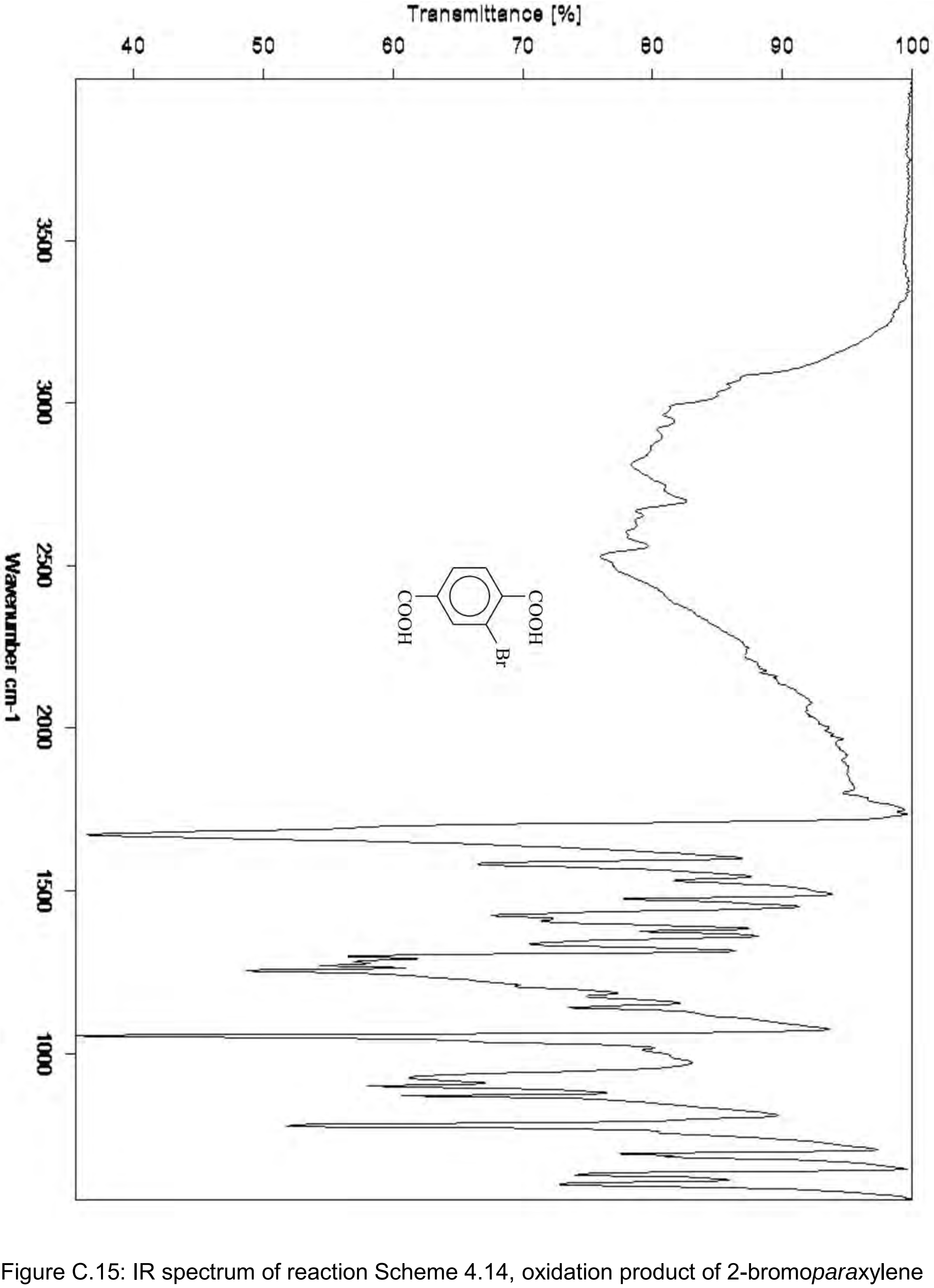


Figure C.15: IR spectrum of reaction Scheme 4.14, oxidation product of 2-bromo*para*xylene

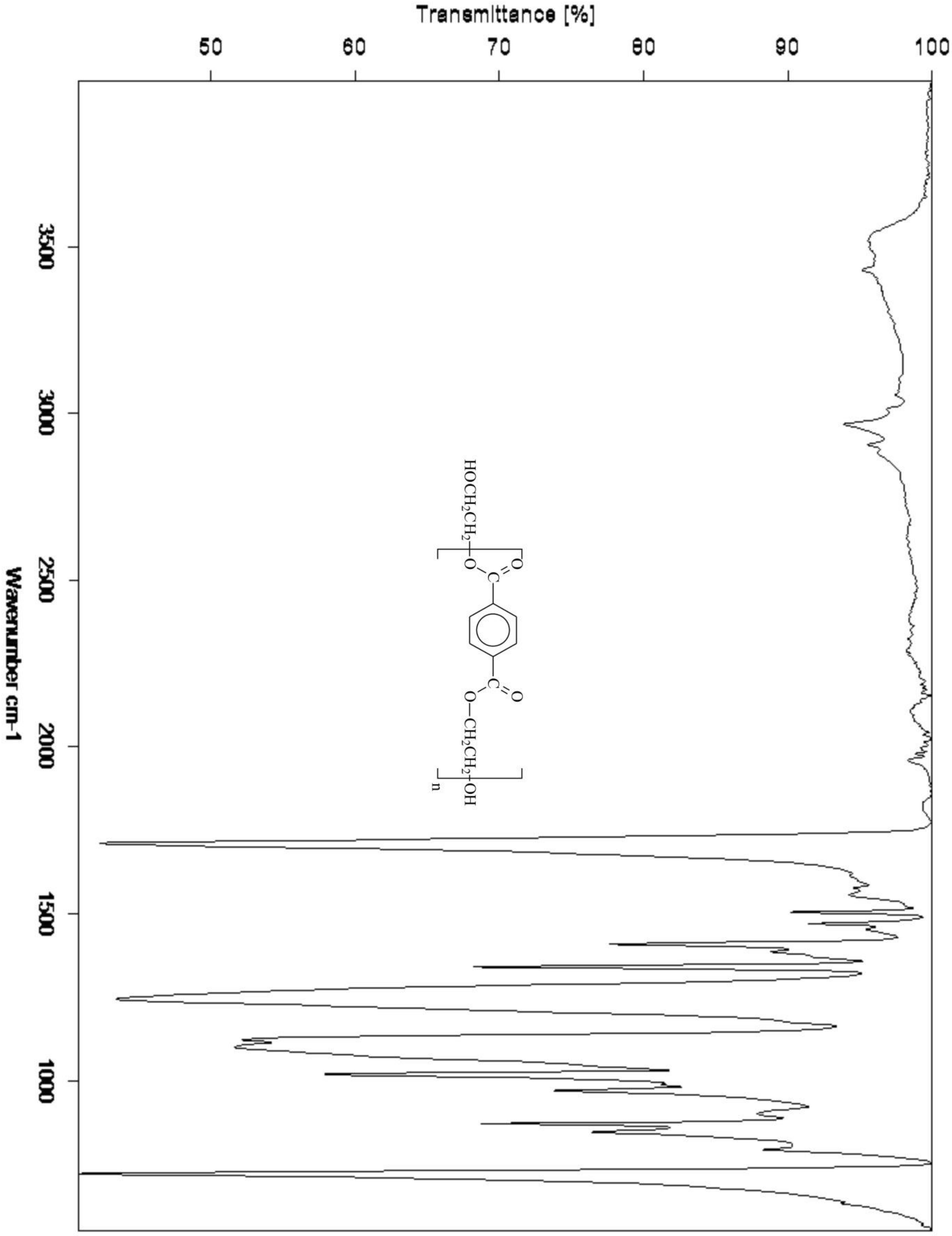


Figure C.16: IR spectrum of Figure 4.5, polyethylene terephthalate

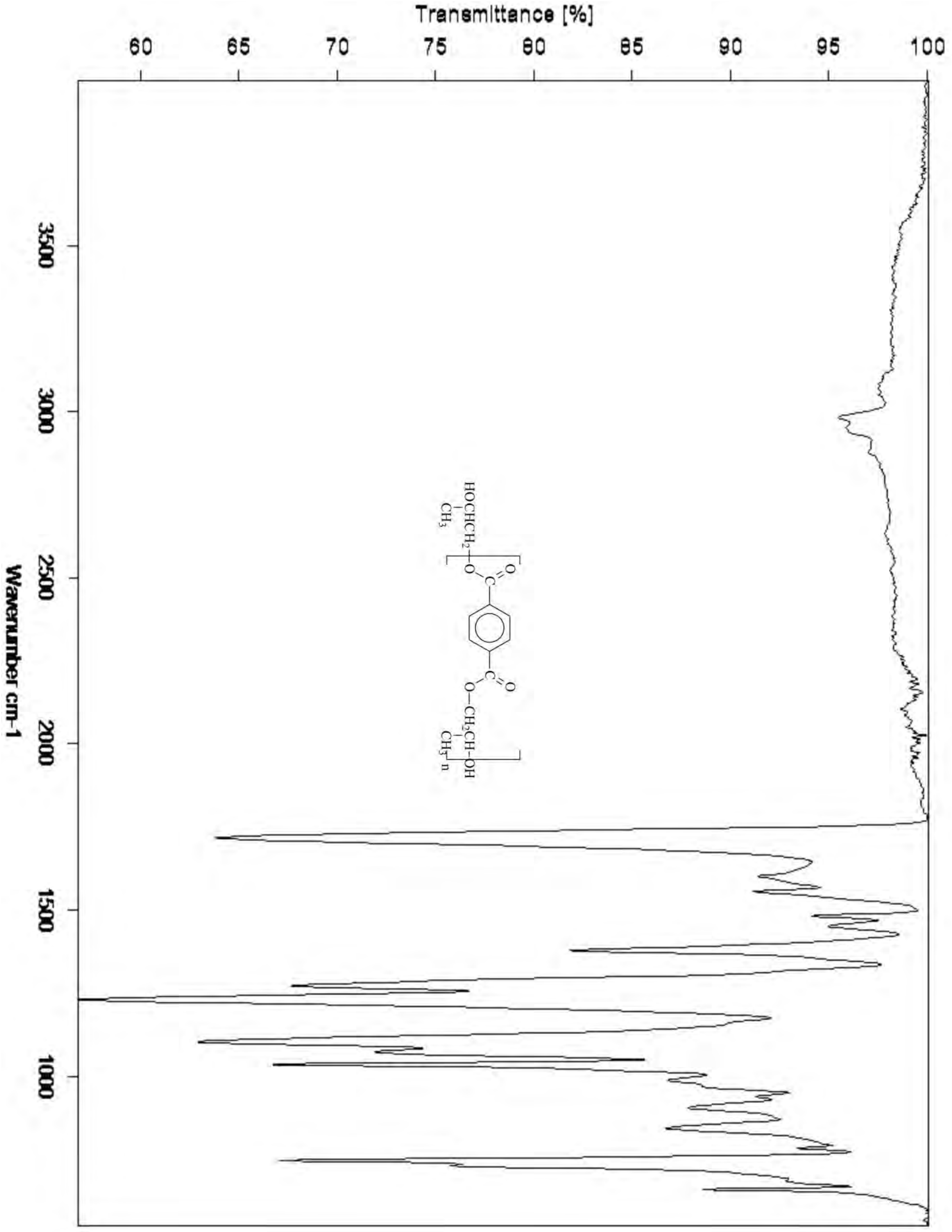


Figure C.17: IR spectrum of Figure 4.6, poly(1,2-propanediol) terephthalate

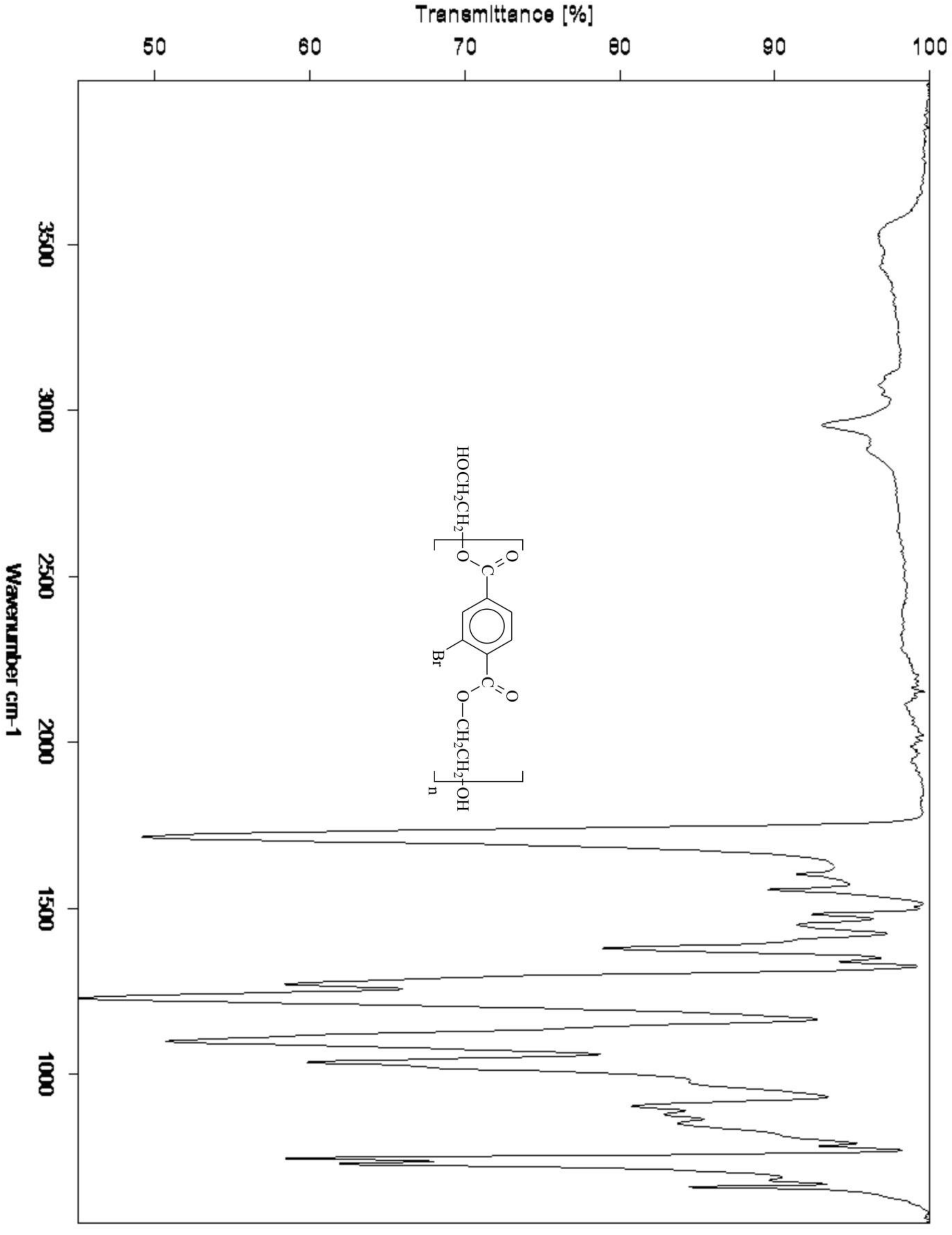


Figure C.18: IR spectrum of Figure 4.7, polyethylene 2-bromoterephthalate

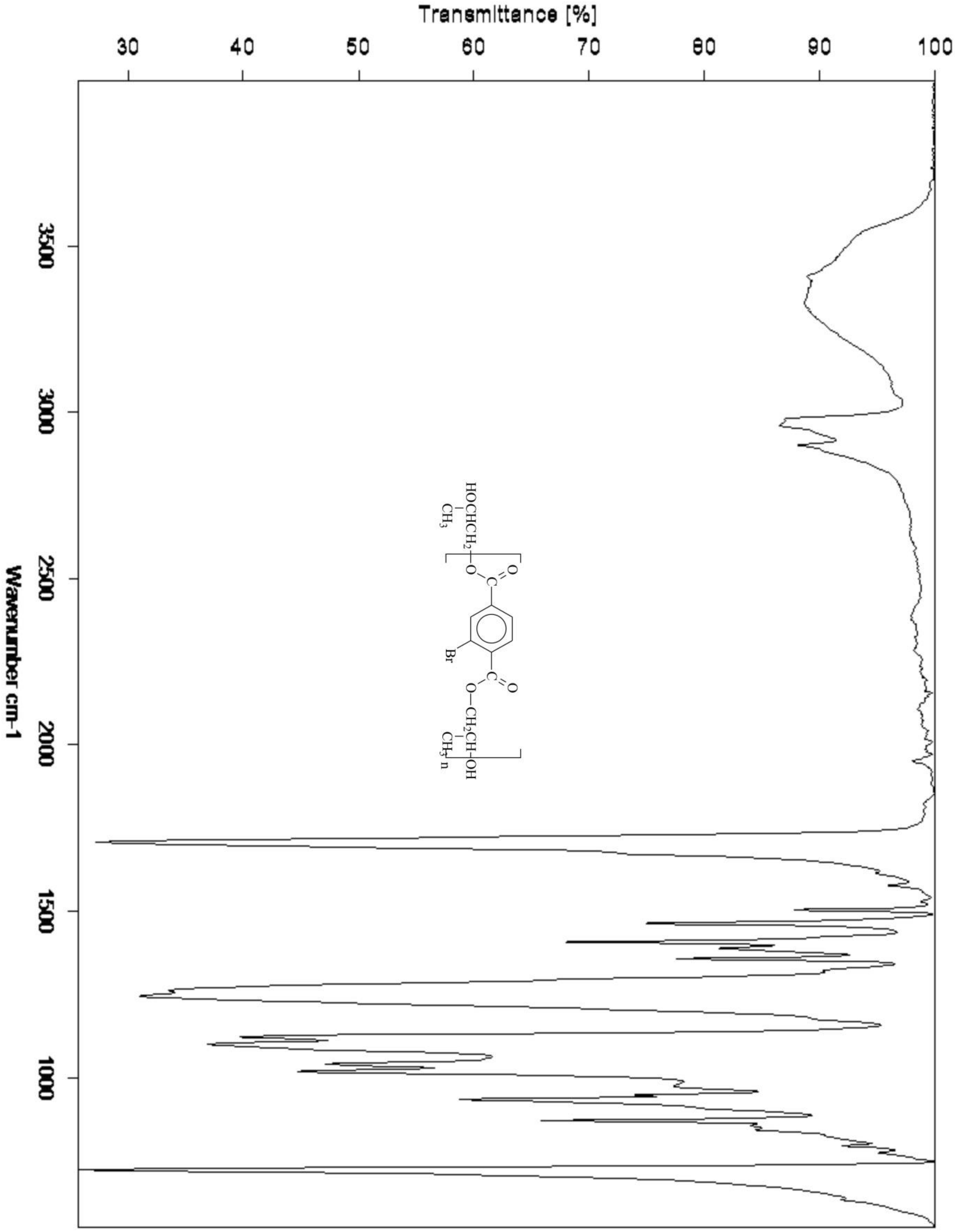


Figure C.19: IR spectrum of Figure 4.8, poly(1,2-propanediol) 2-bromoterephthalte

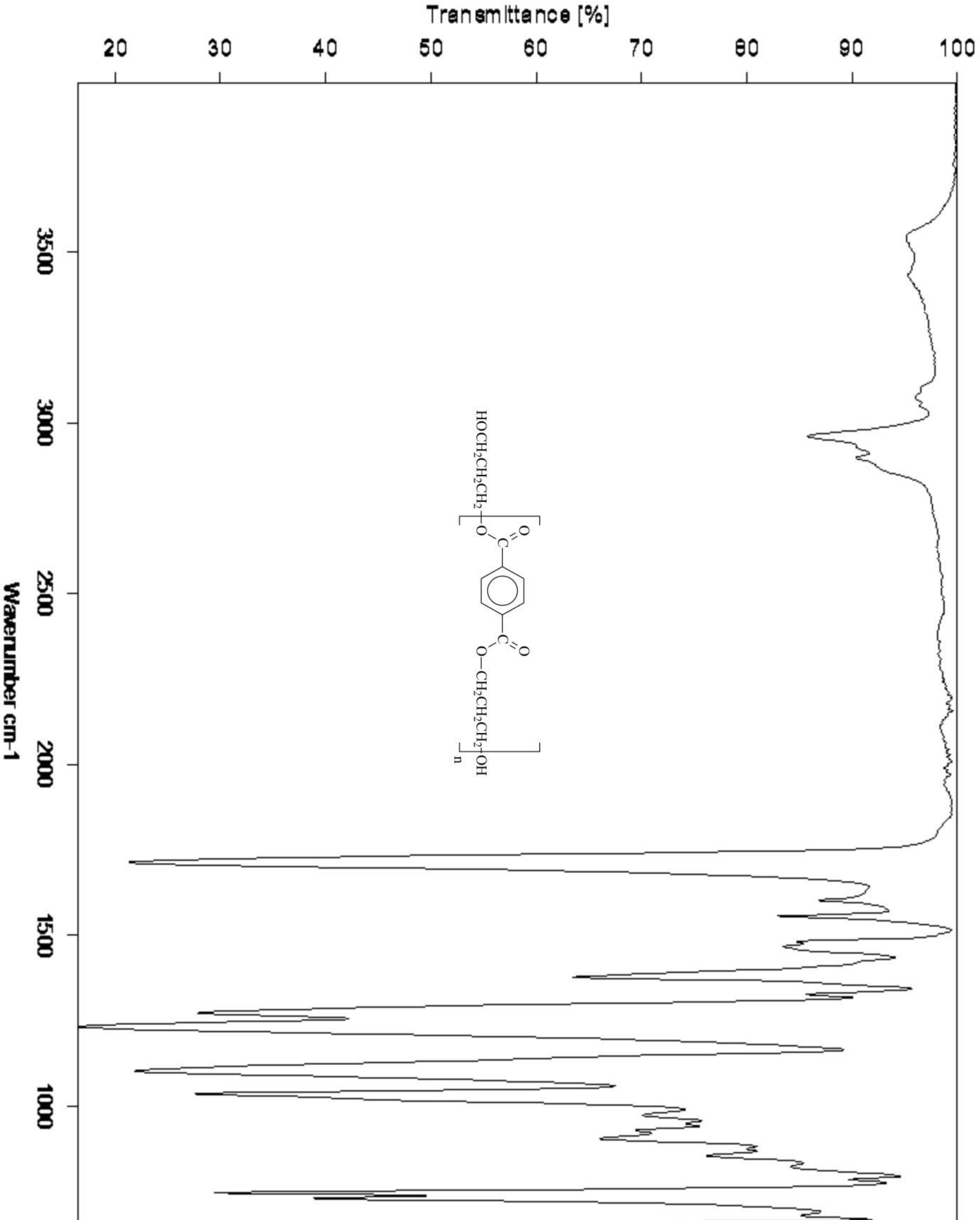


Figure C.20: IR spectrum of Figure 4.9, polypropylene terephthalate

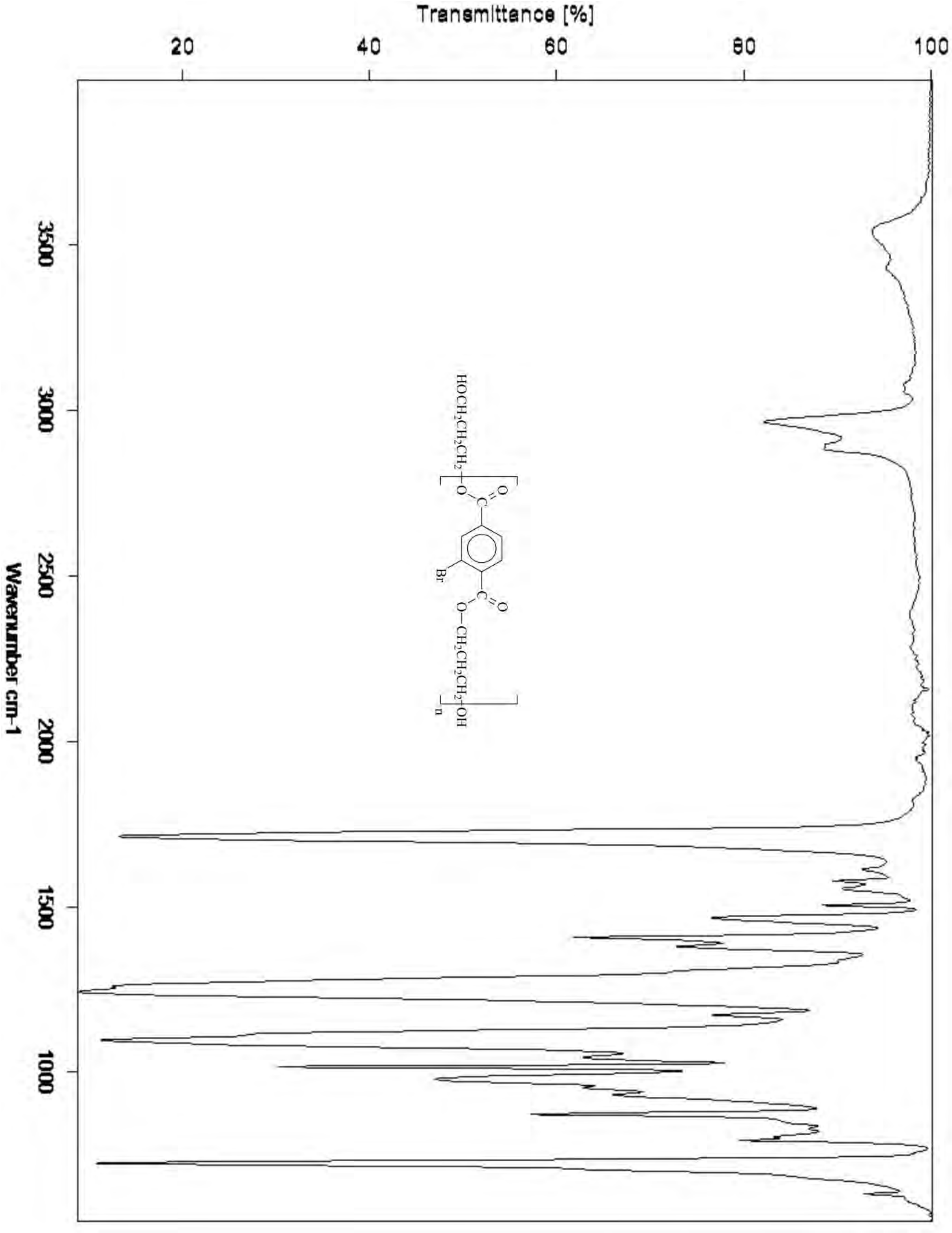


Figure C.21: IR spectrum of Figure 4.10, polypropylene 2-bromoterephthalate

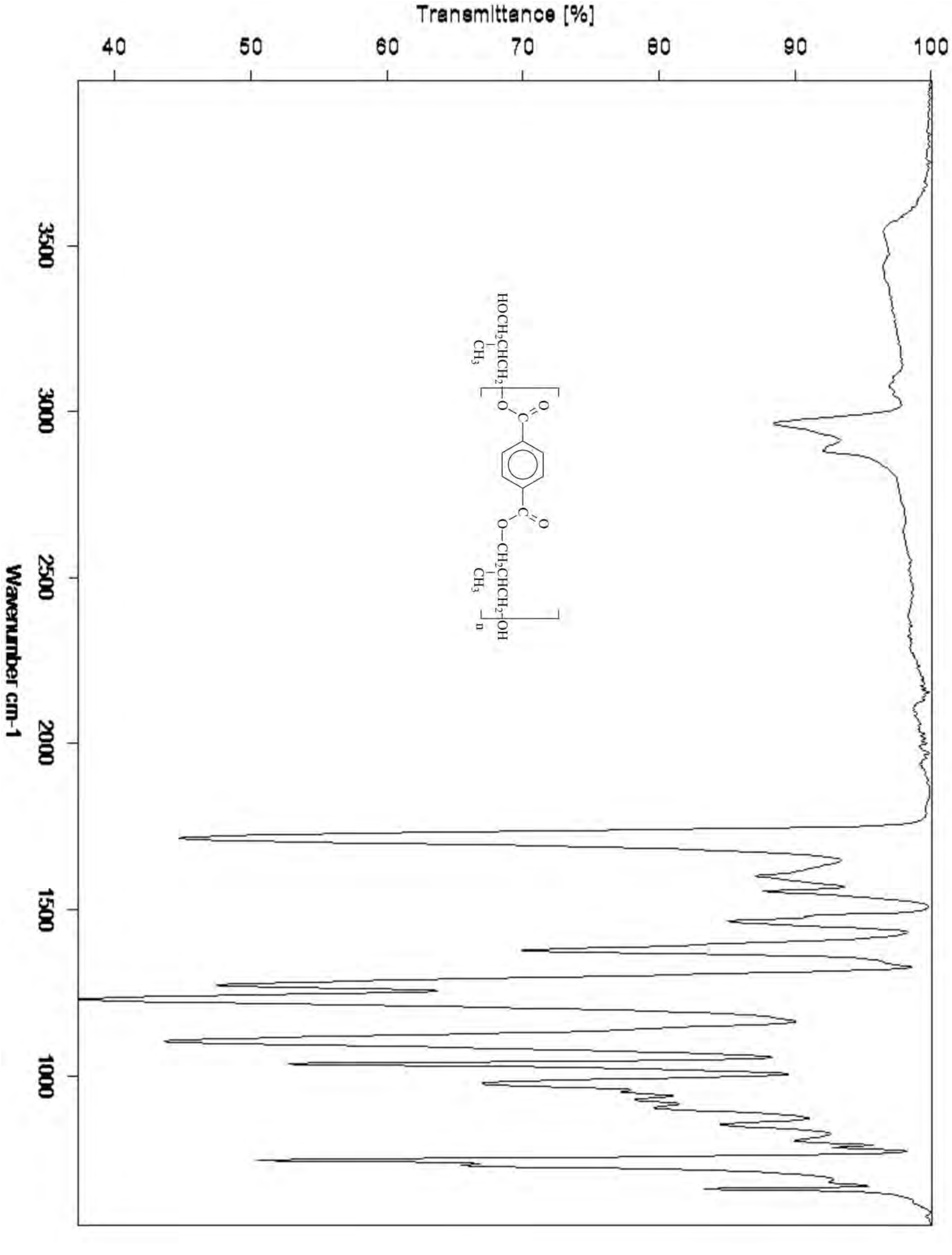


Figure C.22: IR spectrum of Figure 4.11, poly(2-methyl)propylene terephthalate

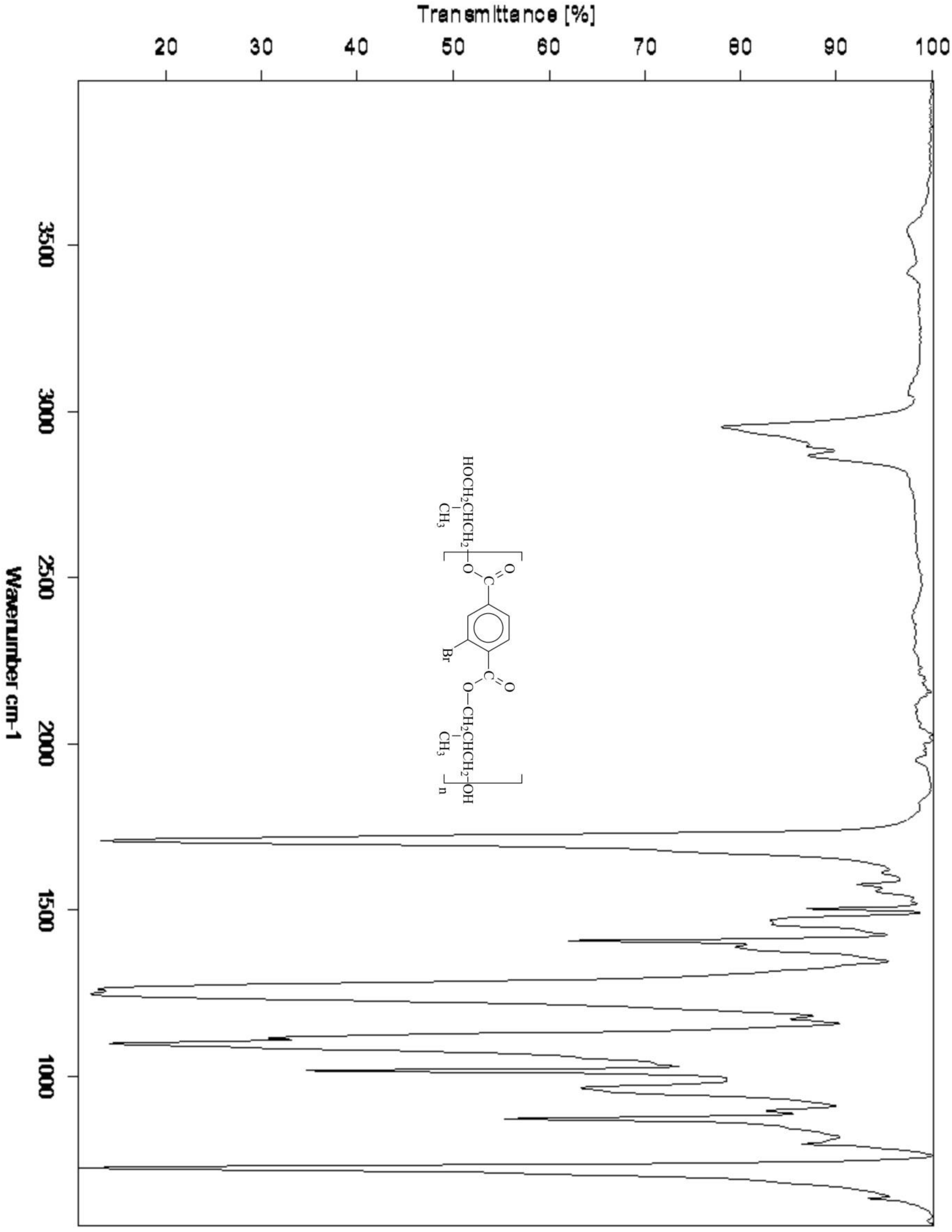


Figure C.23: IR spectrum of Figure 4.12, poly(2-methyl)propylene 2-bromoterephthalate

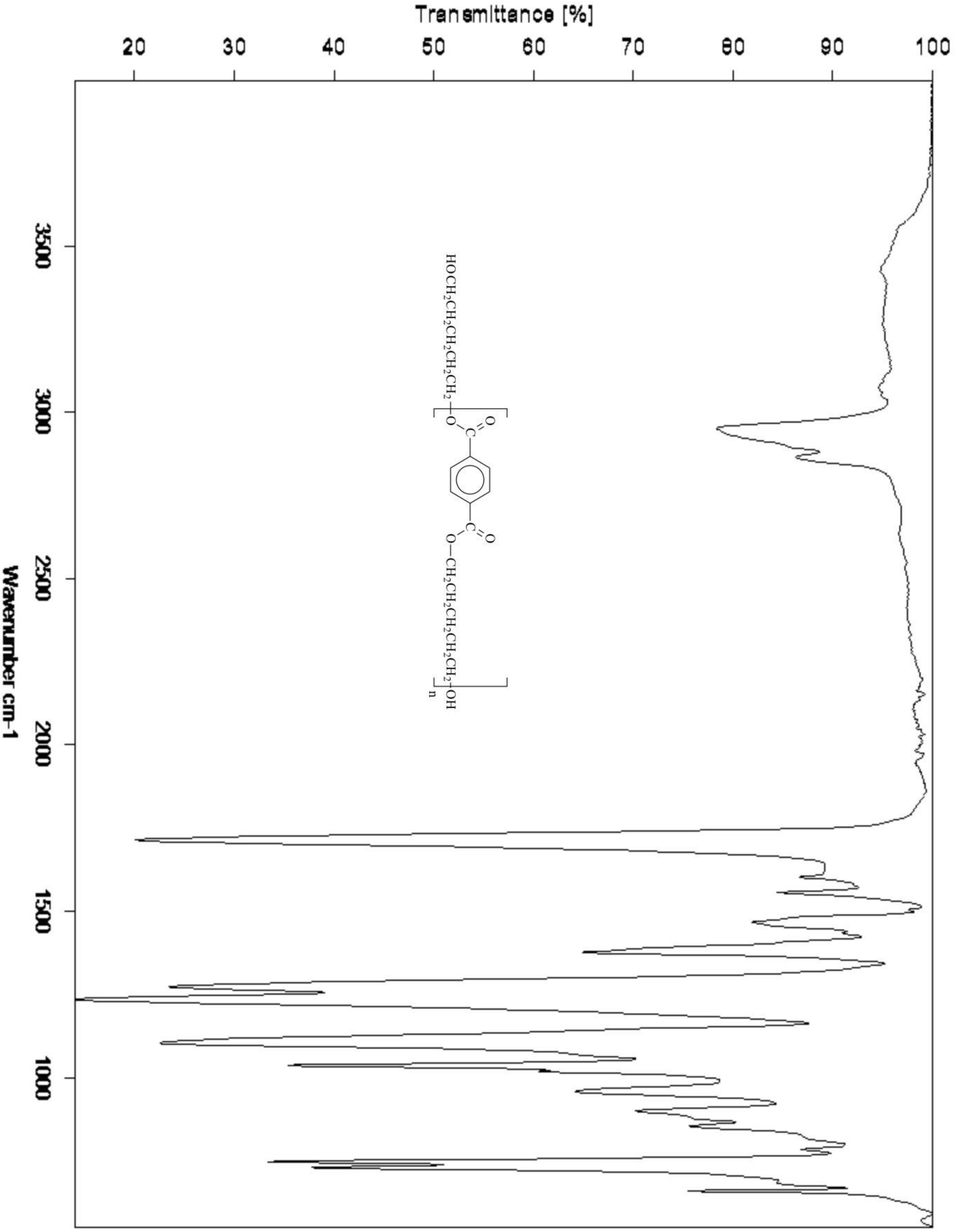


Figure C.24: IR spectrum of Figure 4.13, polypentamethylene terephthalate

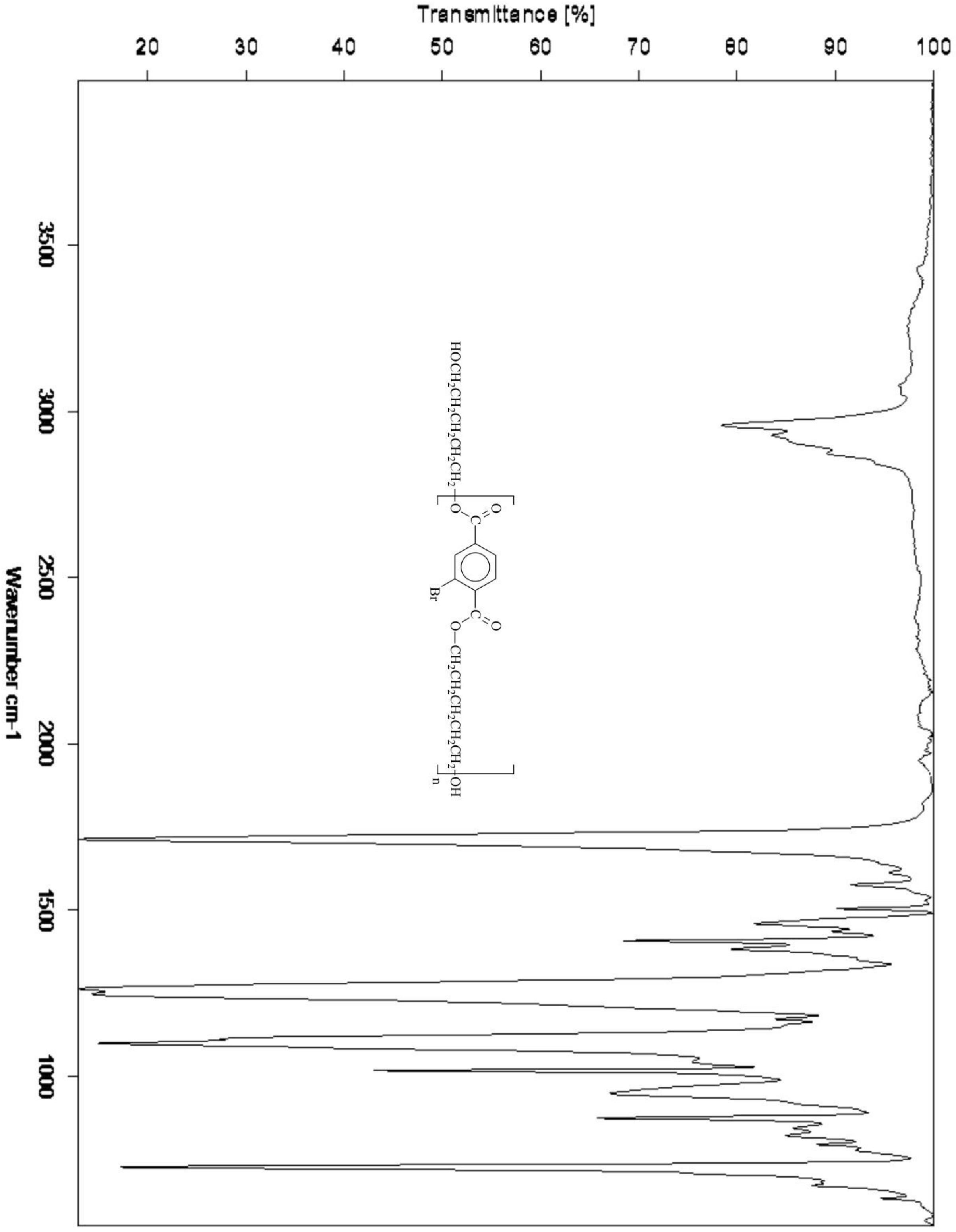


Figure C.25: IR spectrum of Figure 4.14, polypentamethylene 2-bromoterephthalate

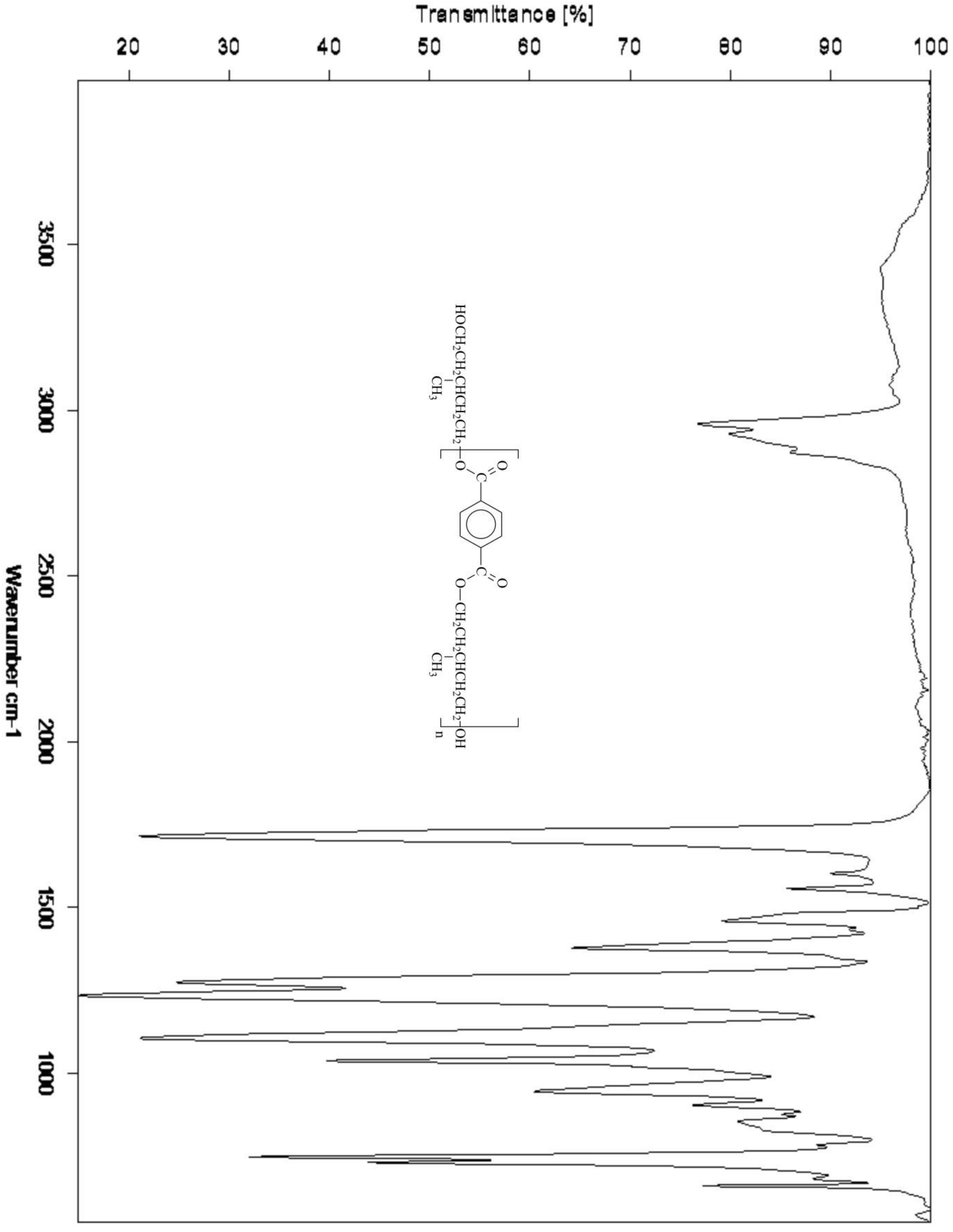


Figure C.26: IR spectrum of Figure 4.15, poly(3-methyl)pentamethylene terephthalate

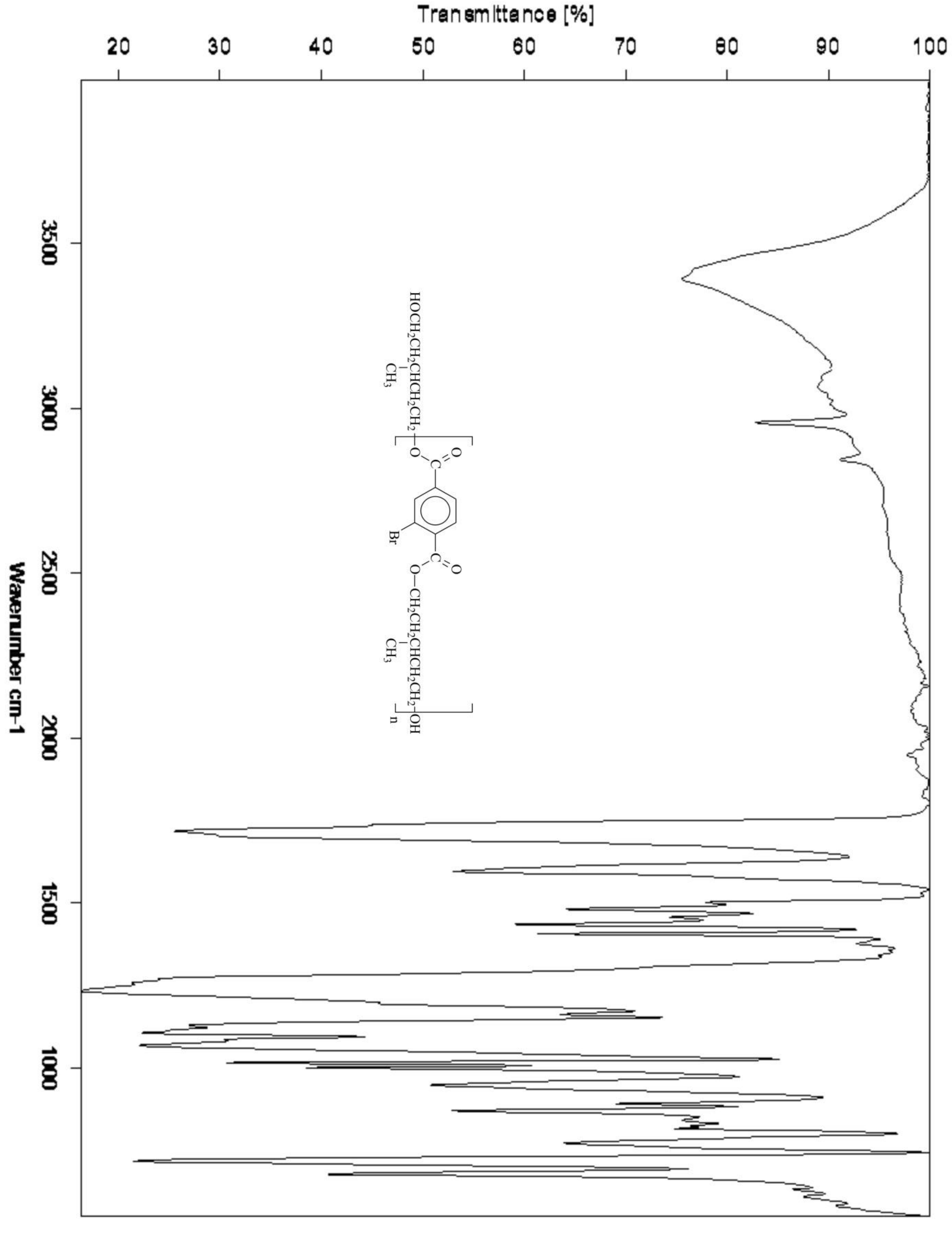
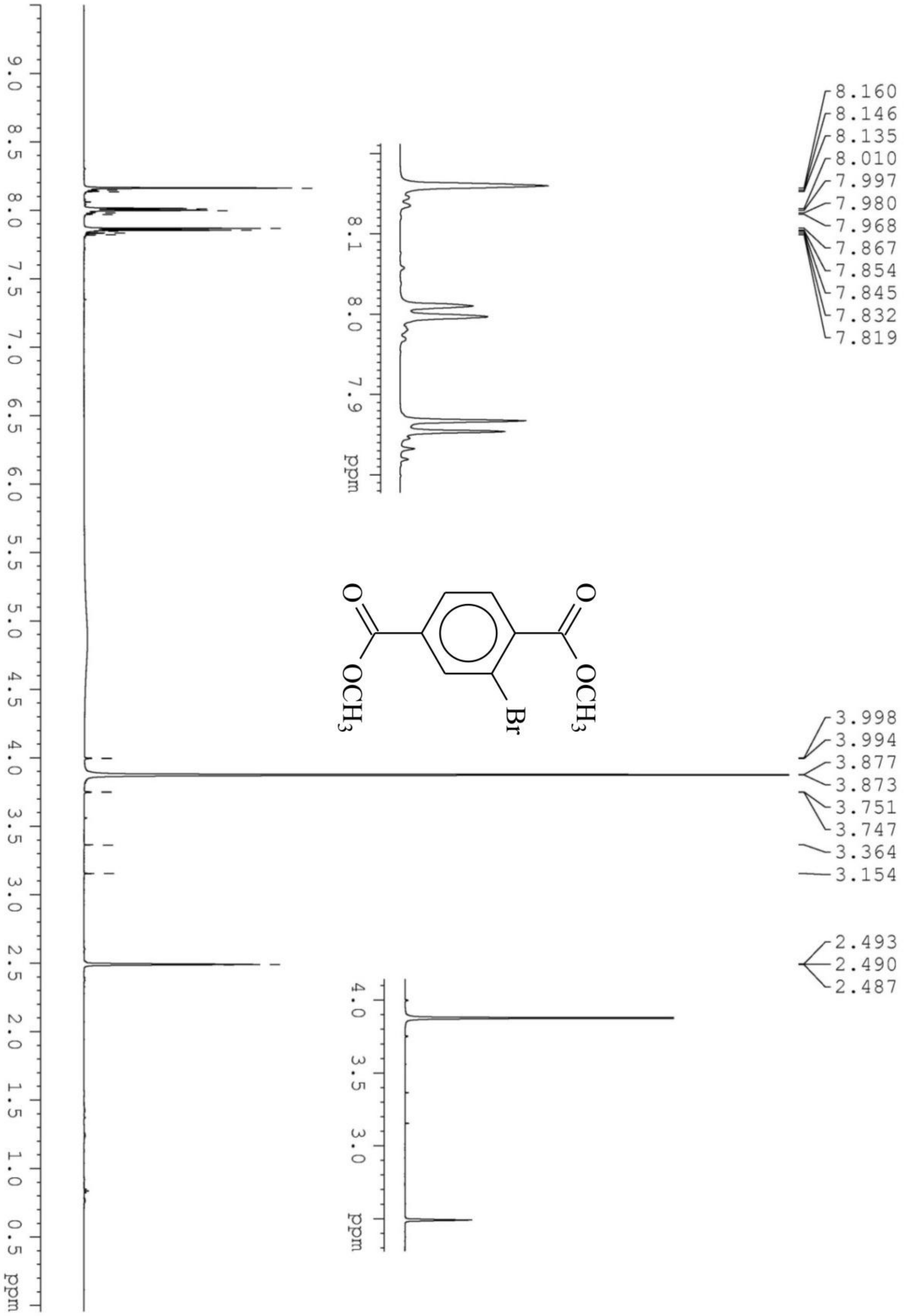


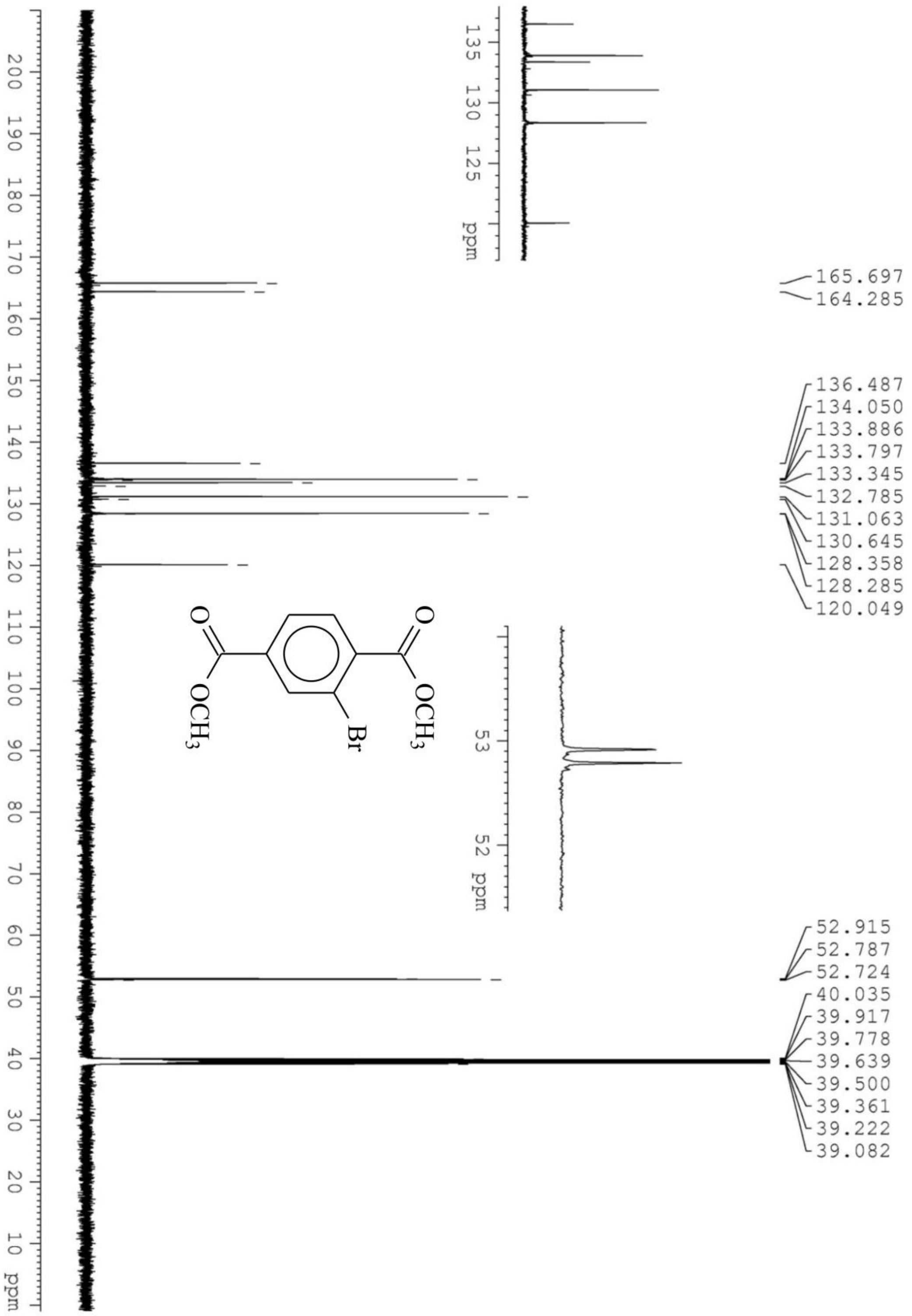
Figure C.27: IR spectrum of Figure 4.16, poly(3-methyl)pentamethylene 2-bromoterephthalate

Appendix D: NMR

(A) ^{1}HNMR, (B) ^{13}CNMR, (C) DEPT90 and (D) DEPT135

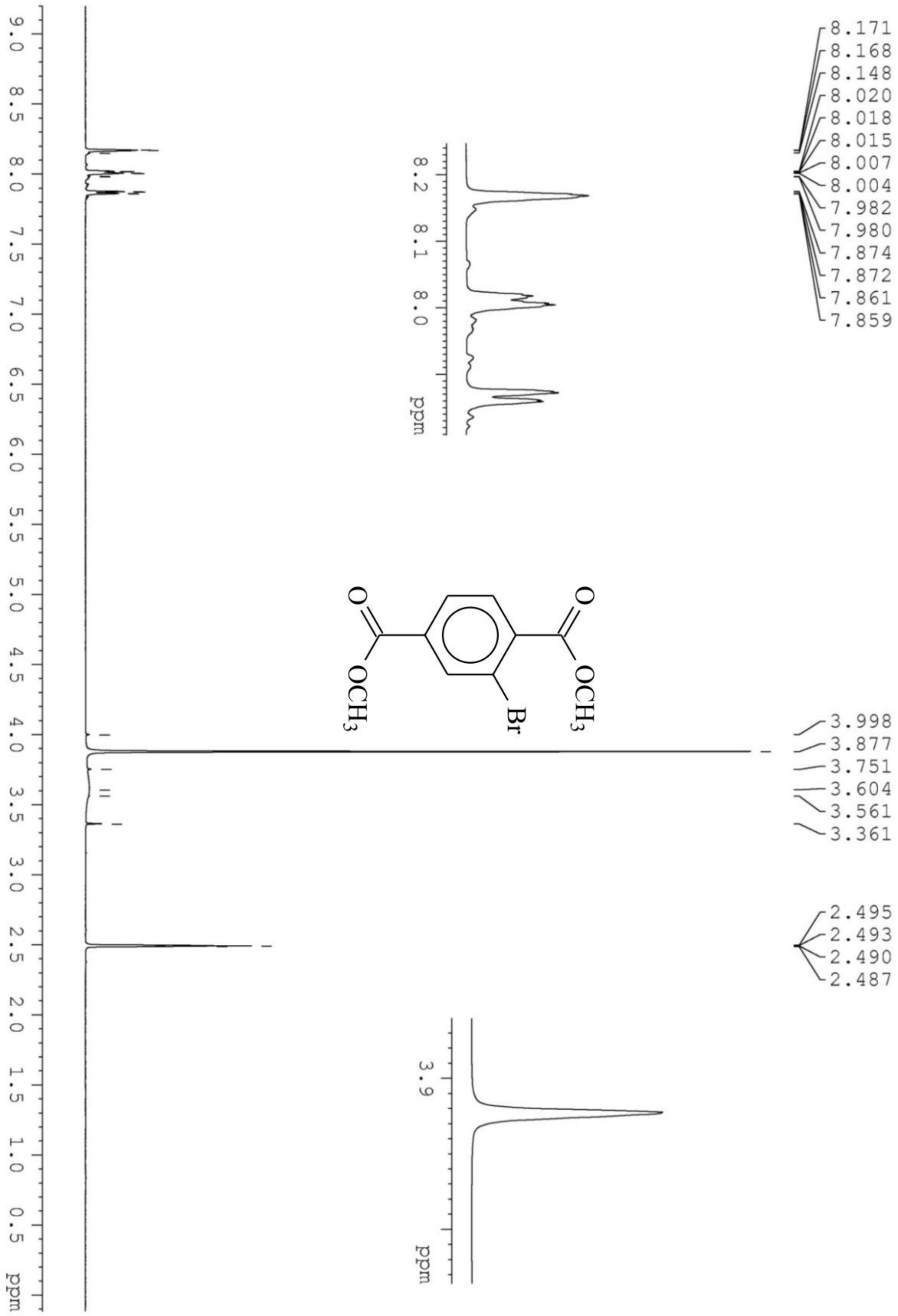

8.160
8.146
8.135
8.010
7.997
7.980
7.968
7.867
7.854
7.845
7.832
7.819
3.998
3.994
3.877
3.873
3.751
3.747
3.364
3.154
2.493
2.490
2.487
O
OCH3
O
OCH3
Br
ppm

(A) ^{1}HNMR

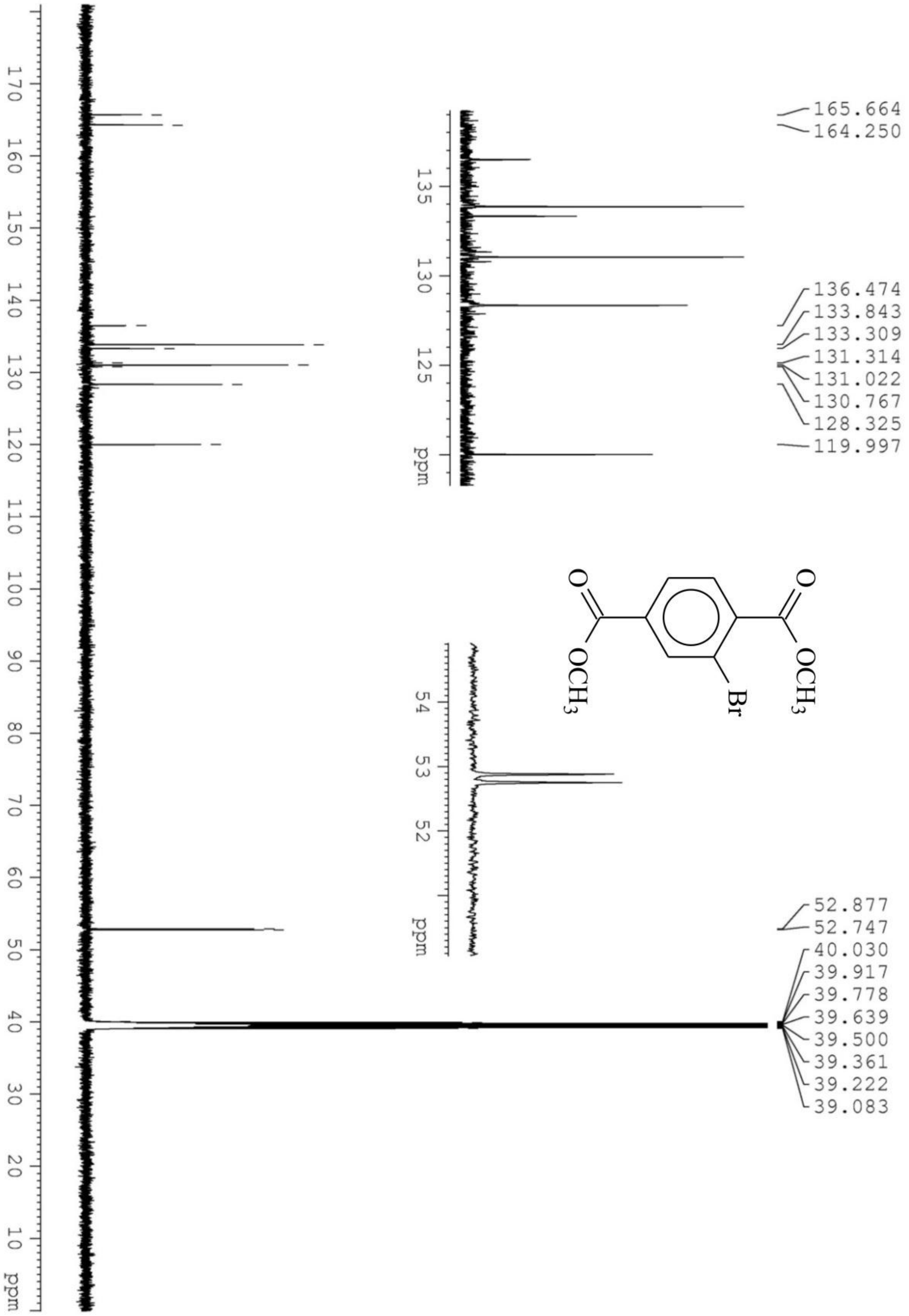


(B) ^{13}CNMR

Figure D.1: NMR spectra of reaction Scheme 4.2, 2-bromodimetyhylterephthalate

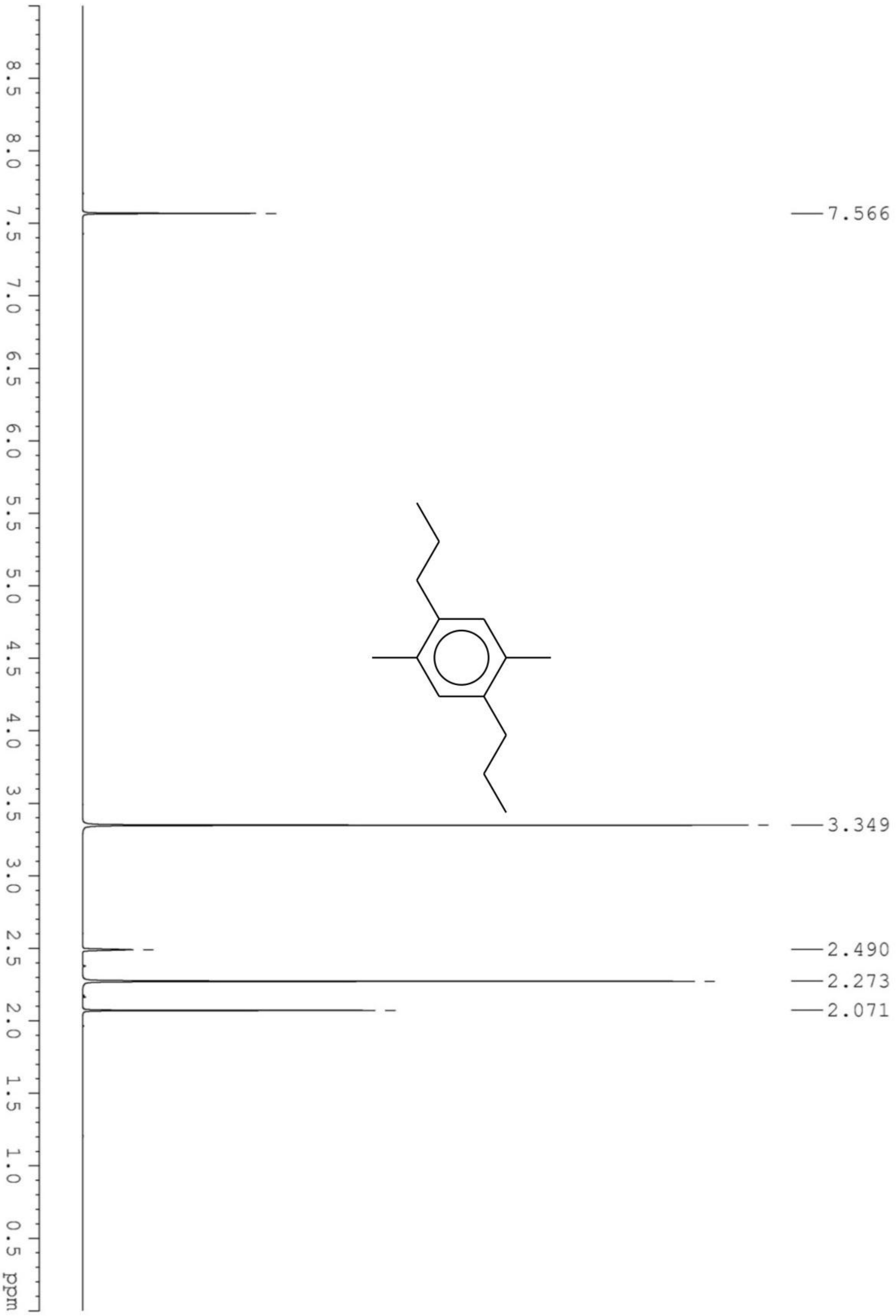

8.171
8.168
8.148
8.020
8.018
8.015
8.007
8.004
7.982
7.980
7.874
7.872
7.861
7.859
3.998
3.877
3.751
3.604
3.561
3.361
2.495
2.493
2.490
2.487
OCH3
Br
O
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
8.2
8.1
3.9

(A) ^{1}HNMR

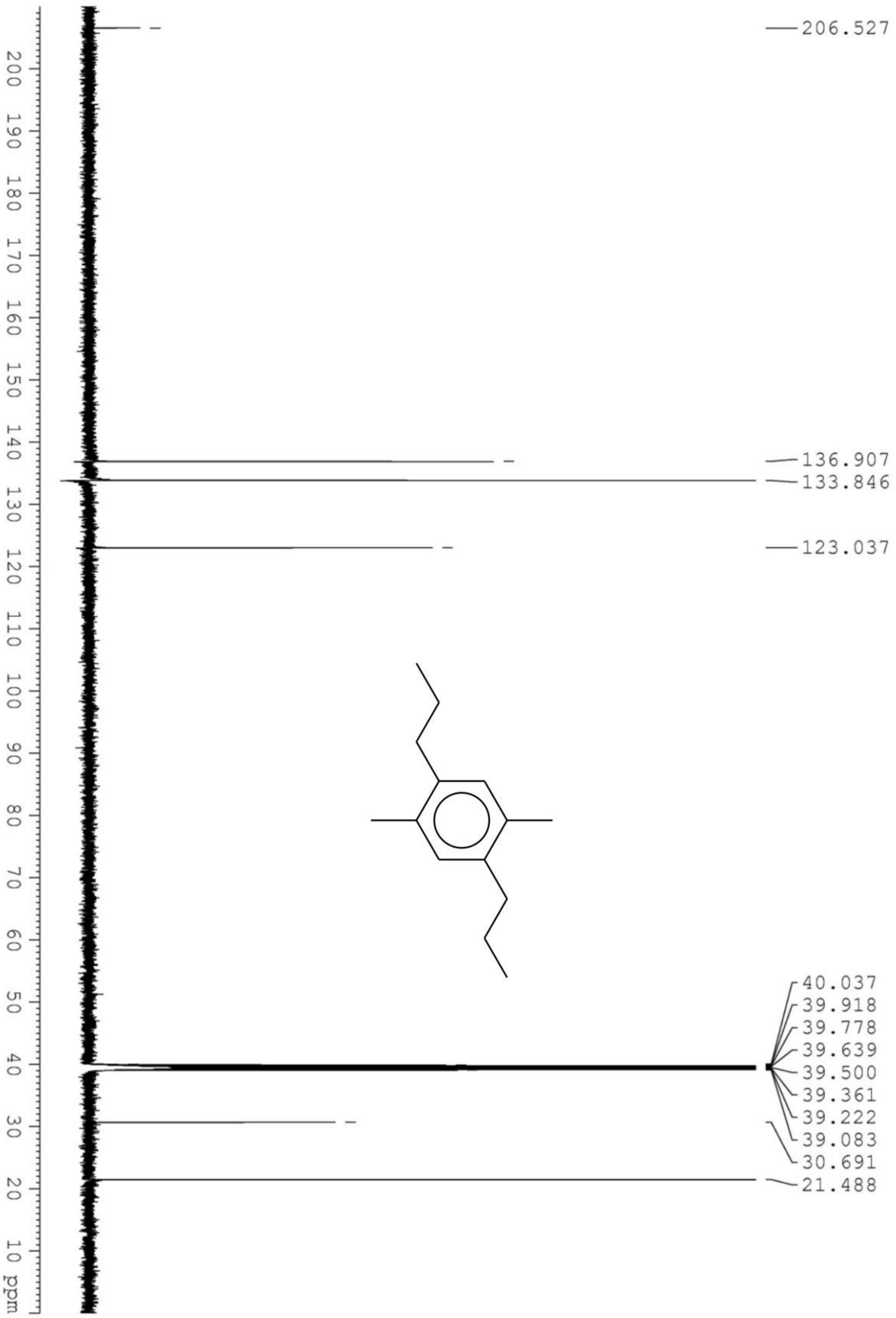


(B) ^{13}CNMR

Figure D.2: NMR spectra of reaction Scheme 4.3, 2-bromodimethylterephthalate

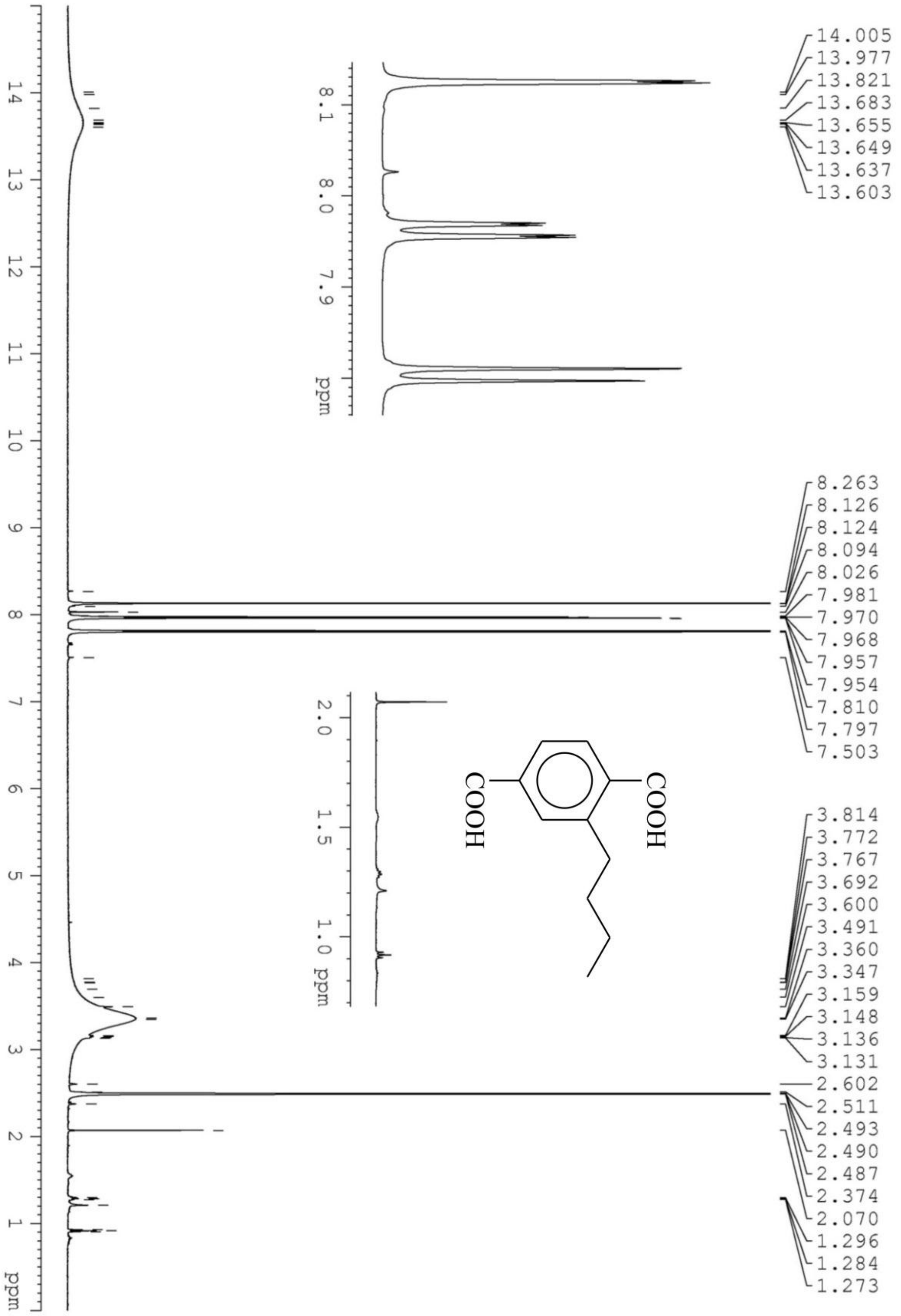

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm
7.566
3.349
2.490
2.273
2.071

(A) ^{1}HNMR

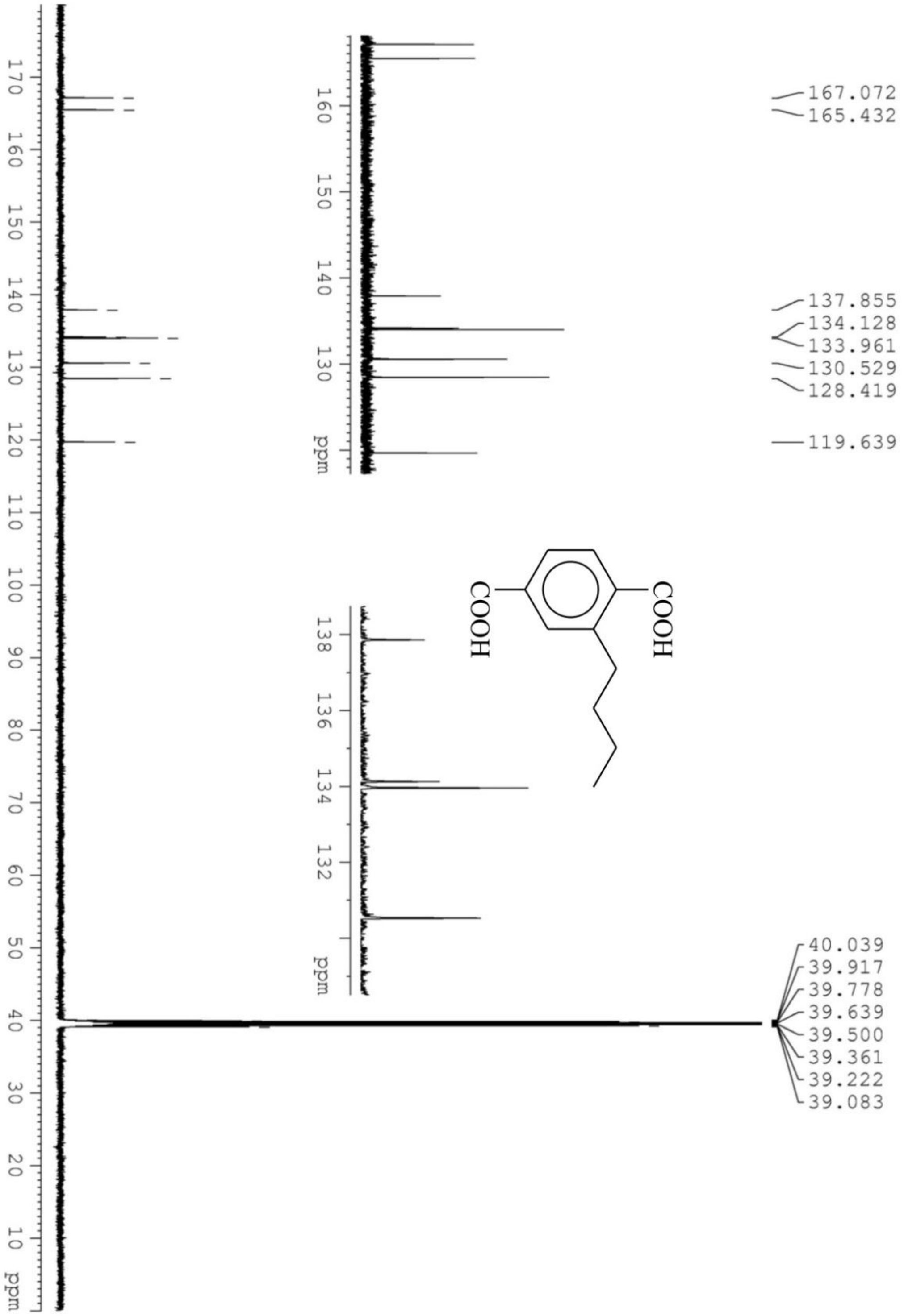


(B) ^{13}CNMR

Figure D.3: NMR spectra of reaction Scheme 4.6, alkylation product of 2,5-dibrom*para*xylene (no reaction)

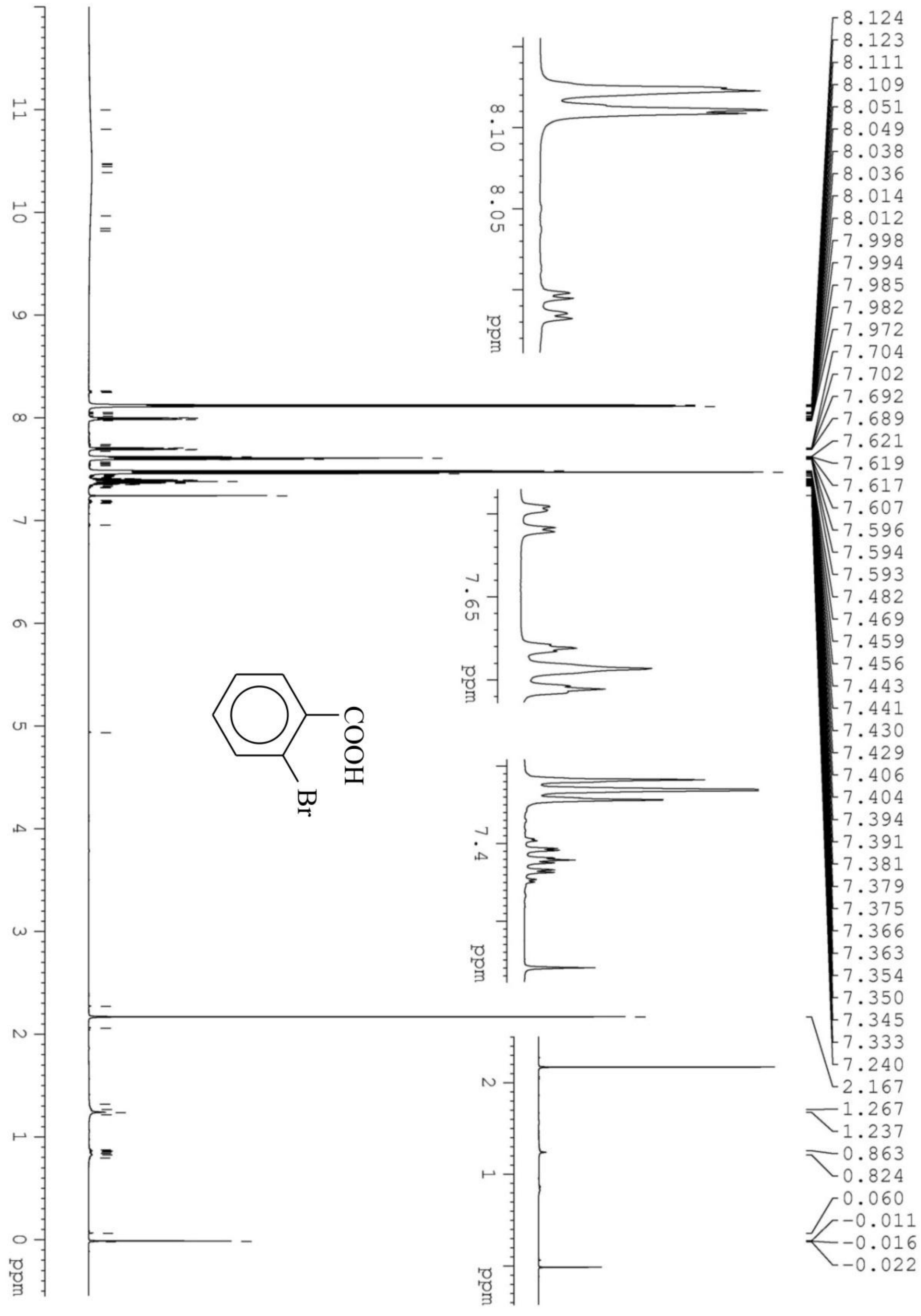

14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
8.1
8.0
7.9
ppm
2.0
1.5
1.0 ppm
COOH
COOH
14.005
13.977
13.821
13.683
13.655
13.649
13.637
13.603
8.263
8.126
8.124
8.094
8.026
7.981
7.970
7.968
7.957
7.954
7.810
7.797
7.503
3.814
3.772
3.767
3.692
3.600
3.491
3.360
3.347
3.159
3.148
3.136
3.131
2.602
2.511
2.493
2.490
2.487
2.374
2.070
1.296
1.284
1.273

(A) ^{1}HNMR

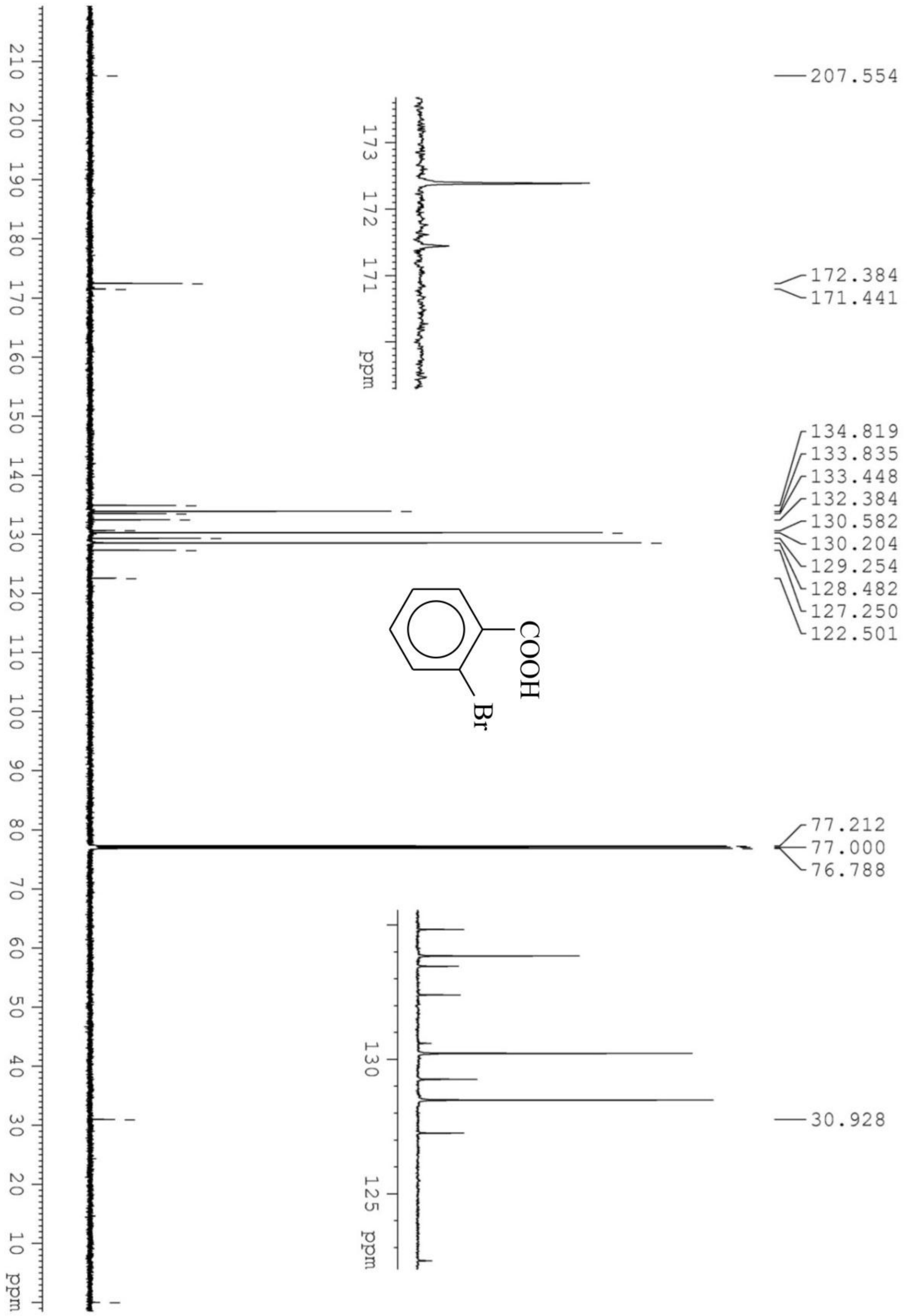


(B) ^{13}CNMR

Figure D.4: NMR spectra of reaction Scheme 4.7, alkylation product of 2-bromoterephthalic acid (no reaction)

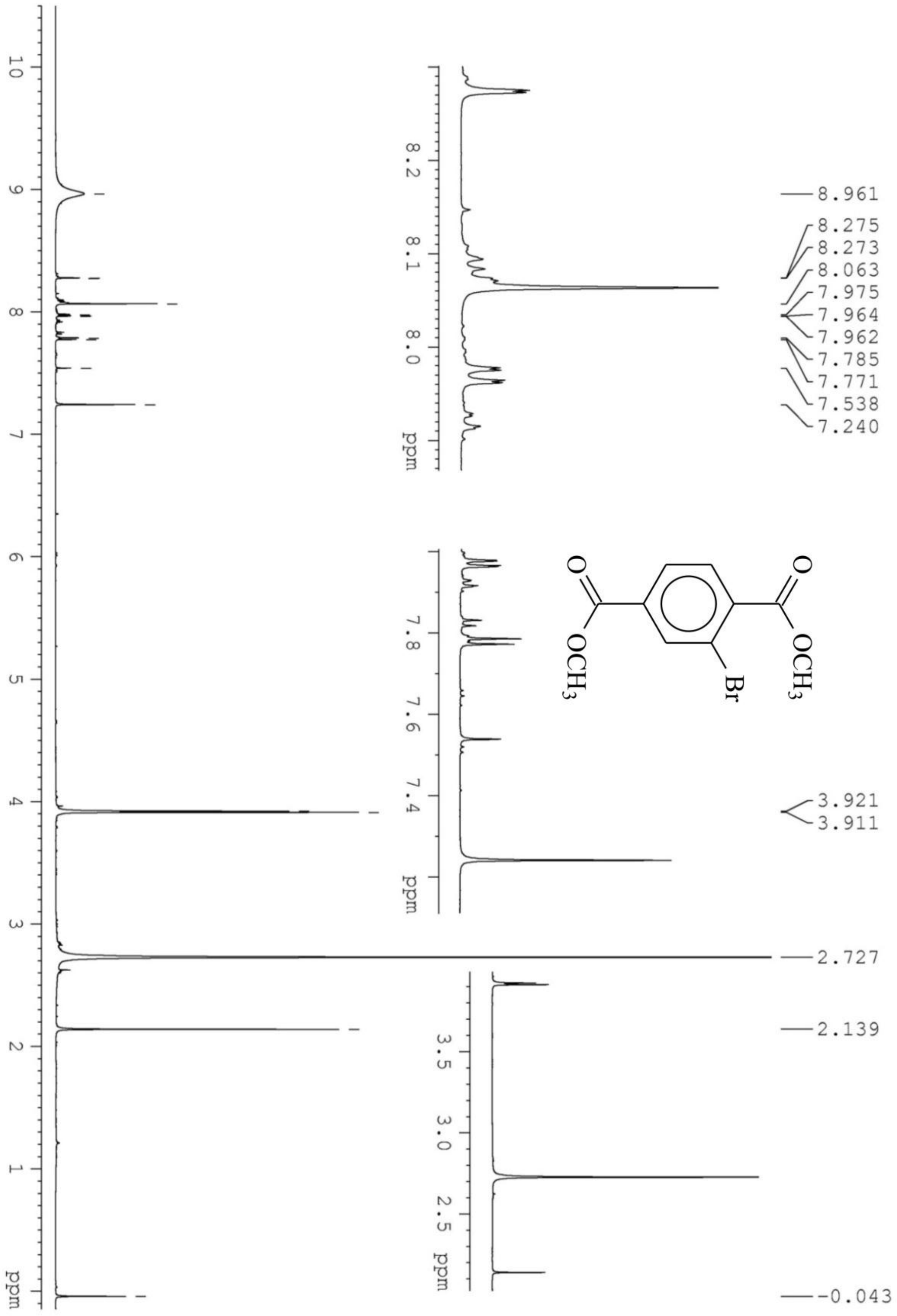

COOH
Br
11
10
9
8
7
6
5
4
3
2
1
0 ppm
8.10
8.05
ppm
7.65
ppm
7.4
ppm
2
1
ppm
8.124
8.123
8.111
8.109
8.051
8.049
8.038
8.036
8.014
8.012
7.998
7.994
7.985
7.982
7.972
7.704
7.702
7.692
7.689
7.621
7.619
7.617
7.607
7.596
7.594
7.593
7.482
7.469
7.459
7.456
7.443
7.441
7.430
7.429
7.406
7.404
7.394
7.391
7.381
7.379
7.375
7.366
7.363
7.354
7.350
7.345
7.333
7.240
2.167
1.267
1.237
0.863
0.824
0.060
−0.011
−0.016
−0.022

(A) ^{1}HNMR

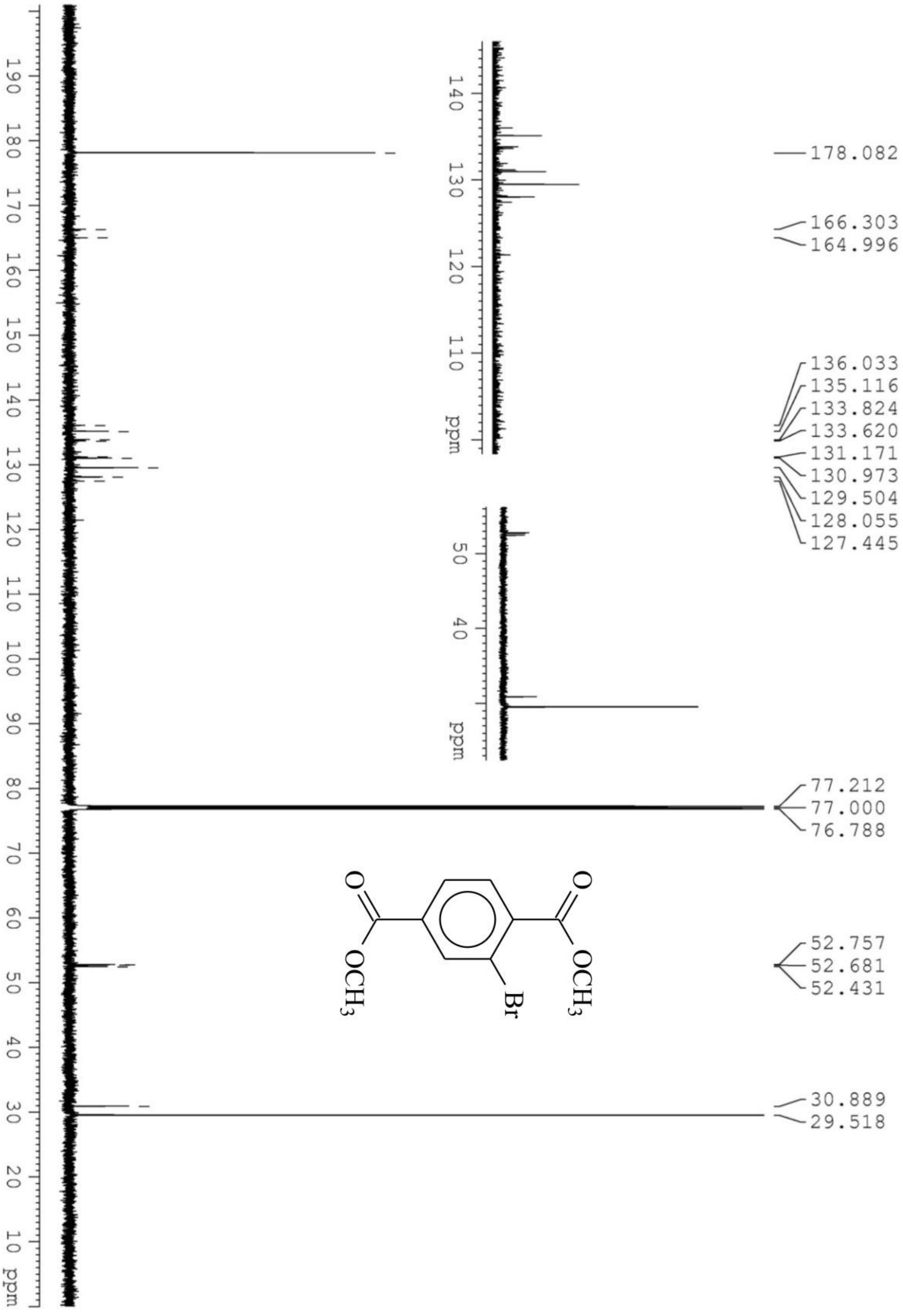


(B) ^{13}CNMR

Figure D.5: NMR spectra of reaction Scheme 4.8, 2-bromobenzoic acid (and 4-Bromobenzoic acid)

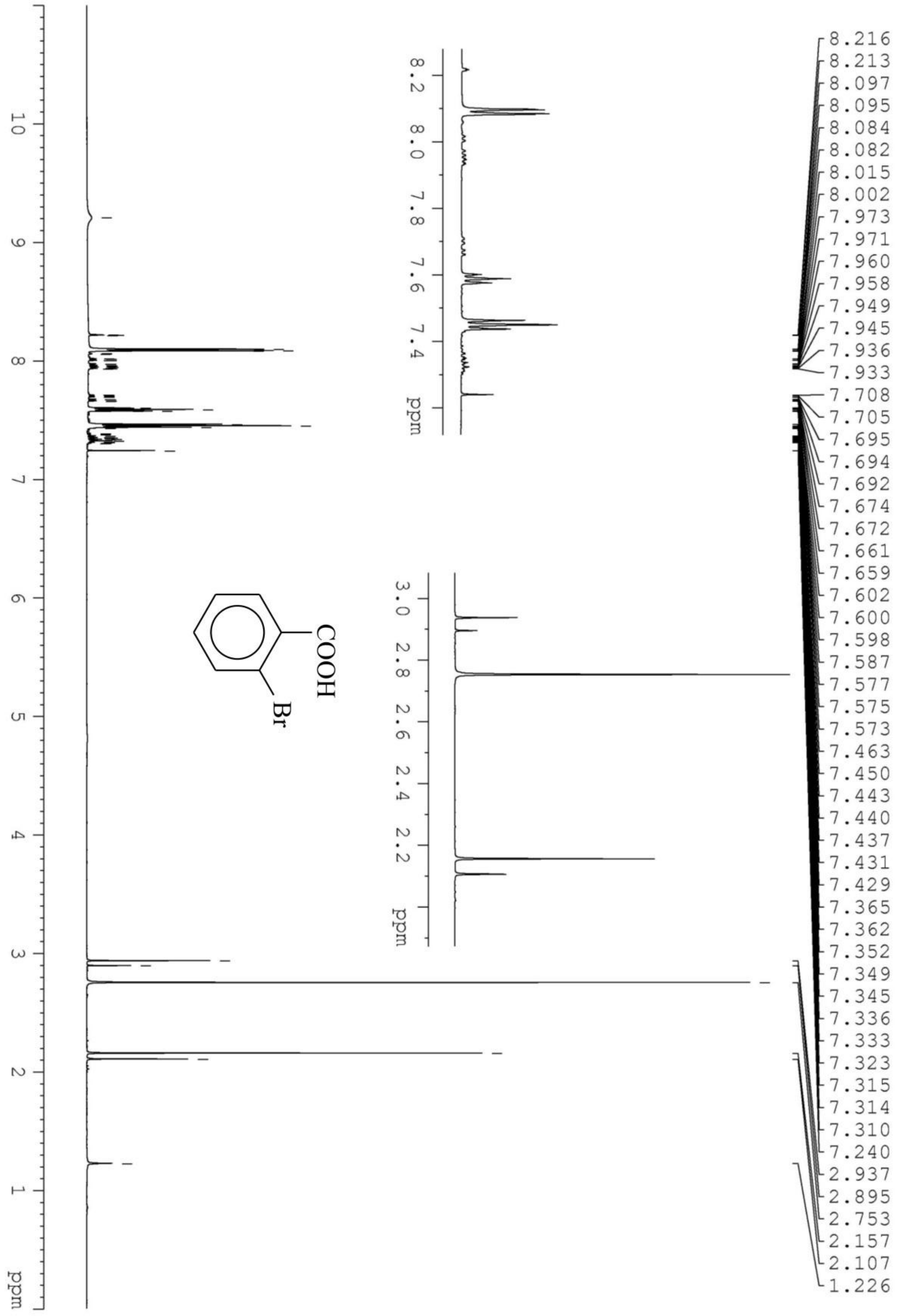

8.961
8.275
8.273
8.063
7.975
7.964
7.962
7.785
7.771
7.538
7.240
3.921
3.911
2.727
2.139
-0.043
O
OCH3
Br
O
OCH3
ppm
10
9
8
7
6
5
4
3
2
1
8.2
8.1
8.0
7.8
7.6
7.4
3.5
3.0
2.5

(A) ^{1}HNMR

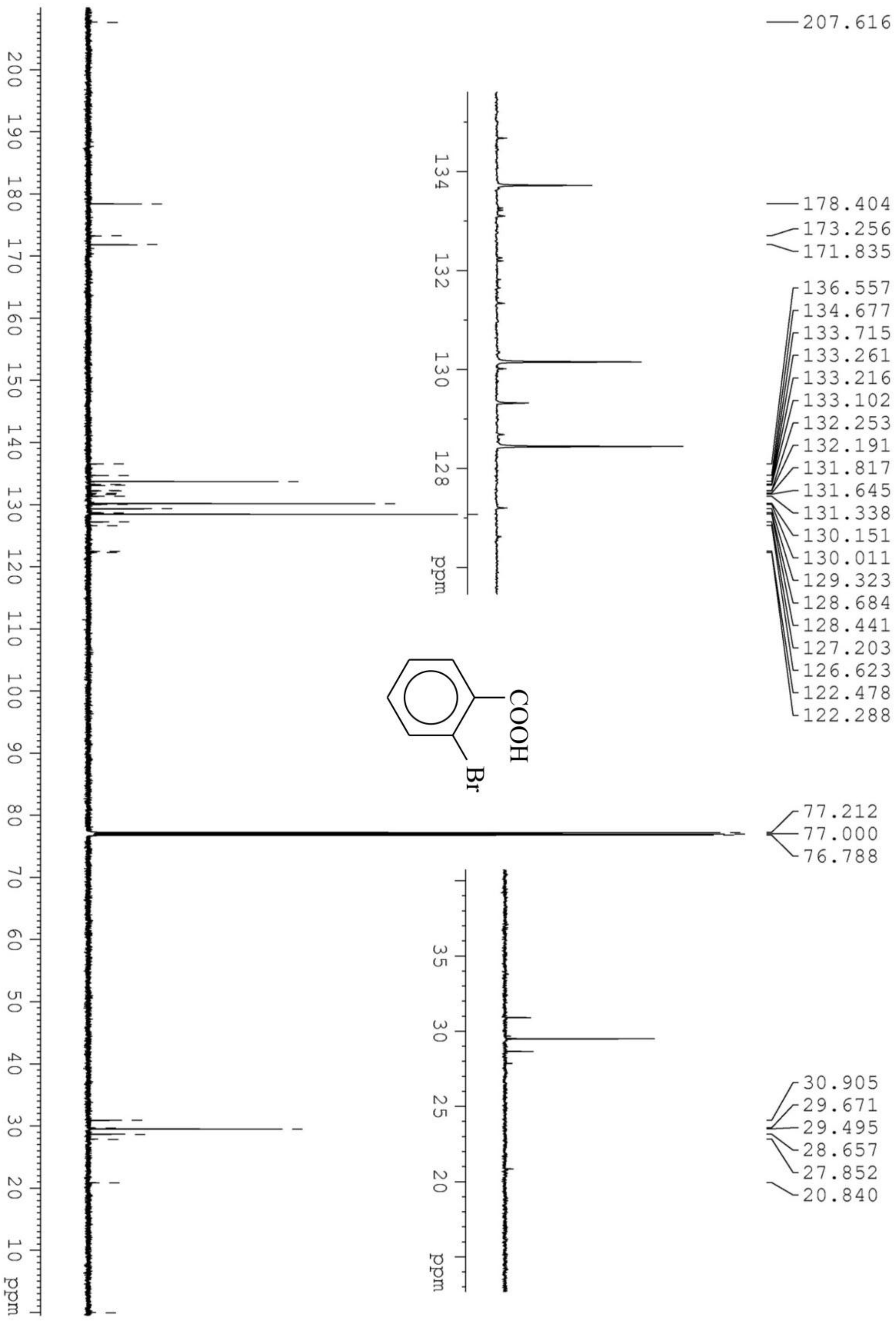


(B) ^{13}CNMR

Figure D.6: NMR spectra of reaction Scheme 4.9, bromination of DMT (no reaction)

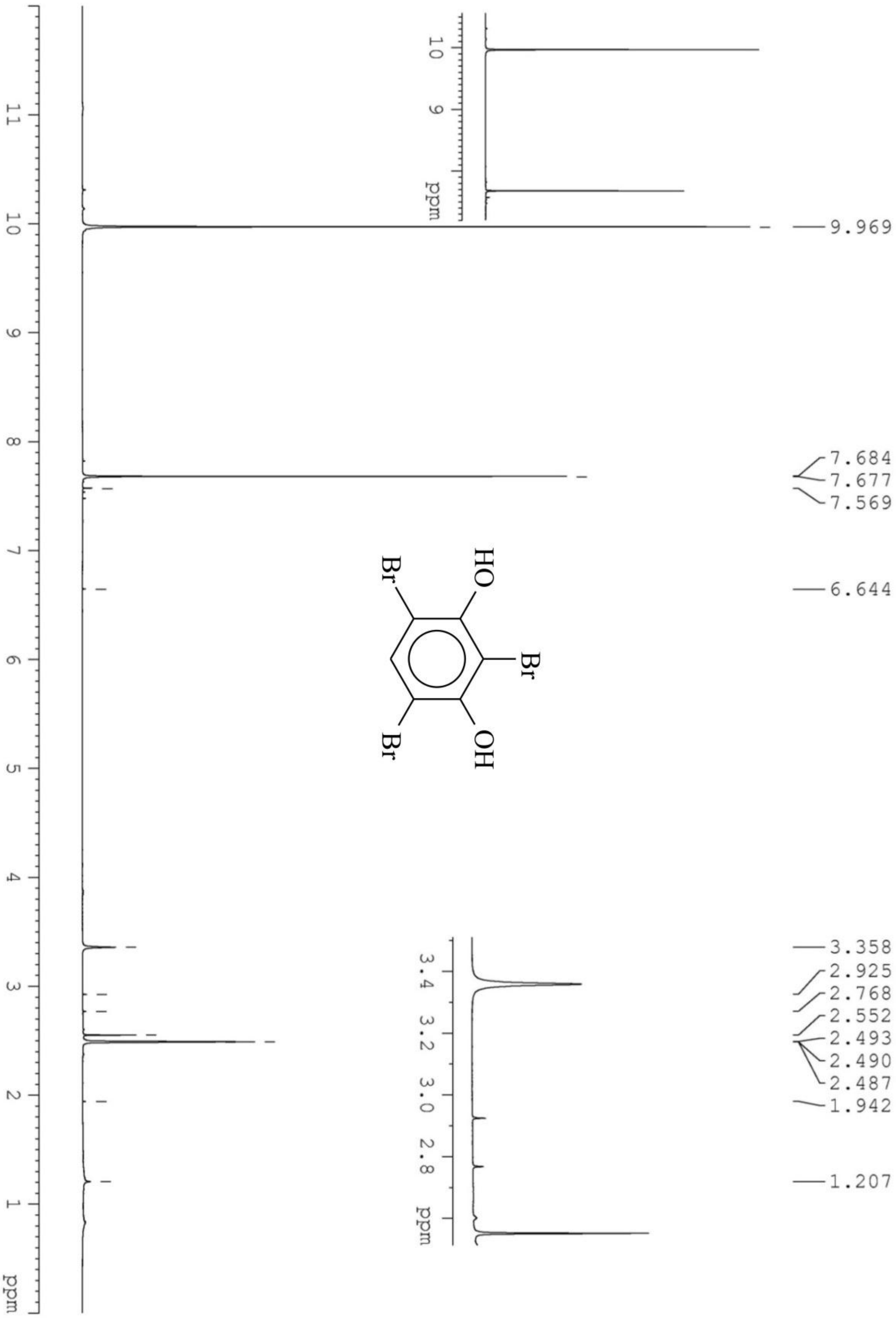

COOH
Br
8.216
8.213
8.097
8.095
8.084
8.082
8.015
8.002
7.973
7.971
7.960
7.958
7.949
7.945
7.936
7.933
7.708
7.705
7.695
7.694
7.692
7.674
7.672
7.661
7.659
7.602
7.600
7.598
7.587
7.577
7.575
7.573
7.463
7.450
7.443
7.440
7.437
7.431
7.429
7.365
7.362
7.352
7.349
7.345
7.336
7.333
7.323
7.315
7.314
7.310
7.240
2.937
2.895
2.753
2.157
2.107
1.226
8.2
8.0
7.8
7.6
7.4
ppm
3.0
2.8
2.6
2.4
2.2
ppm
10
9
8
7
6
5
4
3
2
1
ppm

(A) ^{1}HNMR

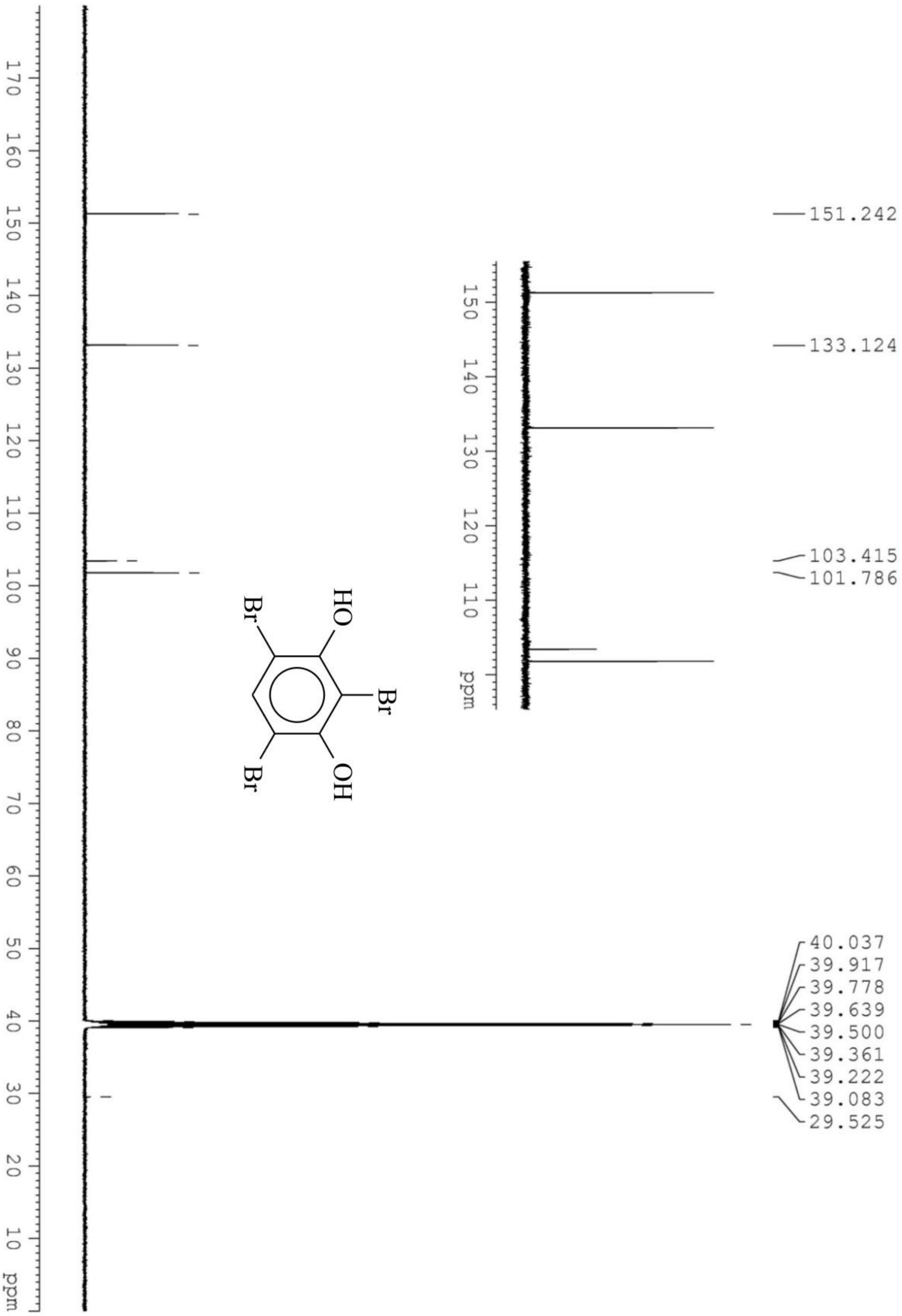


(B) ^{13}CNMR

Figure D.7: NMR spectra of reaction Scheme 4.10, 2-bromobenzoic acid

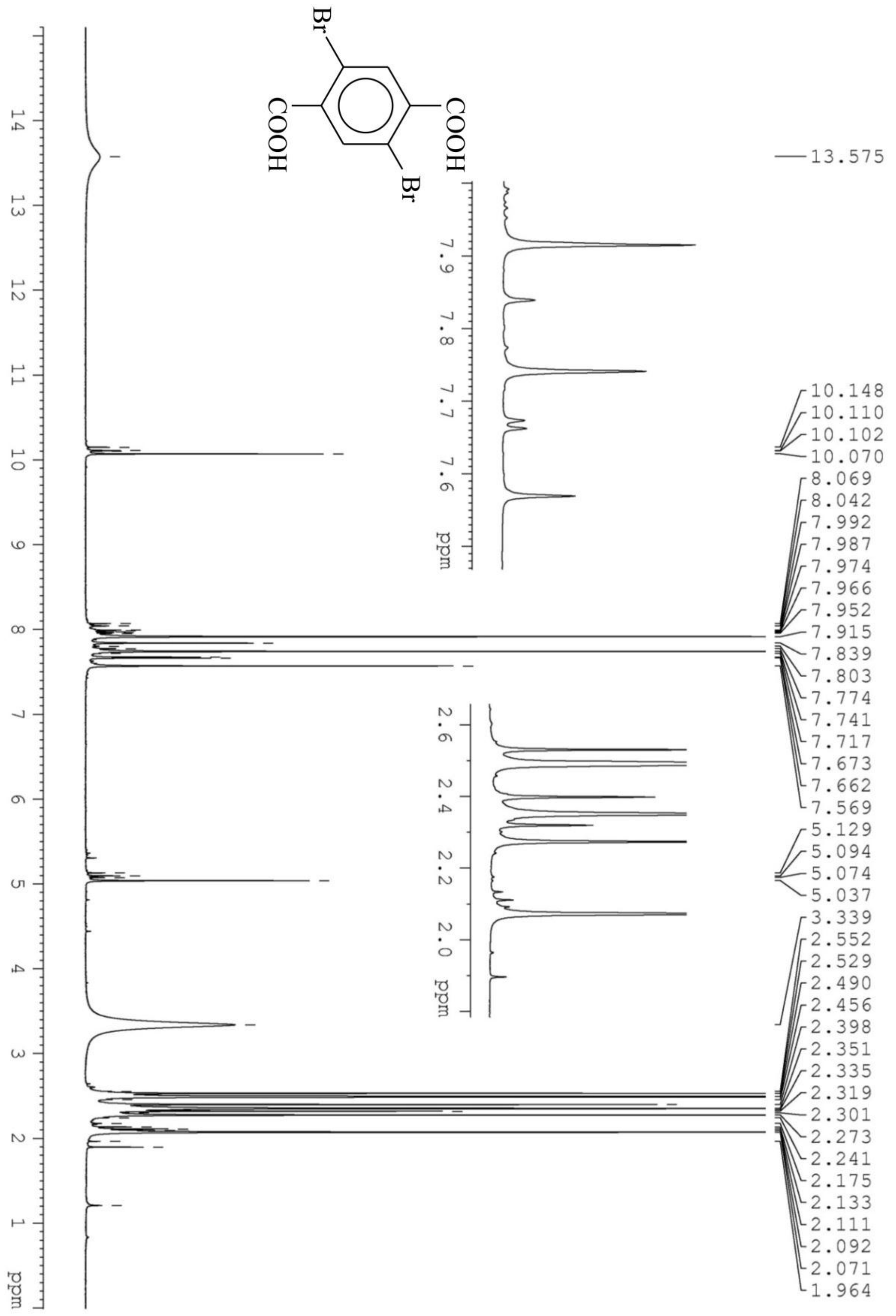

9.969
7.684
7.677
7.569
6.644
3.358
2.925
2.768
2.552
2.493
2.490
2.487
1.942
1.207
ppm
11
10
9
8
7
6
5
4
3
2
1
10
9
ppm
3.4
3.2
3.0
2.8
ppm
HO
Br
Br
Br
OH

(A) ^{1}HNMR



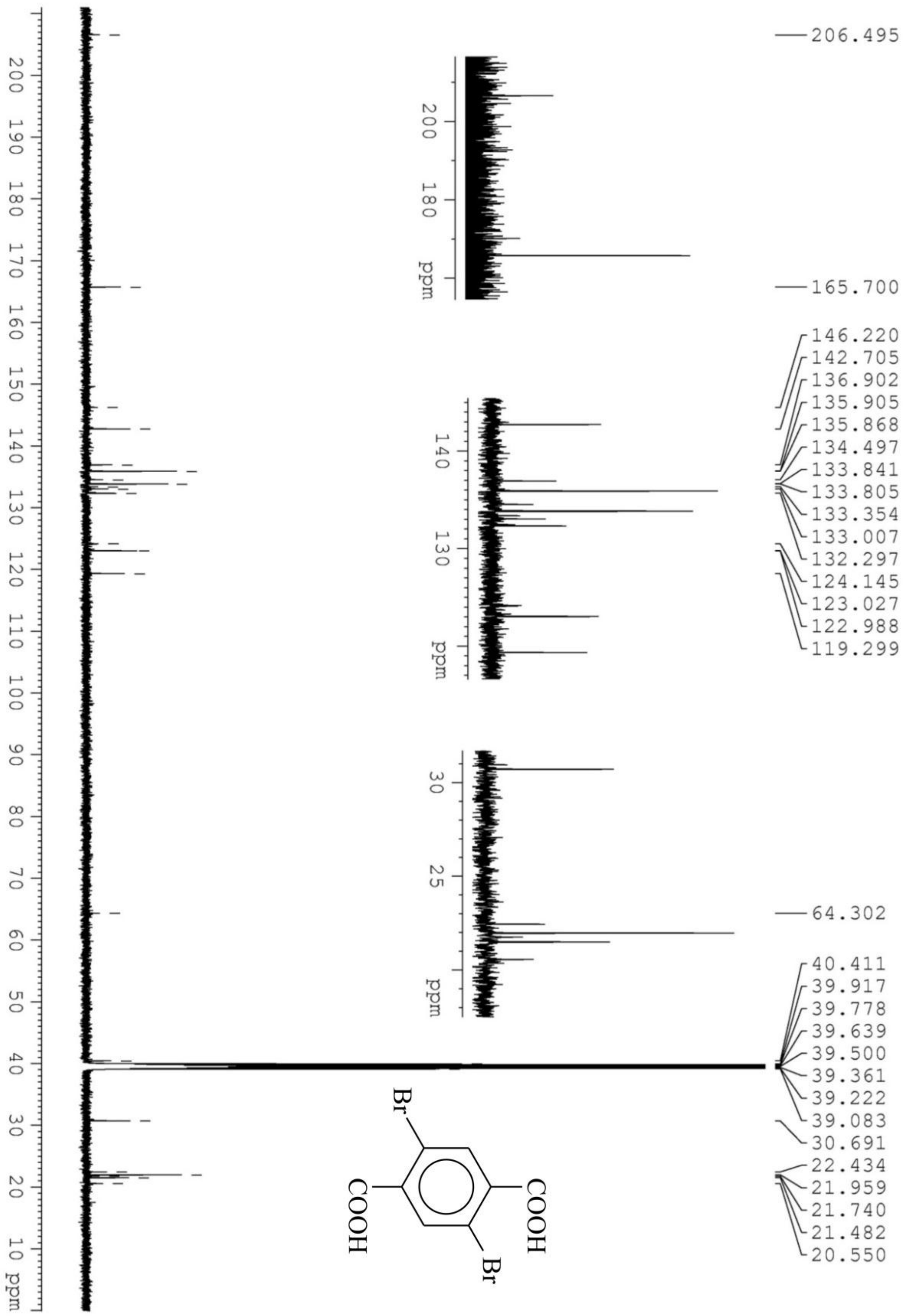
(B) ^{13}CNMR

Figure D.8: NMR spectra of reaction Scheme 4.11, 2,4,6-tribromo-1,3-benzenediol (2,4,6-tribromoresorcinol)



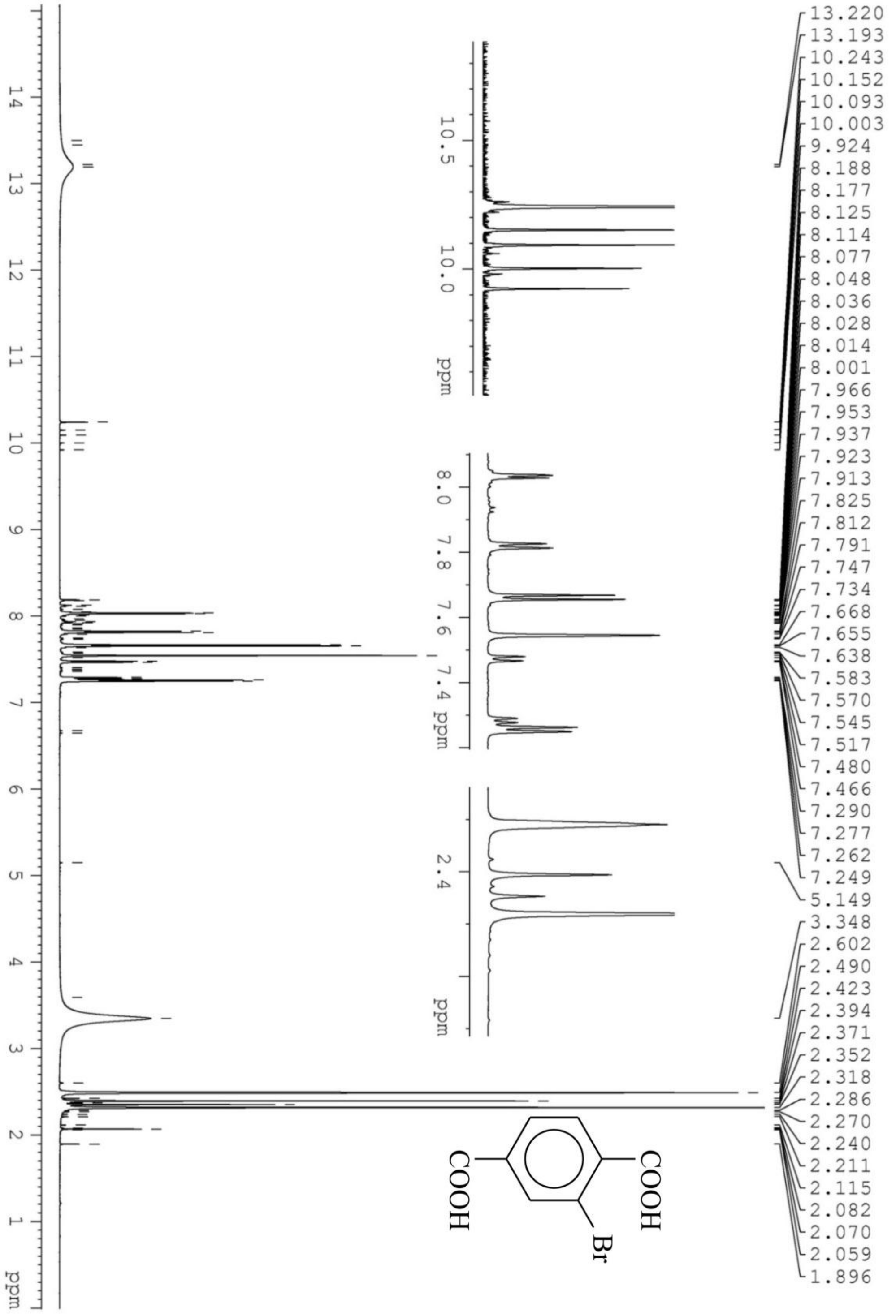
Br
COOH
COOH
Br
13.575
10.148
10.110
10.102
10.070
8.069
8.042
7.992
7.987
7.974
7.966
7.952
7.915
7.839
7.803
7.774
7.741
7.717
7.673
7.662
7.569
5.129
5.094
5.074
5.037
3.339
2.552
2.529
2.490
2.456
2.398
2.351
2.335
2.319
2.301
2.273
2.241
2.175
2.133
2.111
2.092
2.071
1.964
7.9
7.8
7.7
7.6
ppm
2.6
2.4
2.2
2.0
ppm
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm

(A) ^{1}HNMR

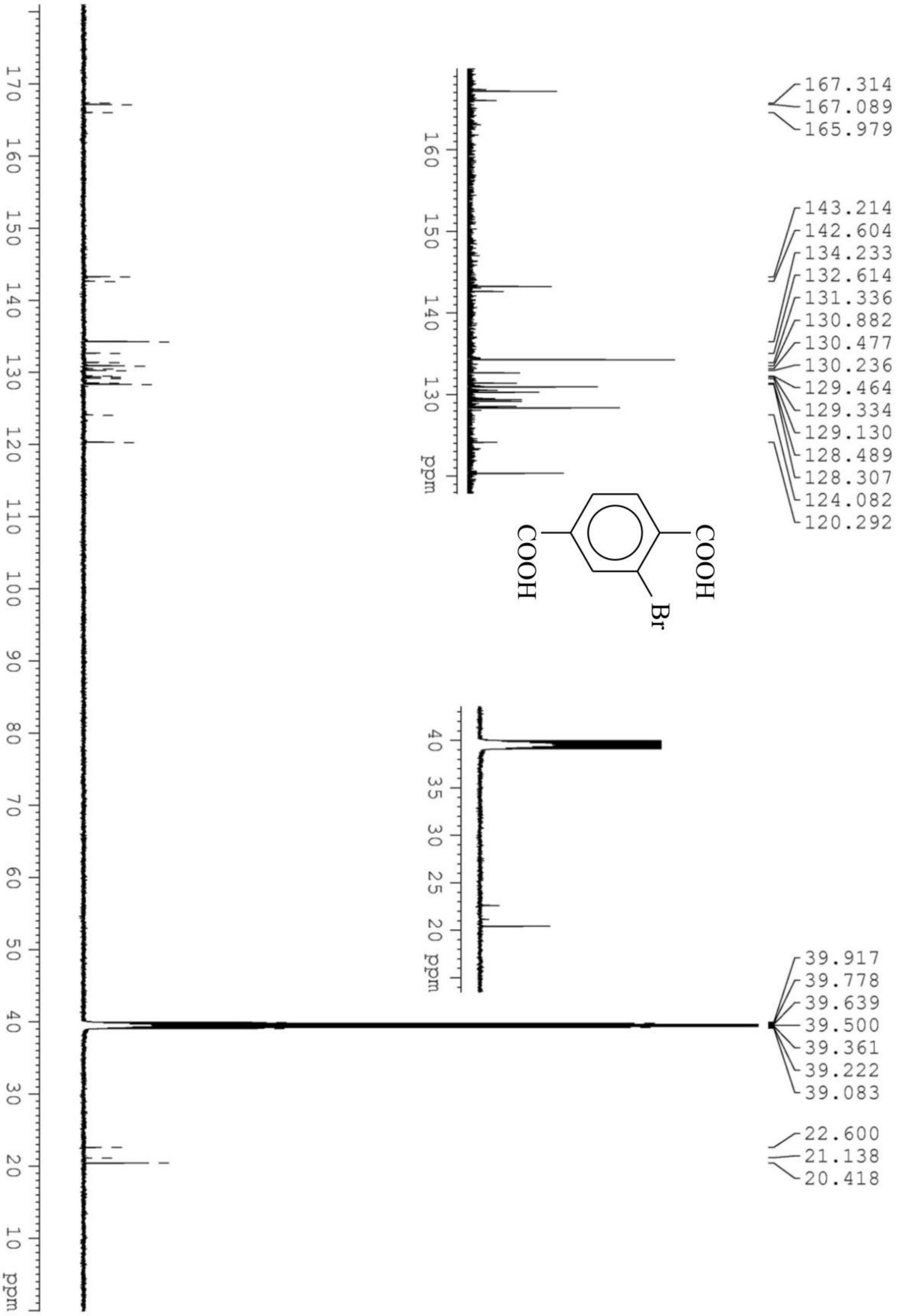


(B) ^{13}CNMR

Figure D.9: NMR spectra of reaction Scheme 4.12, oxidation product of 2,5-dibromo*para*xylene

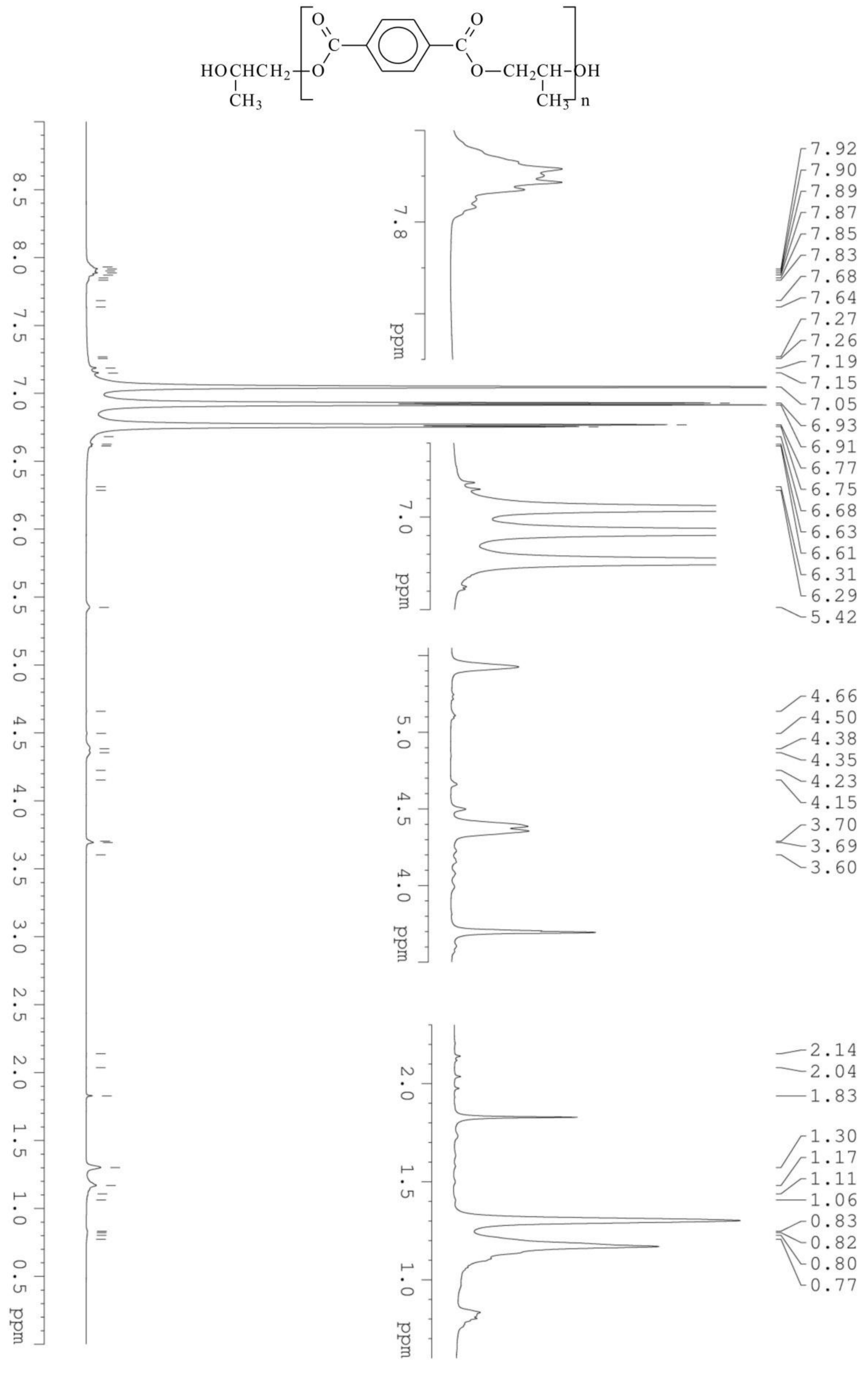

13.220
13.193
10.243
10.152
10.093
10.003
9.924
8.188
8.177
8.125
8.114
8.077
8.048
8.036
8.028
8.014
8.001
7.966
7.953
7.937
7.923
7.913
7.825
7.812
7.791
7.747
7.734
7.668
7.655
7.638
7.583
7.570
7.545
7.517
7.480
7.466
7.290
7.277
7.262
7.249
5.149
3.348
2.602
2.490
2.423
2.394
2.371
2.352
2.318
2.286
2.270
2.240
2.211
2.115
2.082
2.070
2.059
1.896
COOH
COOH
Br
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
10.5
10.0
ppm
8.0
7.8
7.6
7.4
ppm
2.4
ppm

(A) ^{1}HNMR

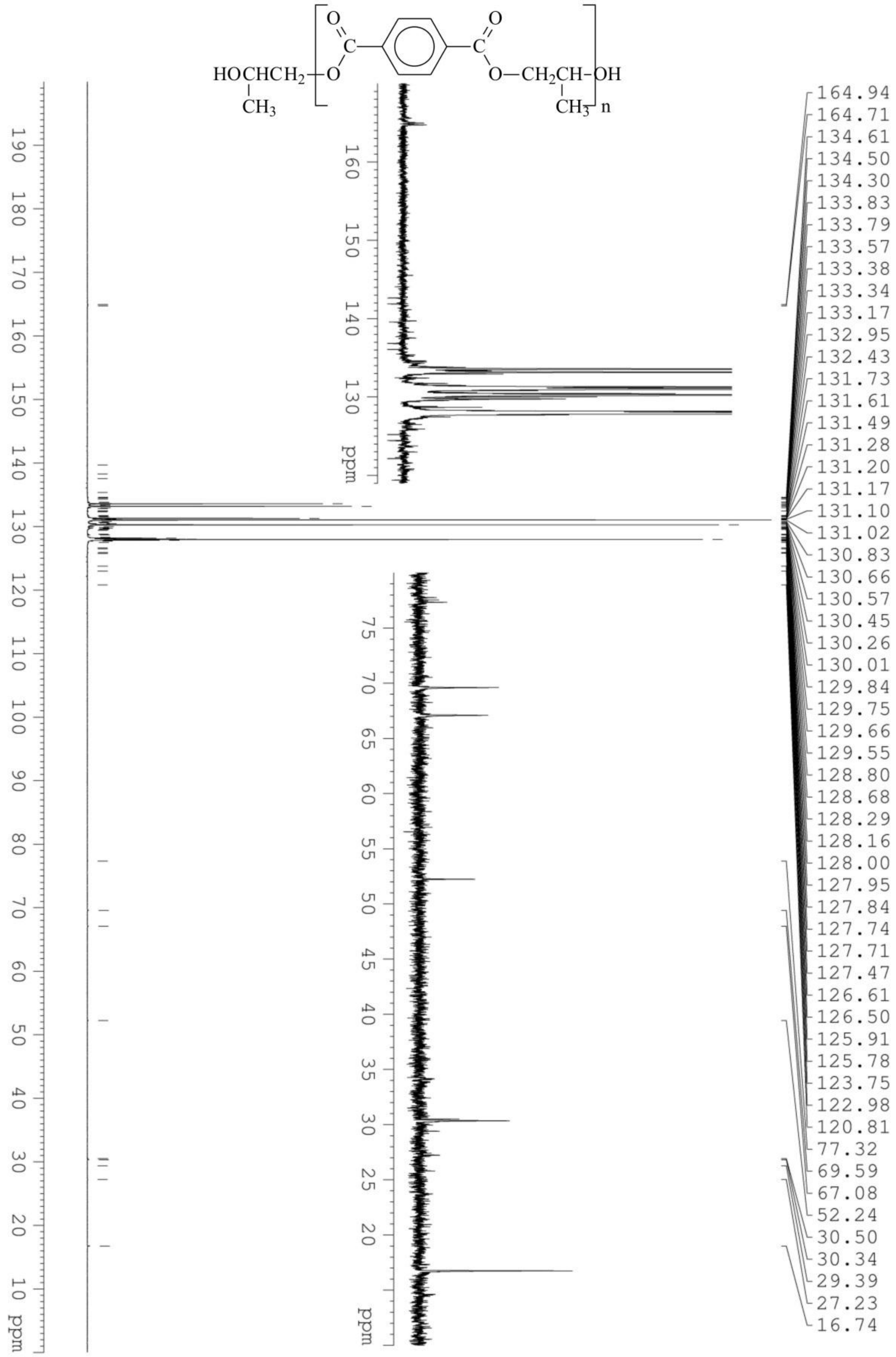


(B) ^{13}CNMR

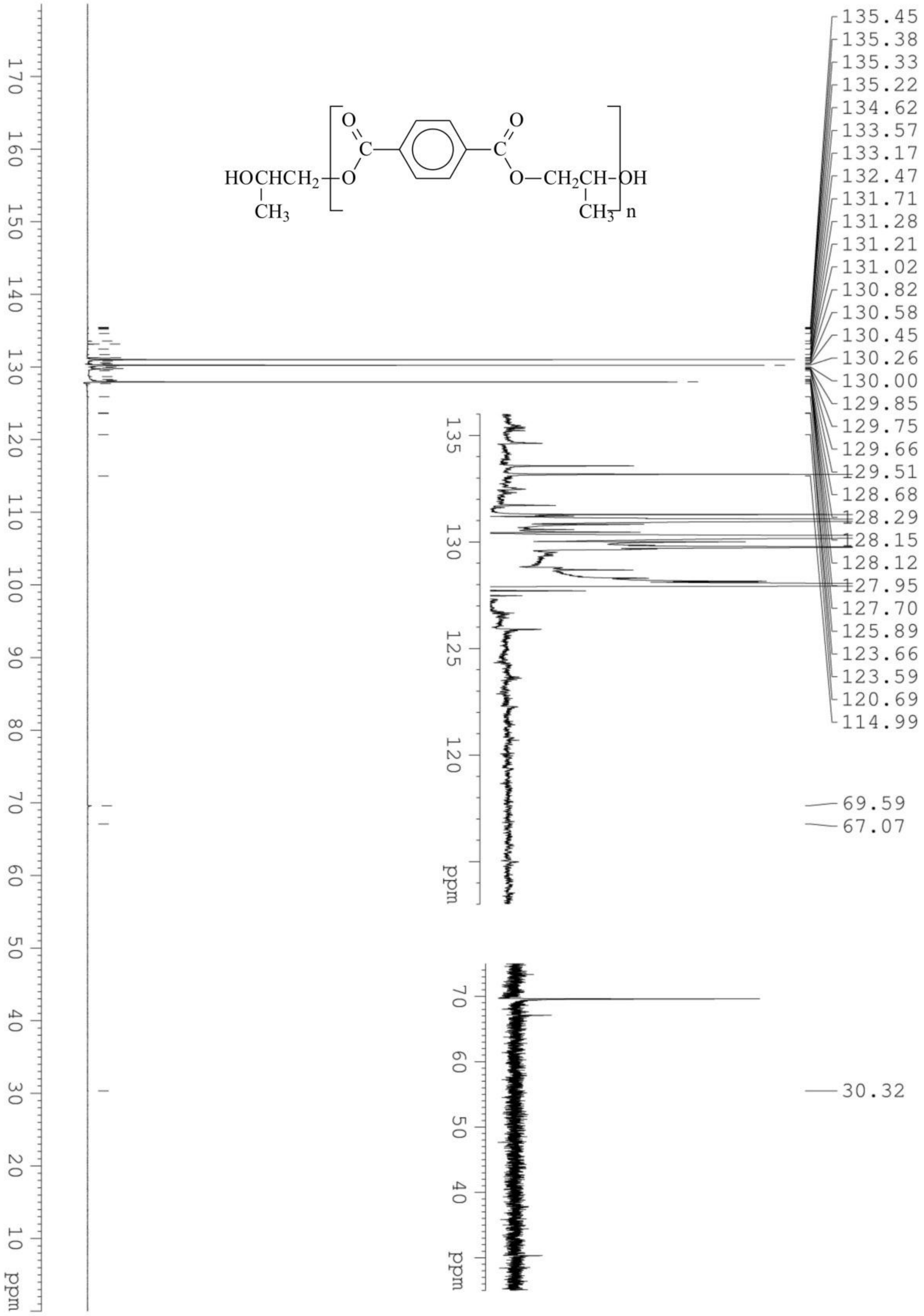
Figure D.10: NMR spectra of reaction Scheme 4.14, oxidation product of 2-Bromo*para*xylene

HOCHCH2
CH3
O
C
O
C
O
O—CH2CH-OH
CH3
n
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm
7.8
ppm
7.0
ppm
5.0
4.5
4.0
ppm
2.0
1.5
1.0
ppm
7.92
7.90
7.89
7.87
7.85
7.83
7.68
7.64
7.27
7.26
7.19
7.15
7.05
6.93
6.91
6.77
6.75
6.68
6.63
6.61
6.31
6.29
5.42
4.66
4.50
4.38
4.35
4.23
4.15
3.70
3.69
3.60
2.14
2.04
1.83
1.30
1.17
1.11
1.06
0.83
0.82
0.80
0.77

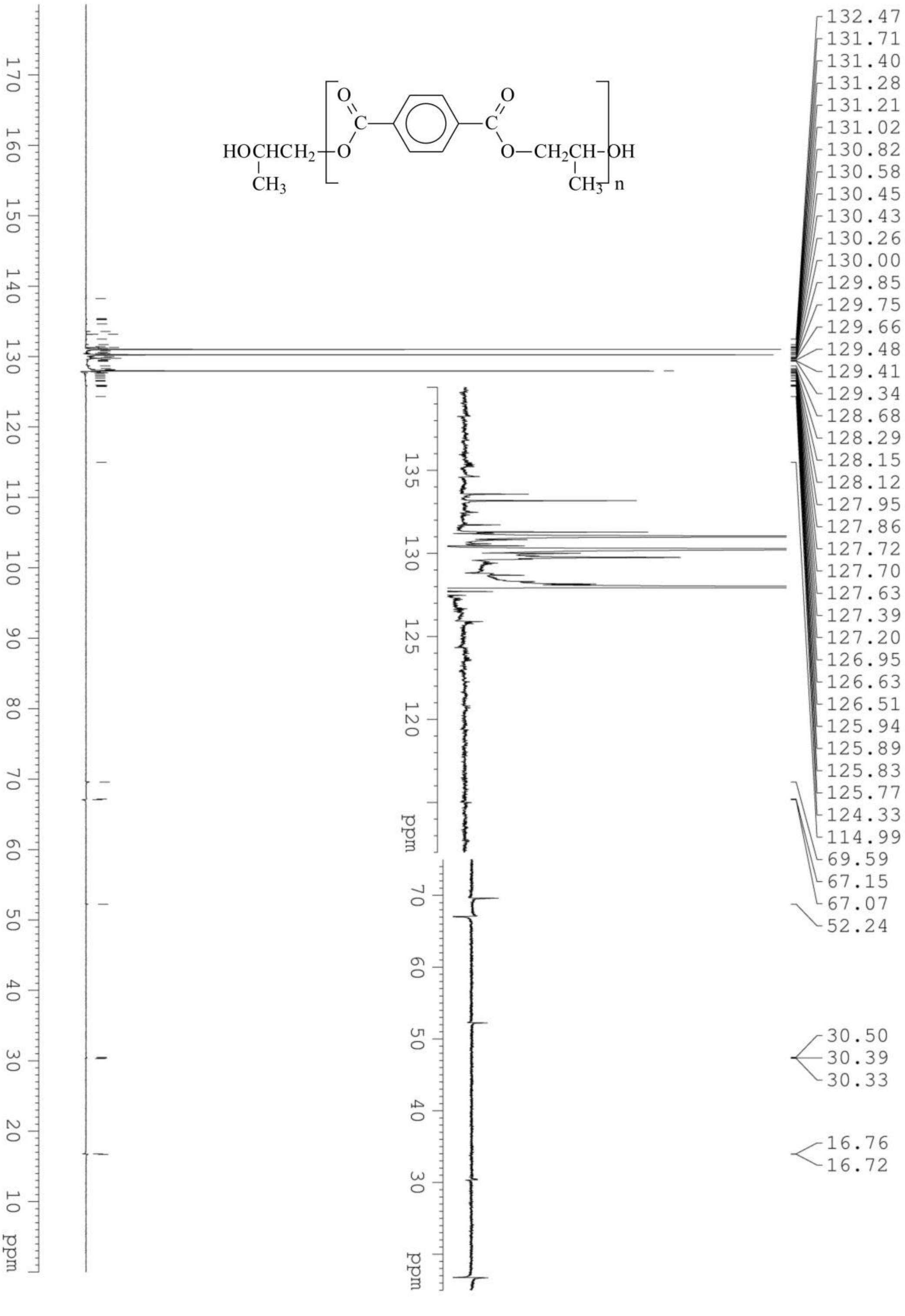
(A) ^{1}HNMR


HOCHCH2 O
CH3
O
C
O
C
O
O—CH2CH-OH
CH3
n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm
160
150
140
130
ppm
75
70
65
60
55
50
45
40
35
30
25
20
ppm
164.94
164.71
134.61
134.50
134.30
133.83
133.79
133.57
133.38
133.34
133.17
132.95
132.43
131.73
131.61
131.49
131.28
131.20
131.17
131.10
131.02
130.83
130.66
130.57
130.45
130.26
130.01
129.84
129.75
129.66
129.55
128.80
128.68
128.29
128.16
128.00
127.95
127.84
127.74
127.71
127.47
126.61
126.50
125.91
125.78
123.75
122.98
120.81
77.32
69.59
67.08
52.24
30.50
30.34
29.39
27.23
16.74

(B) ^{13}CNMR

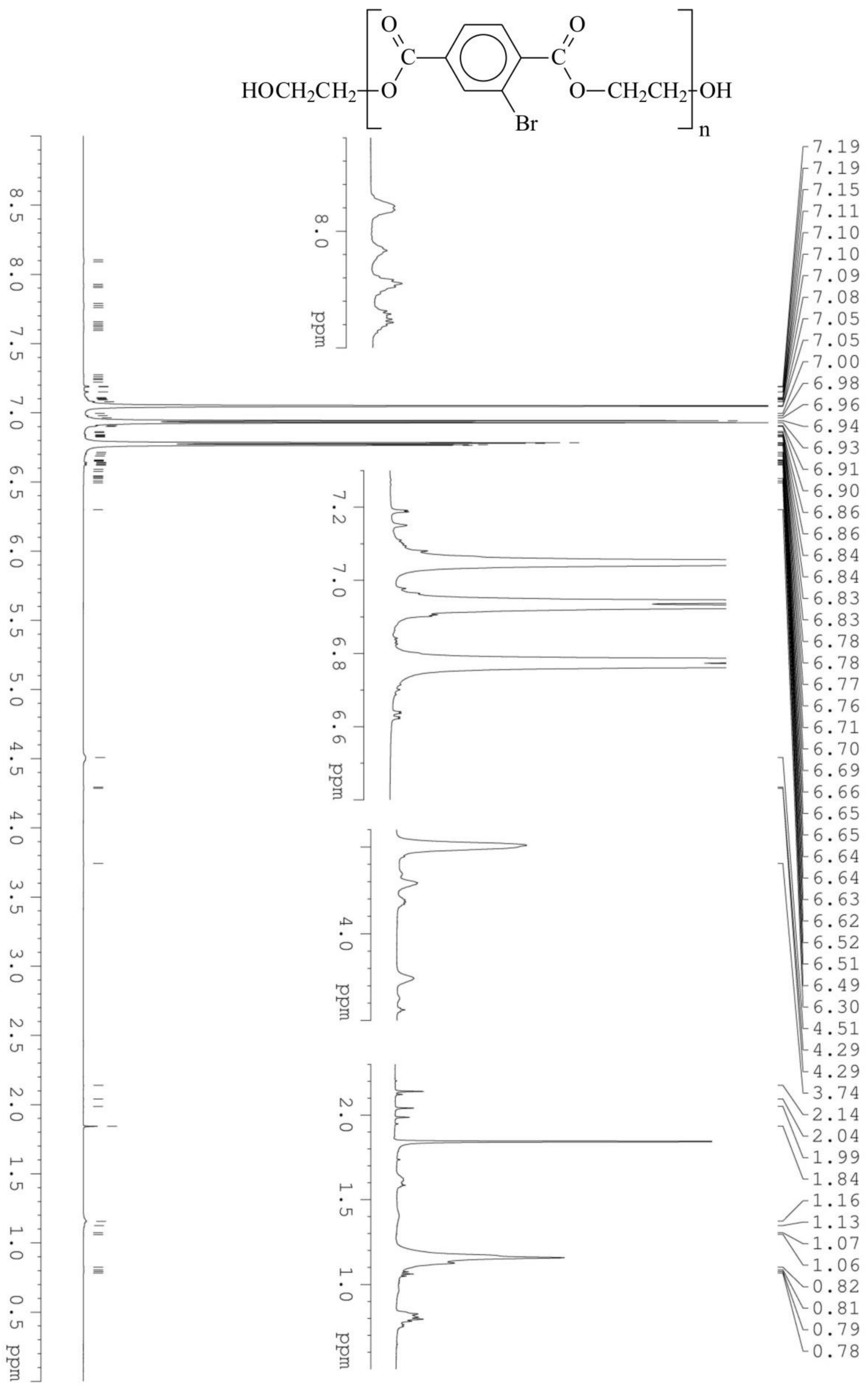

HOCHCH2
CH3
O
C
O
O
C
O–CH2CH–OH
CH3
n
135.45
135.38
135.33
135.22
134.62
133.57
133.17
132.47
131.71
131.28
131.21
131.02
130.82
130.58
130.45
130.26
130.00
129.85
129.75
129.66
129.51
128.68
128.29
128.15
128.12
127.95
127.70
125.89
123.66
123.59
120.69
114.99
69.59
67.07
30.32
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
135
130
125
120
ppm
70
60
50
40
ppm

(C) DEPT90

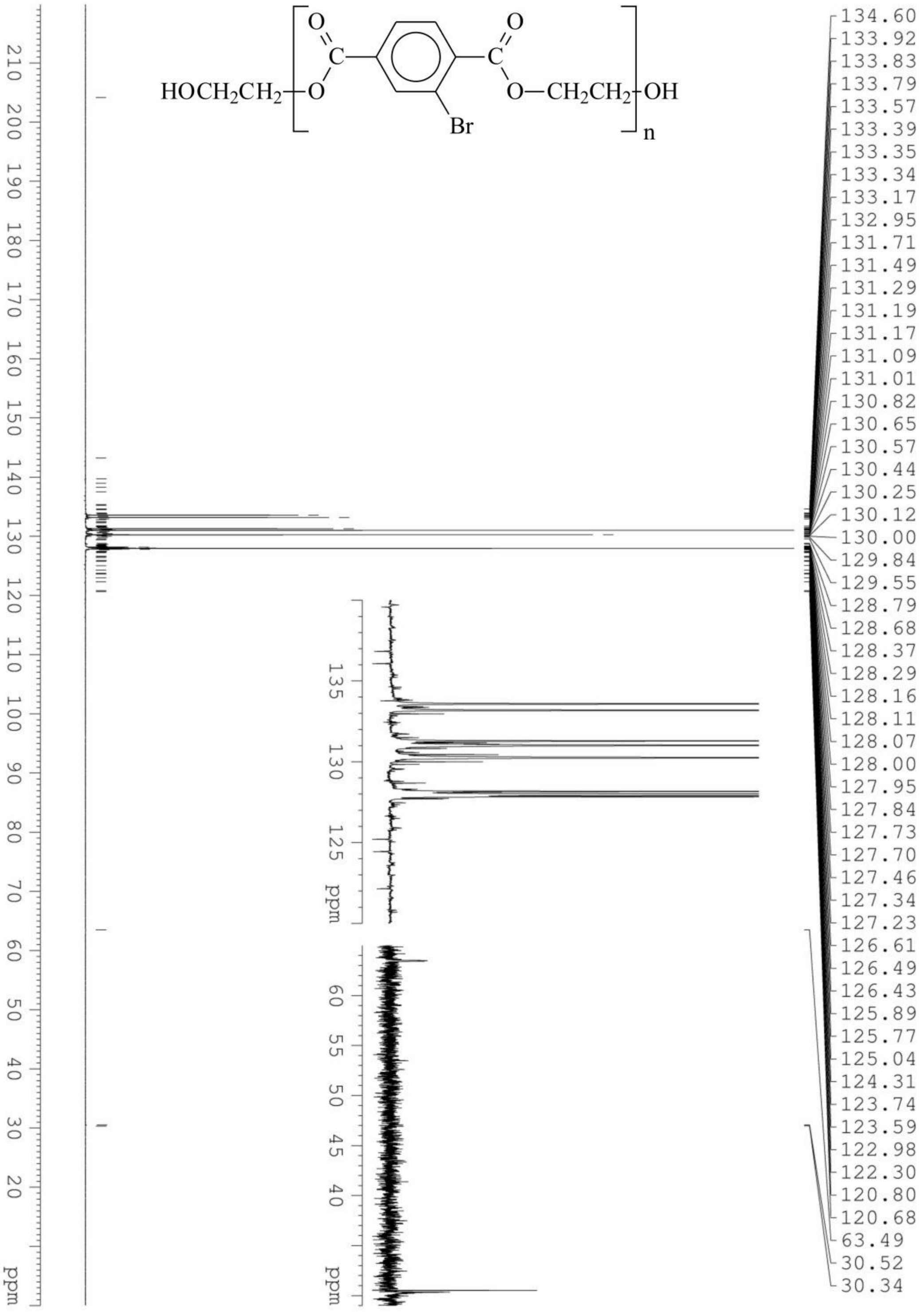


(D) DEPT135

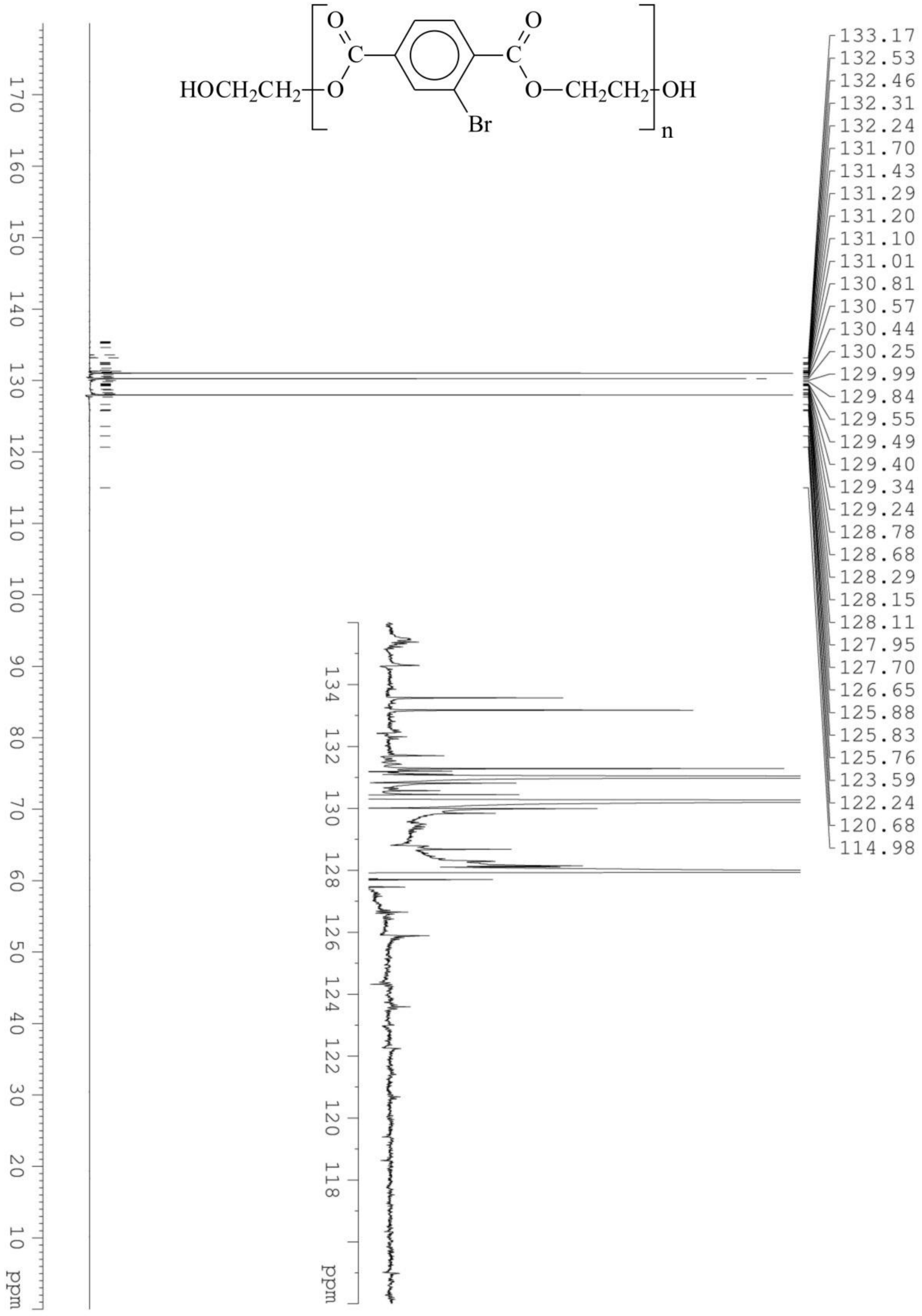
Figure D.11: NMR spectra of Figure 4.6 poly(1,2-propanediol) terephthalate


HOCH2CH2
O
C
O
Br
O
C
O
O—CH2CH2
OH
n
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm
8.0
ppm
7.2
7.0
6.8
6.6
ppm
4.0
ppm
2.0
1.5
1.0
ppm
7.19
7.19
7.15
7.11
7.10
7.10
7.09
7.08
7.05
7.05
7.00
6.98
6.96
6.94
6.93
6.91
6.90
6.86
6.86
6.84
6.84
6.83
6.83
6.78
6.78
6.77
6.76
6.71
6.70
6.69
6.66
6.65
6.65
6.64
6.64
6.63
6.62
6.52
6.51
6.49
6.30
4.51
4.29
4.29
3.74
2.14
2.04
1.99
1.84
1.16
1.13
1.07
1.06
0.82
0.81
0.79
0.78

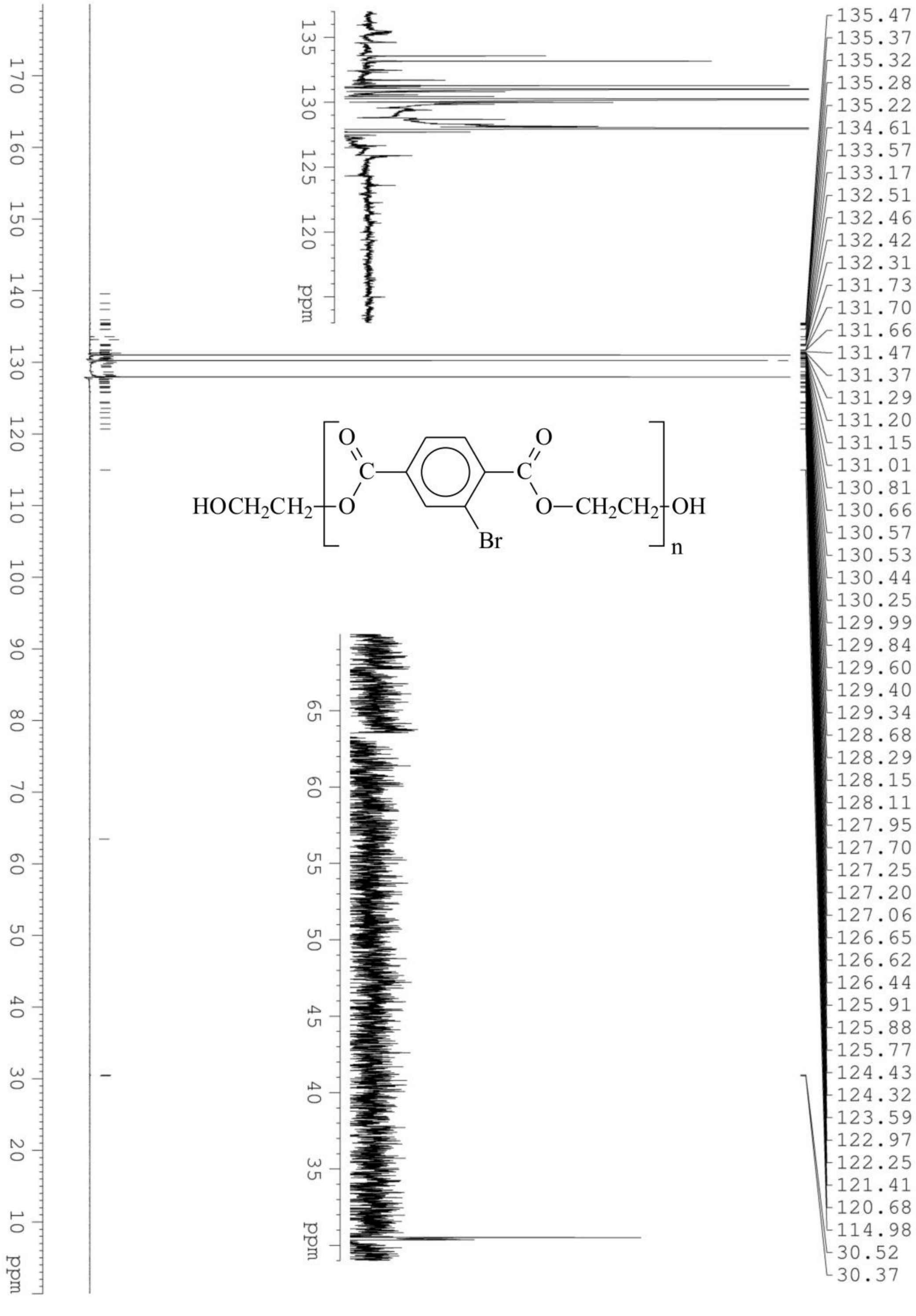
(A) ^{1}HNMR


HOCH$_2$CH$_2$–O–C(=O)–C$_6$H$_3$Br–C(=O)–O–CH$_2$CH$_2$–OH
Br
n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm
135
130
125
ppm
60
55
50
45
40
ppm
134.60
133.92
133.83
133.79
133.57
133.39
133.35
133.34
133.17
132.95
131.71
131.49
131.29
131.19
131.17
131.09
131.01
130.82
130.65
130.57
130.44
130.25
130.12
130.00
129.84
129.55
128.79
128.68
128.37
128.29
128.16
128.11
128.07
128.00
127.95
127.84
127.73
127.70
127.46
127.34
127.23
126.61
126.49
126.43
125.89
125.77
125.04
124.31
123.74
123.59
122.98
122.30
120.80
120.68
63.49
30.52
30.34

(B) ^{13}CNMR

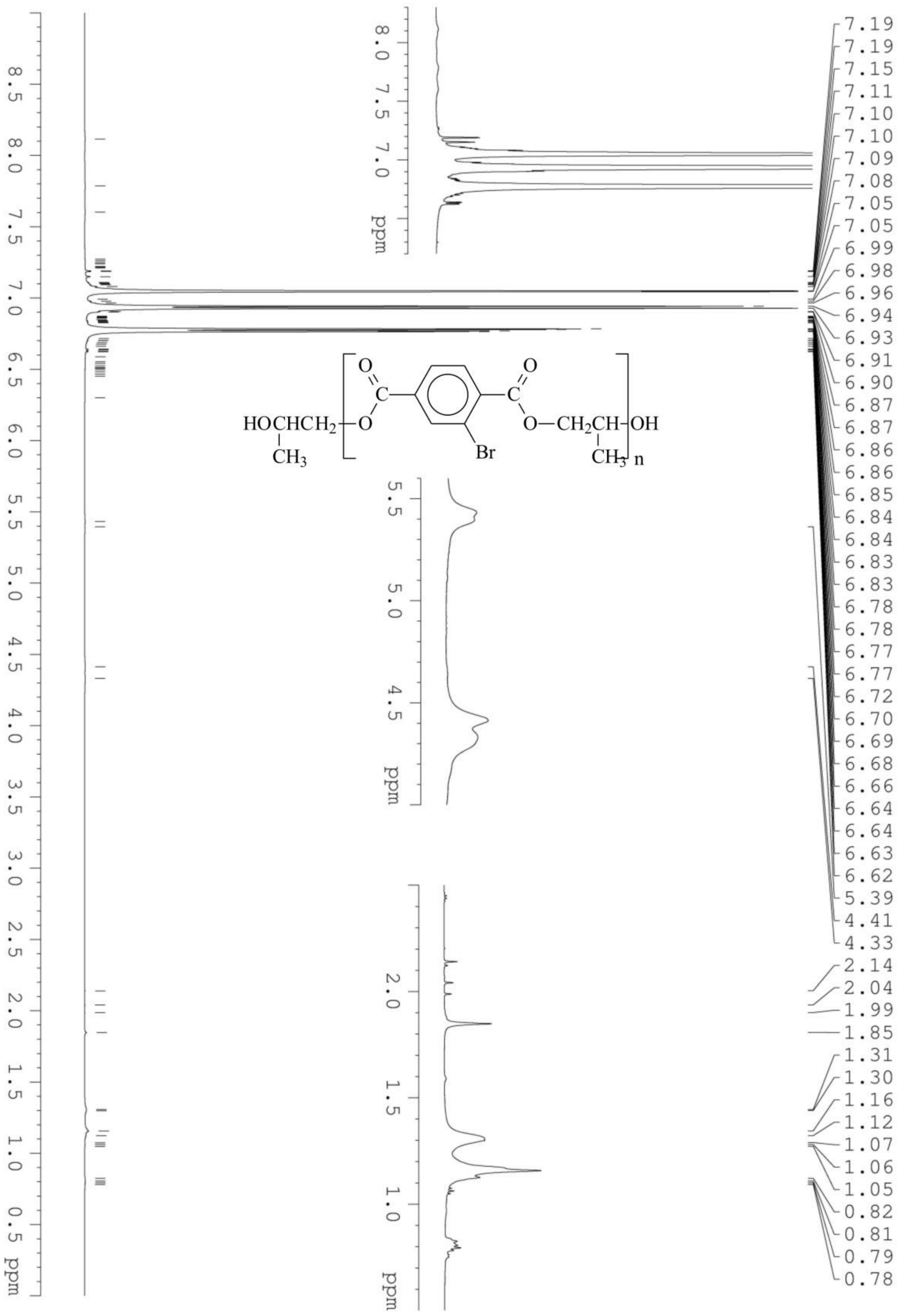

HOCH2CH2
O
C
O
O
C
O
O–CH2CH2
OH
Br
n
133.17
132.53
132.46
132.31
132.24
131.70
131.43
131.29
131.20
131.10
131.01
130.81
130.57
130.44
130.25
129.99
129.84
129.55
129.49
129.40
129.34
129.24
128.78
128.68
128.29
128.15
128.11
127.95
127.70
126.65
125.88
125.83
125.76
123.59
122.24
120.68
114.98
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
134 132 130 128 126 124 122 120 118 ppm

(C) DEPT90



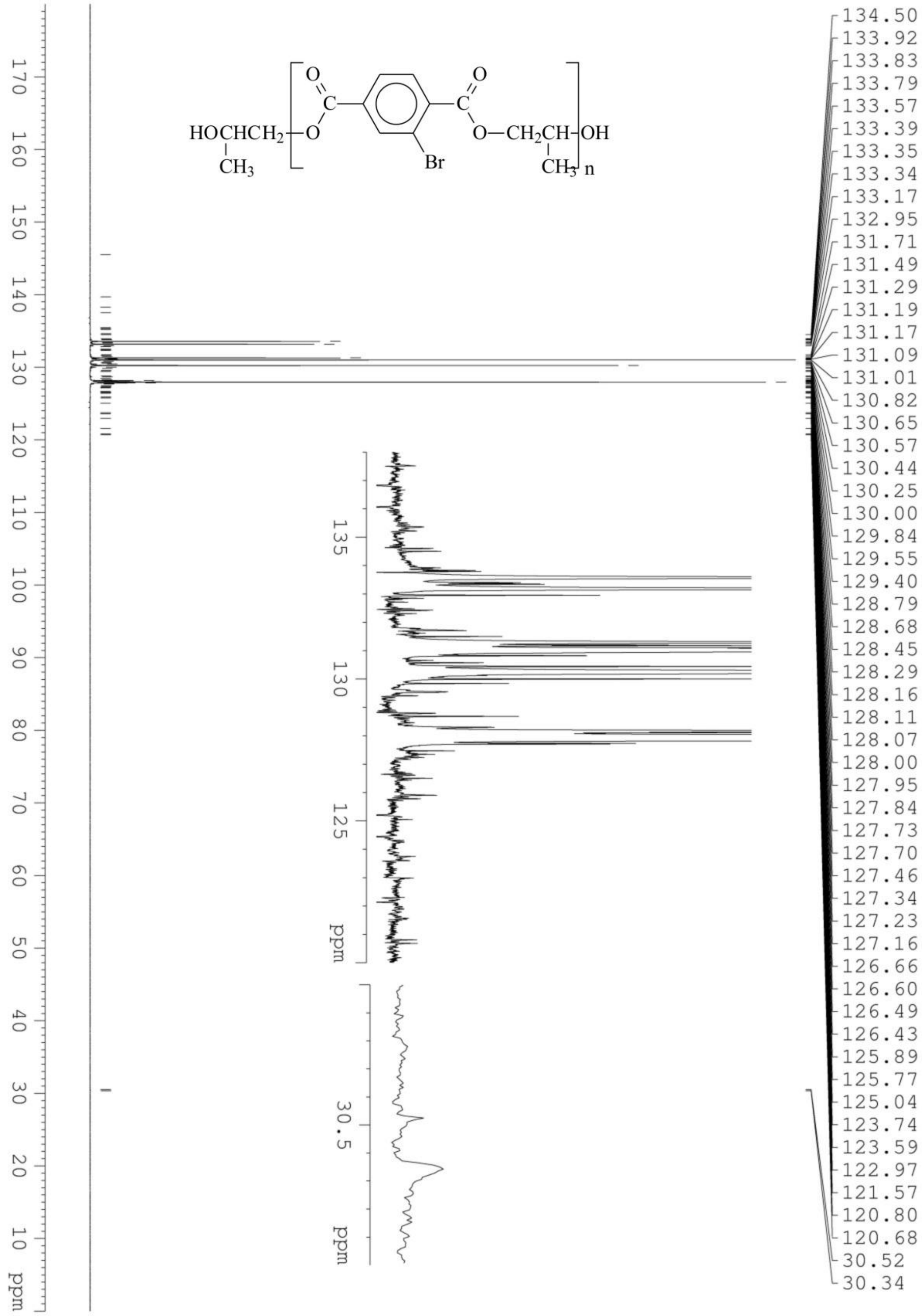
(D) DEPT135

Figure D.12: NMR spectra of Figure 4.7 polyethylene 2-bromoterephthalate

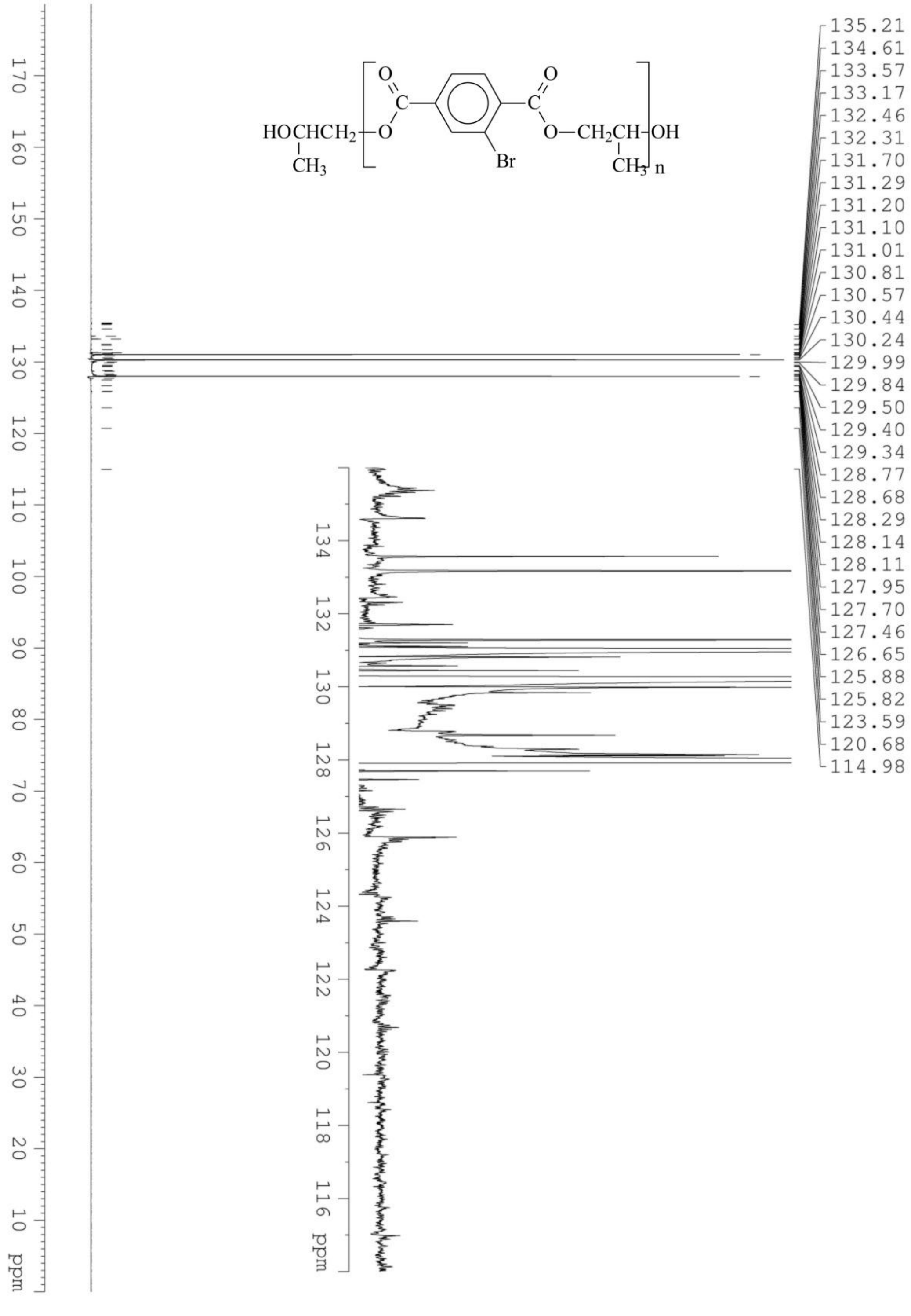


7.19
7.19
7.15
7.11
7.10
7.10
7.09
7.08
7.05
7.05
6.99
6.98
6.96
6.94
6.93
6.91
6.90
6.87
6.87
6.86
6.86
6.85
6.84
6.84
6.83
6.83
6.78
6.78
6.77
6.77
6.72
6.70
6.69
6.68
6.66
6.64
6.64
6.63
6.62
5.39
4.41
4.33
2.14
2.04
1.99
1.85
1.31
1.30
1.16
1.12
1.07
1.06
1.05
0.82
0.81
0.79
0.78
HOCHCH2
CH3
O
C
O
Br
O—CH2CH
OH
CH3
n
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm

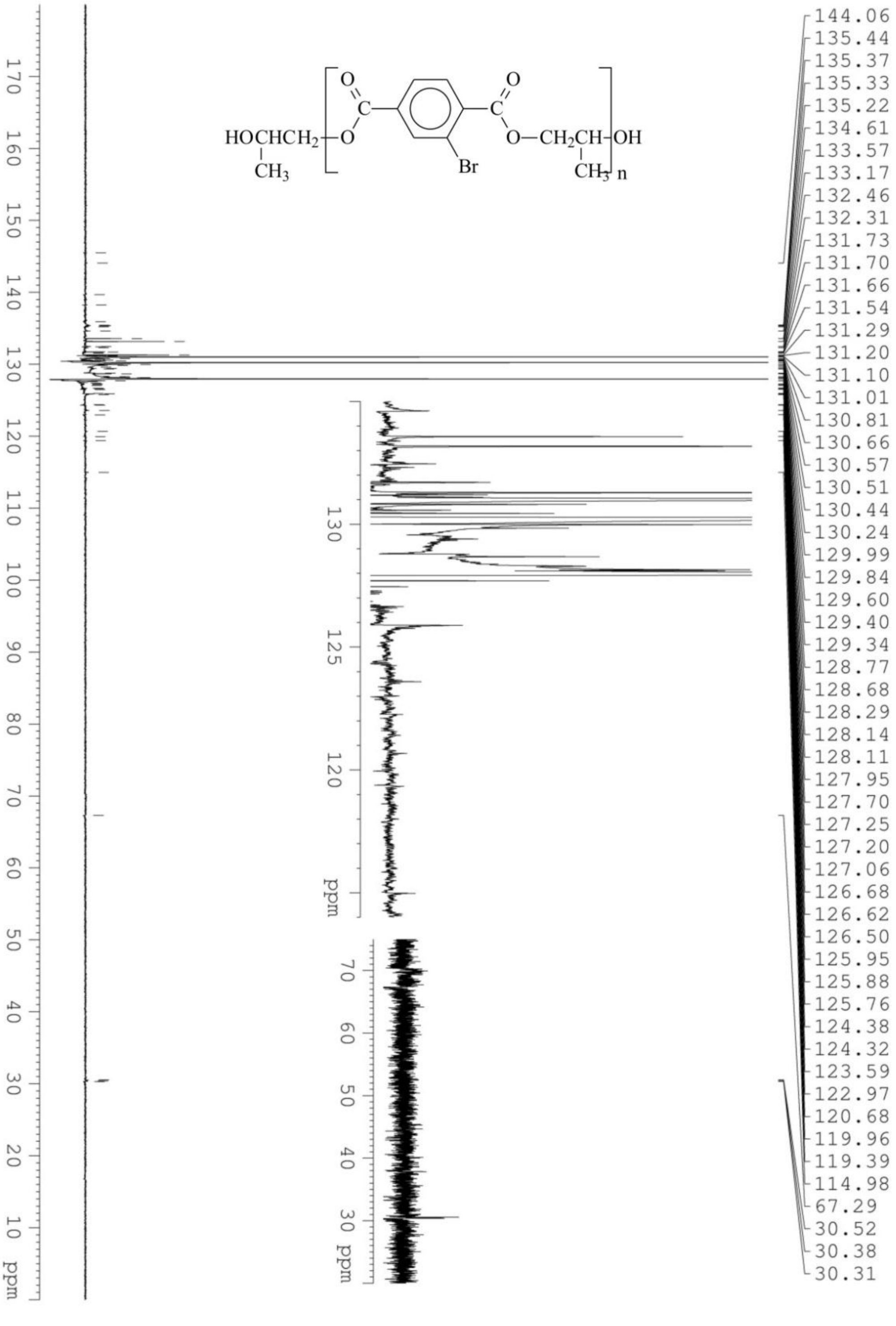
(A) ^{1}HNMR


HOCHCH$_2$
CH$_3$
O
C
O
Br
O
C
O—CH$_2$CH
OH
CH$_3$
n
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
135
130
125
ppm
30.5
ppm
134.50
133.92
133.83
133.79
133.57
133.39
133.35
133.34
133.17
132.95
131.71
131.49
131.29
131.19
131.17
131.09
131.01
130.82
130.65
130.57
130.44
130.25
130.00
129.84
129.55
129.40
128.79
128.68
128.45
128.29
128.16
128.11
128.07
128.00
127.95
127.84
127.73
127.70
127.46
127.34
127.23
127.16
126.66
126.60
126.49
126.43
125.89
125.77
125.04
123.74
123.59
122.97
121.57
120.80
120.68
30.52
30.34

(B) ^{13}CNMR

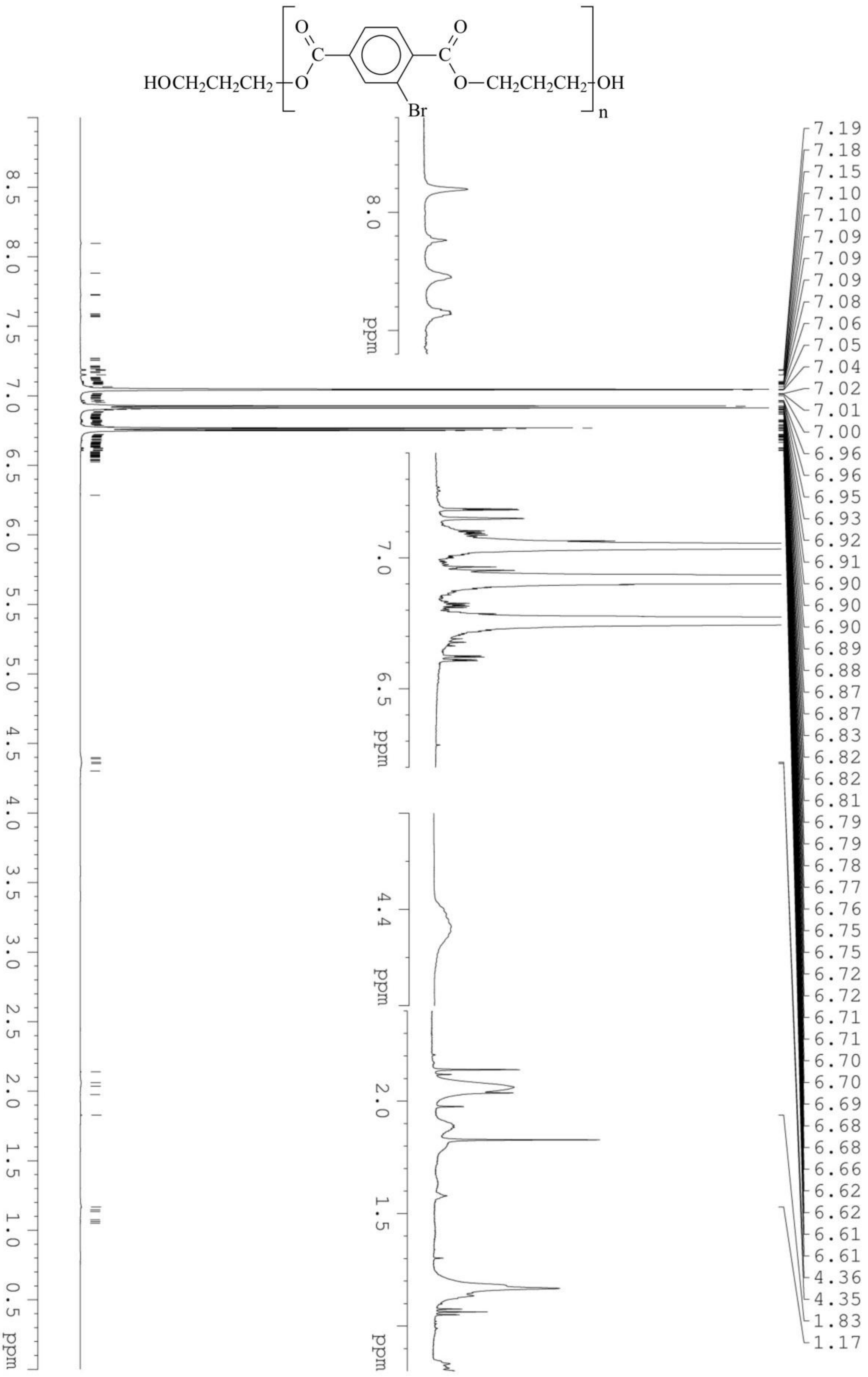

HOCHCH2
CH3
O
C
O
Br
O
C
O—CH2CH
OH
CH3
n
135.21
134.61
133.57
133.17
132.46
132.31
131.70
131.29
131.20
131.10
131.01
130.81
130.57
130.44
130.24
129.99
129.84
129.50
129.40
129.34
128.77
128.68
128.29
128.14
128.11
127.95
127.70
127.46
126.65
125.88
125.82
123.59
120.68
114.98
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
134
132
130
128
126
124
122
120
118
116
ppm

(C) DEPT90

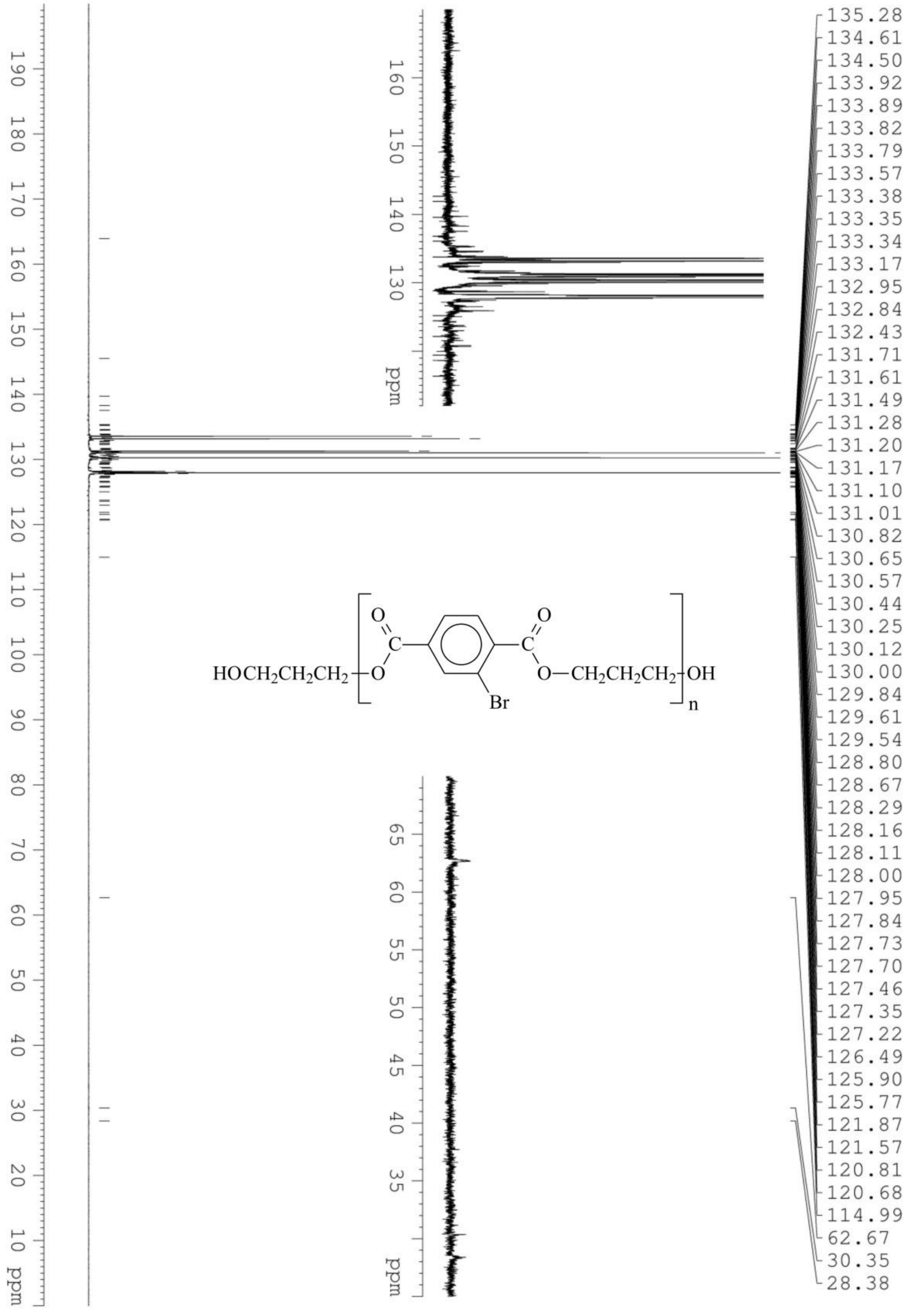


(D) DEPT135

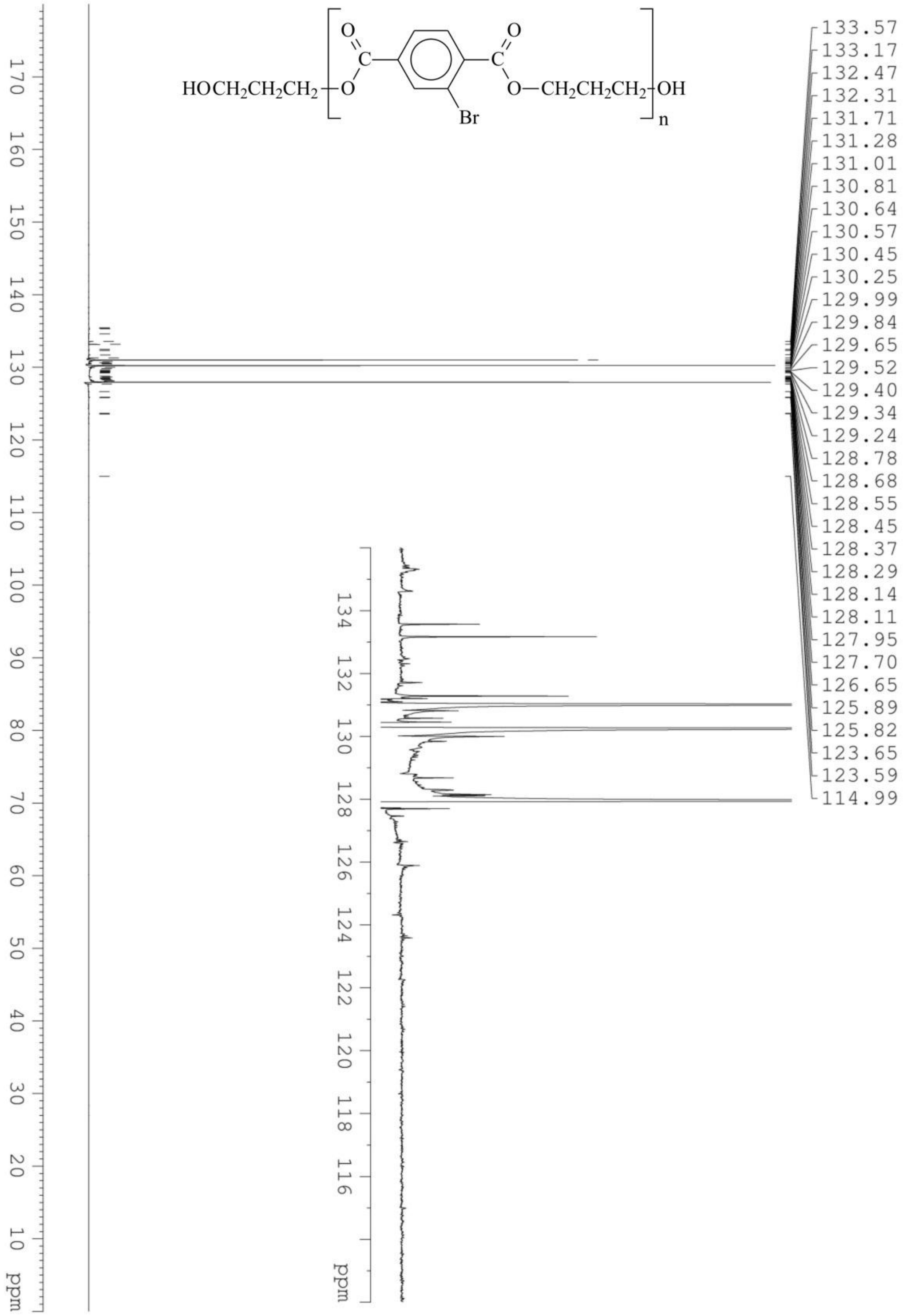
Figure D.13: NMR spectra of Figure 4.8 poly(1,2-propanediol) 2-bromoterephthalate


HOCH2CH2CH2
O
C
O
Br
O
C
O
O—CH2CH2CH2
OH
n
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm
8.0
ppm
7.0
6.5 ppm
4.4
ppm
2.0
1.5
ppm
7.19
7.18
7.15
7.10
7.10
7.09
7.09
7.09
7.08
7.06
7.05
7.04
7.02
7.01
7.00
6.96
6.96
6.95
6.93
6.92
6.91
6.90
6.90
6.90
6.89
6.88
6.87
6.87
6.83
6.82
6.82
6.81
6.79
6.79
6.78
6.77
6.76
6.75
6.75
6.72
6.72
6.71
6.71
6.70
6.70
6.69
6.68
6.68
6.66
6.62
6.62
6.61
6.61
4.36
4.35
1.83
1.17

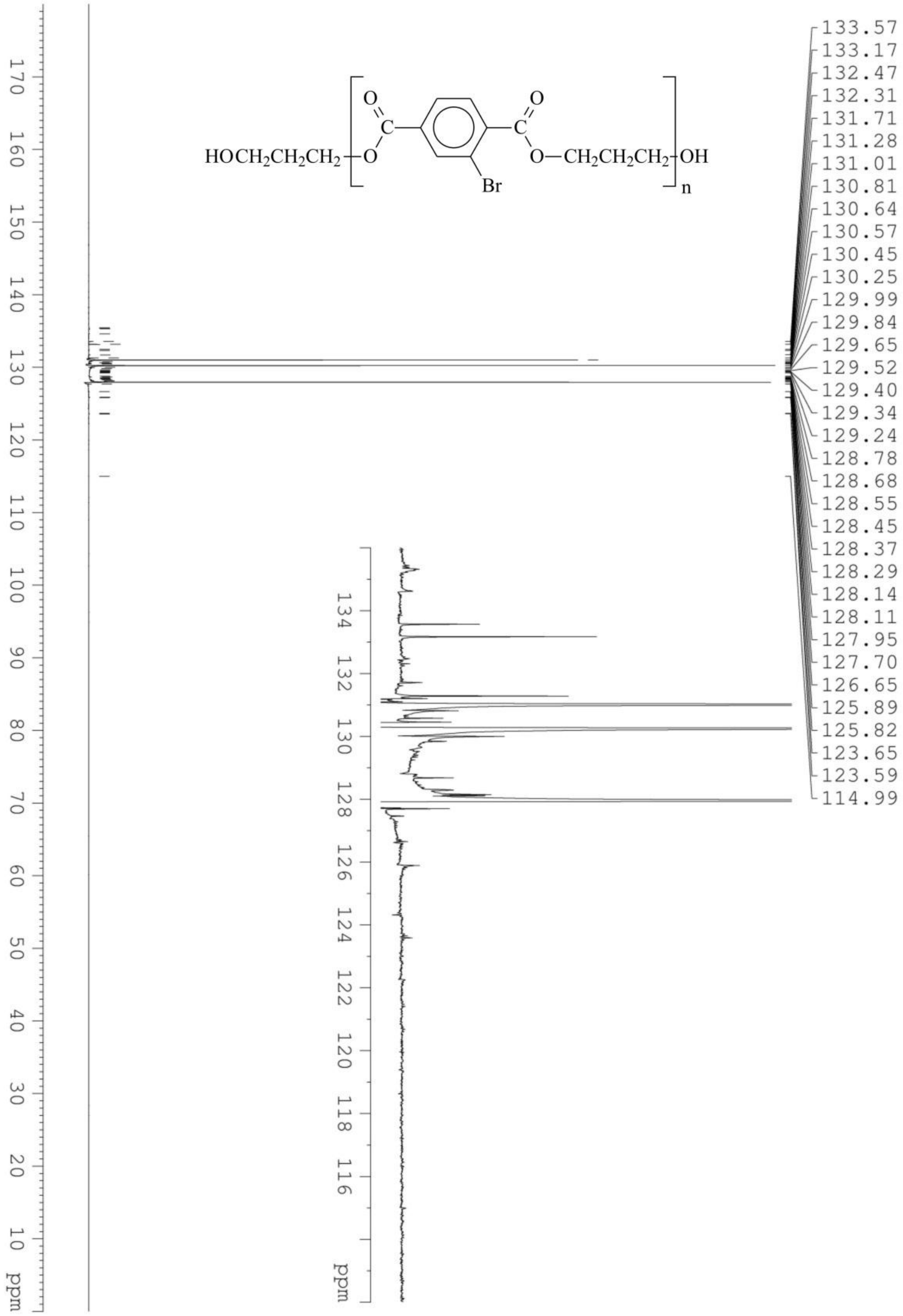
(A) ^{1}HNMR


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm
160
150
140
130
ppm
65
60
55
50
45
40
35
ppm
HOCH2CH2CH2
O
C
O
C
O
O—CH2CH2CH2
OH
Br
n
135.28
134.61
134.50
133.92
133.89
133.82
133.79
133.57
133.38
133.35
133.34
133.17
132.95
132.84
132.43
131.71
131.61
131.49
131.28
131.20
131.17
131.10
131.01
130.82
130.65
130.57
130.44
130.25
130.12
130.00
129.84
129.61
129.54
128.80
128.67
128.29
128.16
128.11
128.00
127.95
127.84
127.73
127.70
127.46
127.35
127.22
126.49
125.90
125.77
121.87
121.57
120.81
120.68
114.99
62.67
30.35
28.38

(B) ^{13}CNMR

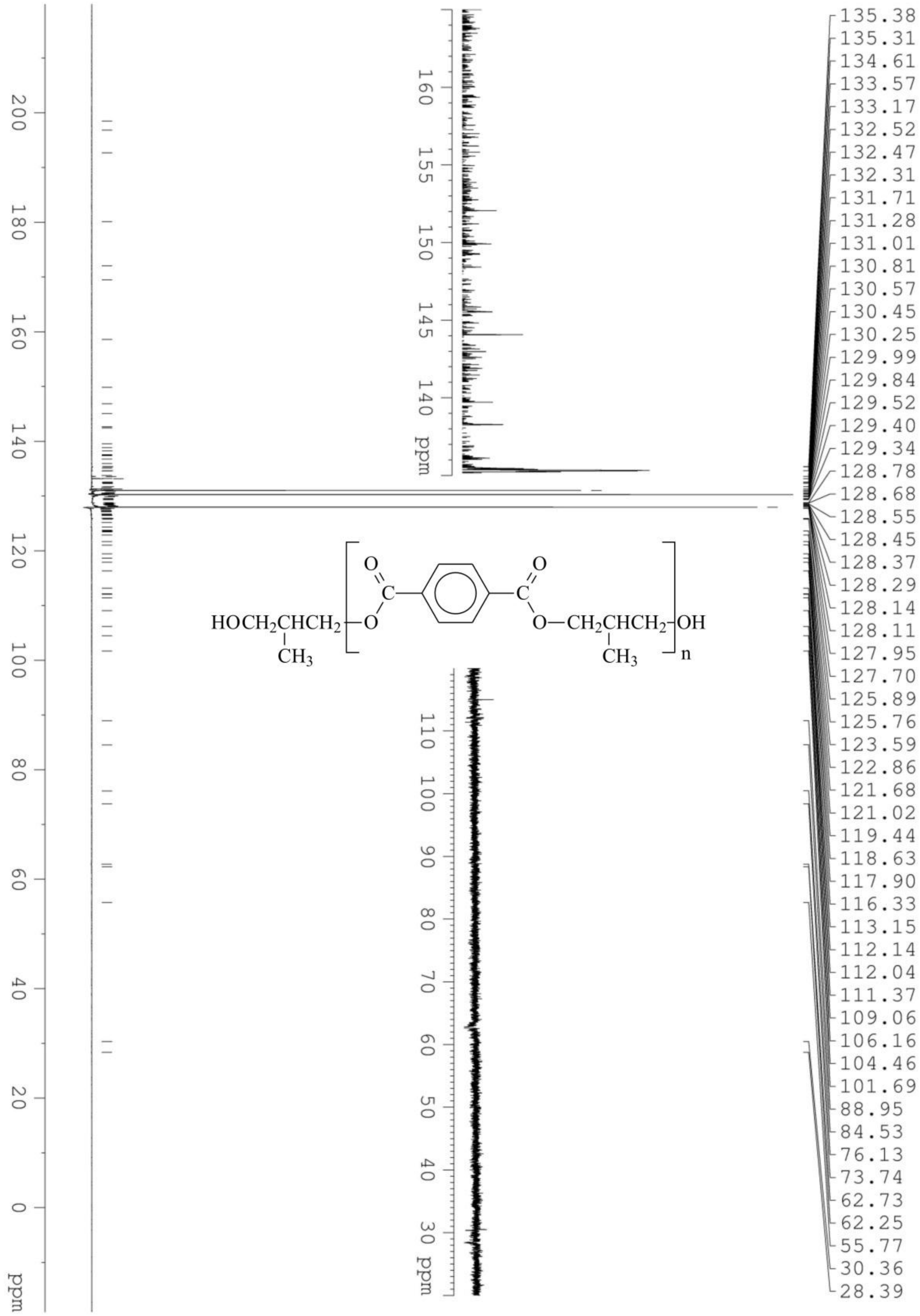

HOCH2CH2CH2
O
C
O
C
O
O—CH2CH2CH2
OH
Br
n
133.57
133.17
132.47
132.31
131.71
131.28
131.01
130.81
130.64
130.57
130.45
130.25
129.99
129.84
129.65
129.52
129.40
129.34
129.24
128.78
128.68
128.55
128.45
128.37
128.29
128.14
128.11
127.95
127.70
126.65
125.89
125.82
123.65
123.59
114.99
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
134
132
130
128
126
124
122
120
118
116
ppm

(C) DEPT90

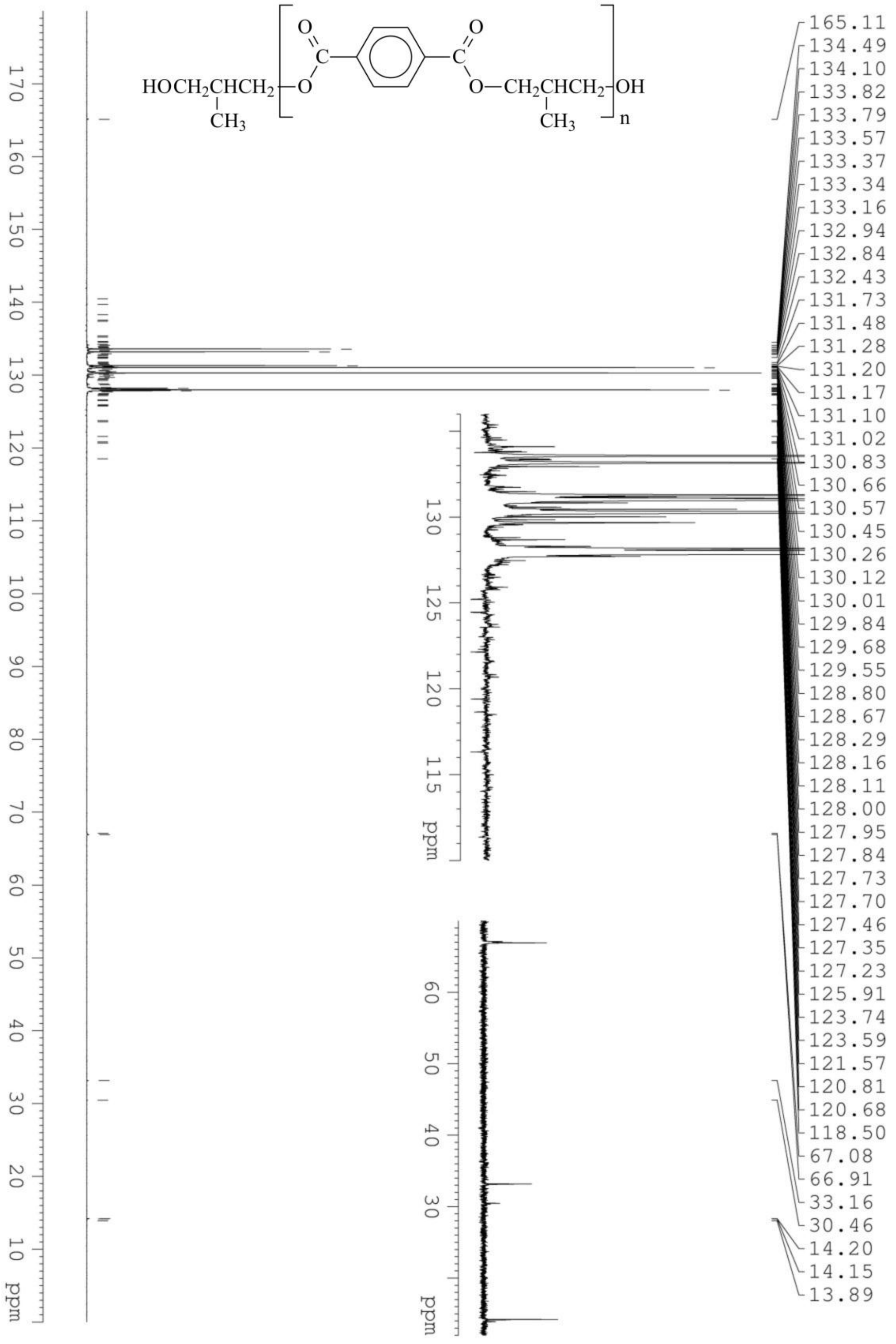


(D) DEPT135

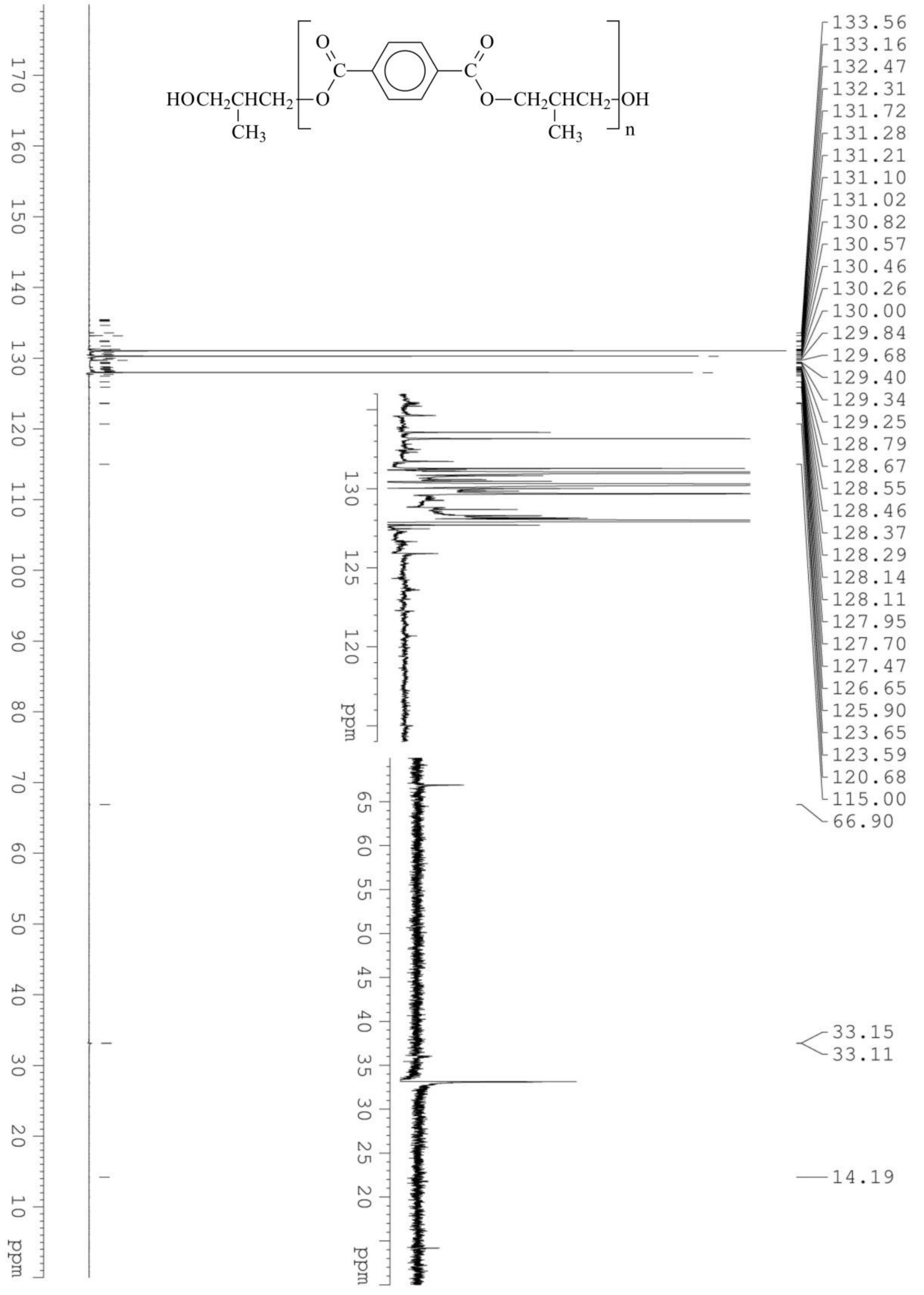
Figure D.14: NMR spectra of Figure 4.10 polypropylene 2-bromoterephthalate


135.38
135.31
134.61
133.57
133.17
132.52
132.47
132.31
131.71
131.28
131.01
130.81
130.57
130.45
130.25
129.99
129.84
129.52
129.40
129.34
128.78
128.68
128.55
128.45
128.37
128.29
128.14
128.11
127.95
127.70
125.89
125.76
123.59
122.86
121.68
121.02
119.44
118.63
117.90
116.33
113.15
112.14
112.04
111.37
109.06
106.16
104.46
101.69
88.95
84.53
76.13
73.74
62.73
62.25
55.77
30.36
28.39
ppm

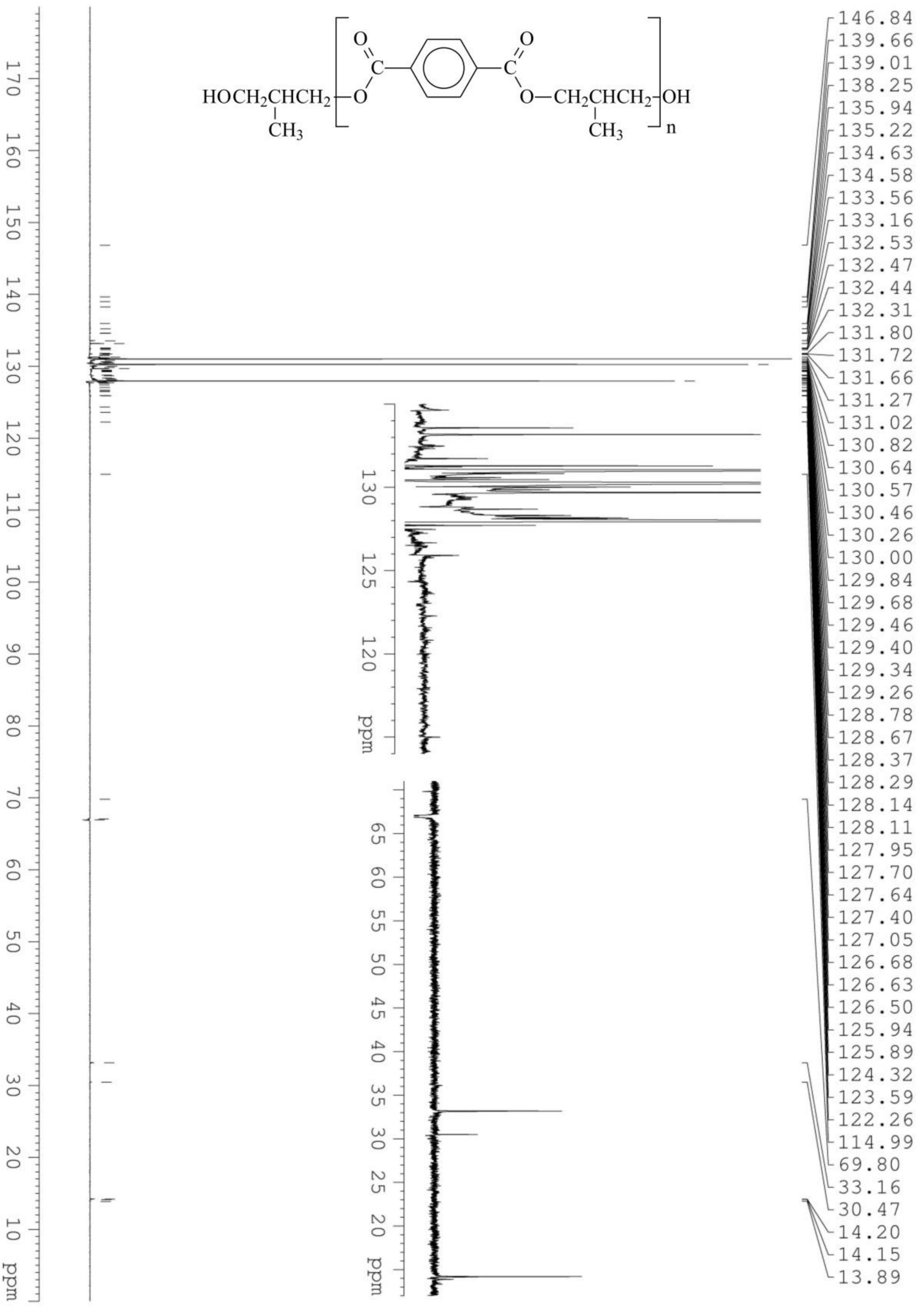
(A) ^{1}HNMR


HOCH2CHCH2 CH3 O C O C O O CH2CHCH2 CH3 OH n
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
130
125
120
115
ppm
60
50
40
30
ppm
165.11
134.49
134.10
133.82
133.79
133.57
133.37
133.34
133.16
132.94
132.84
132.43
131.73
131.48
131.28
131.20
131.17
131.10
131.02
130.83
130.66
130.57
130.45
130.26
130.12
130.01
129.84
129.68
129.55
128.80
128.67
128.29
128.16
128.11
128.00
127.95
127.84
127.73
127.70
127.46
127.35
127.23
125.91
123.74
123.59
121.57
120.81
120.68
118.50
67.08
66.91
33.16
30.46
14.20
14.15
13.89

(B) ^{13}CNMR

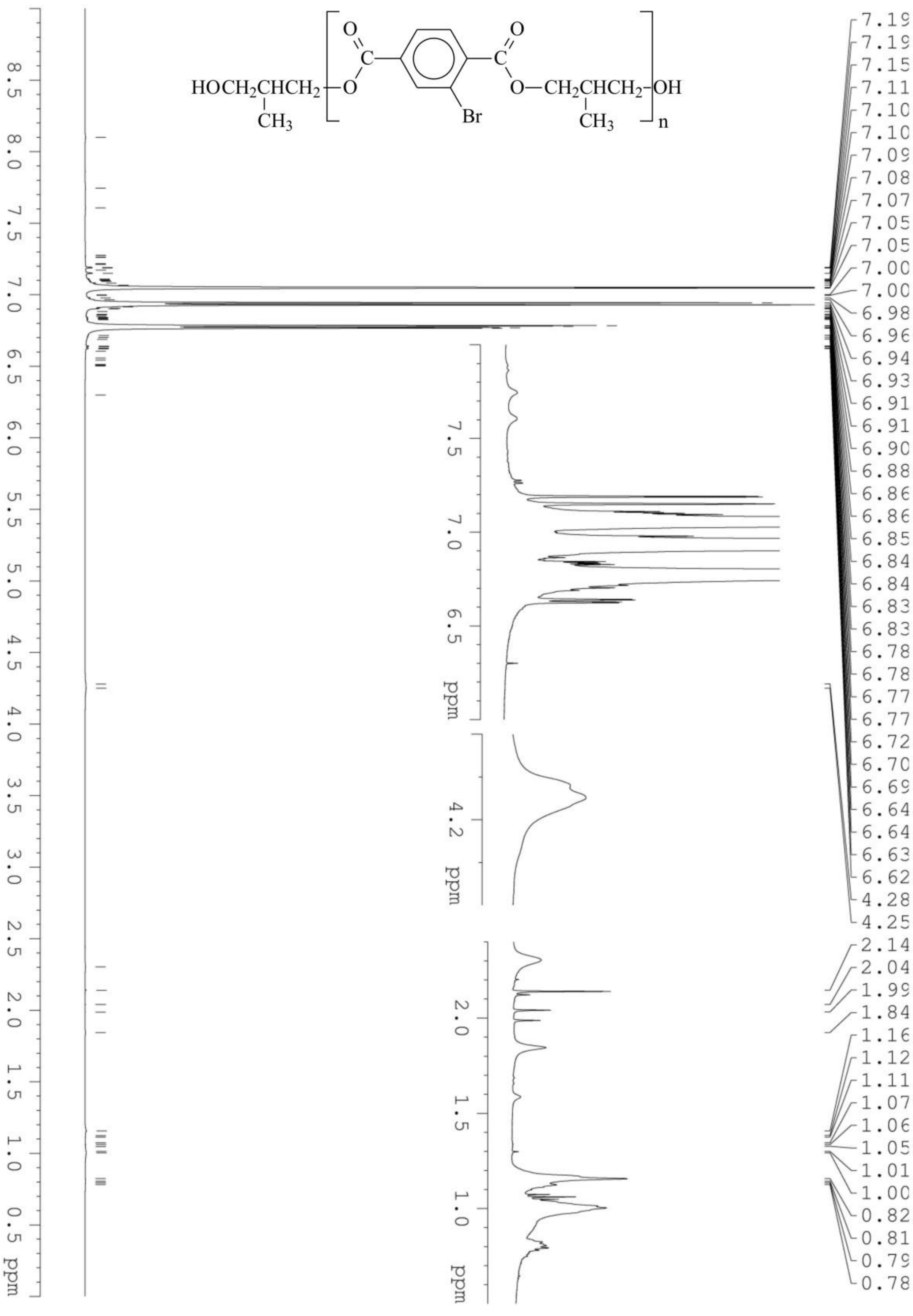

HOCH2CHCH2
CH3
O
C
O
O
C
O
O—CH2CHCH2
CH3
OH
n
133.56
133.16
132.47
132.31
131.72
131.28
131.21
131.10
131.02
130.82
130.57
130.46
130.26
130.00
129.84
129.68
129.40
129.34
129.25
128.79
128.67
128.55
128.46
128.37
128.29
128.14
128.11
127.95
127.70
127.47
126.65
125.90
123.65
123.59
120.68
115.00
66.90
33.15
33.11
14.19
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
130
125
120
ppm
65
60
55
50
45
40
35
30
25
20
ppm

(C) DEPT90

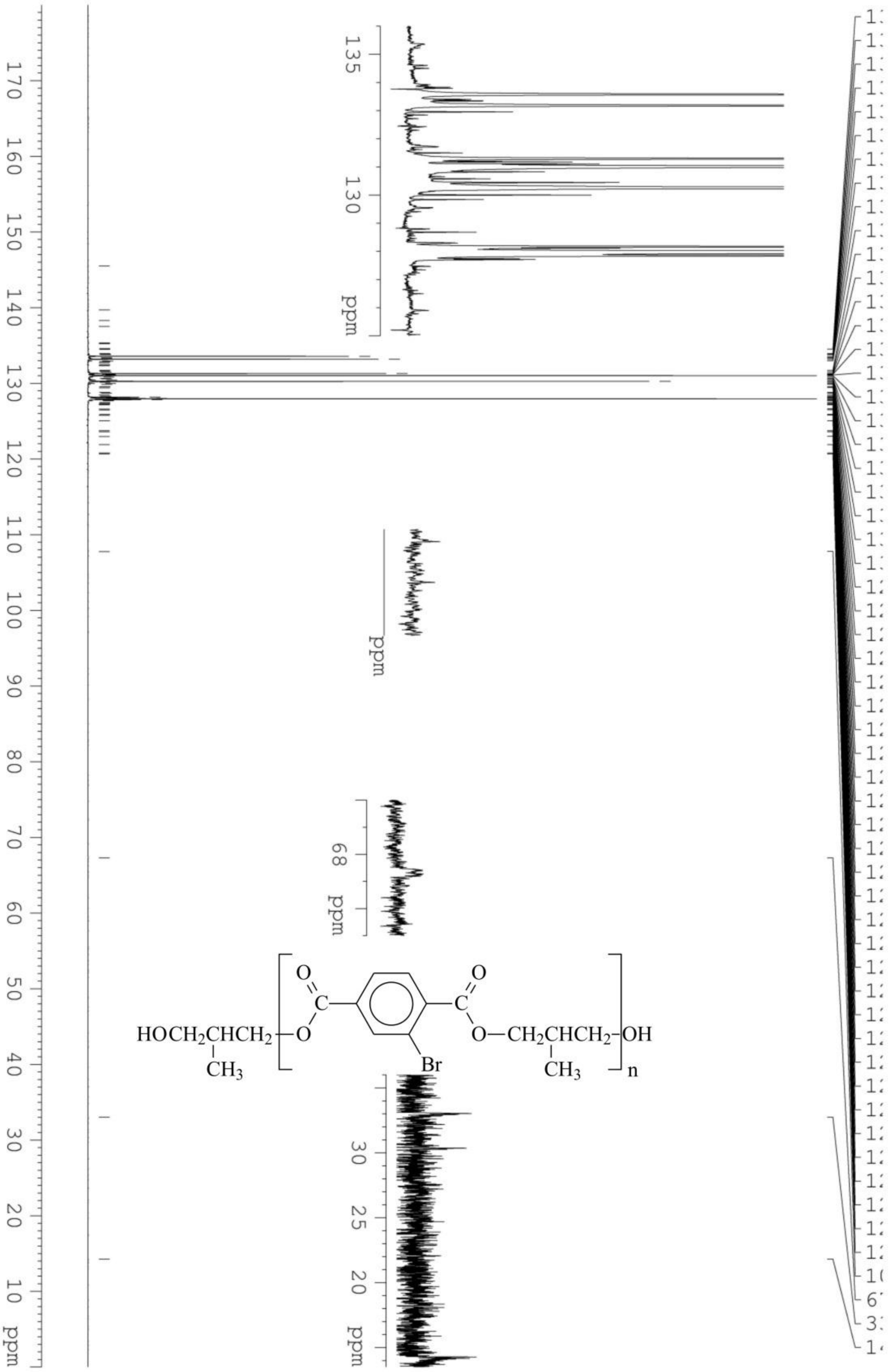


(D) DEPT135

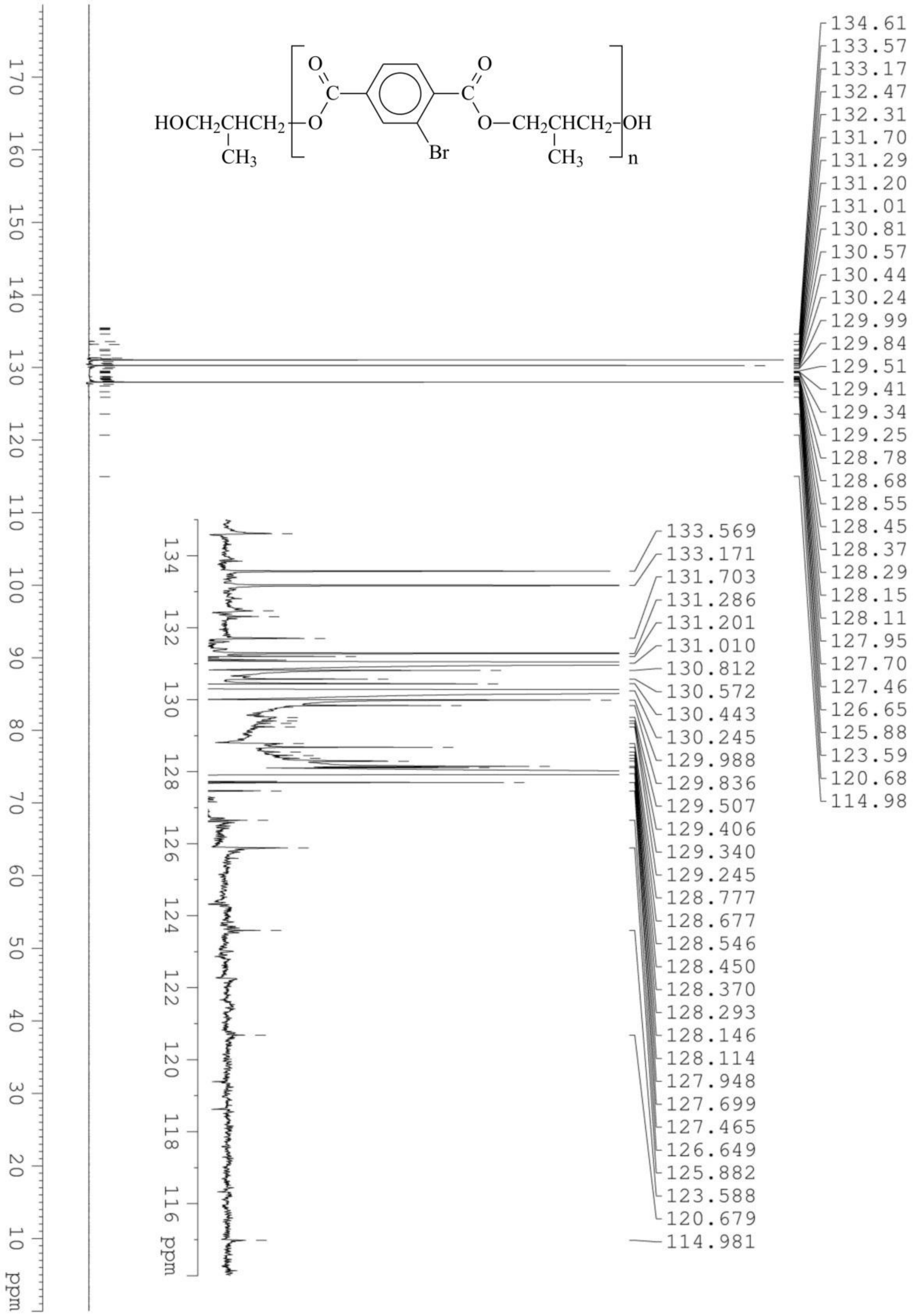
Figure D.15: NMR spectra of Figure 4.11 poly(2-methyl)trimethylene terephthalate


HOCH2CHCH2
CH3
O
C
O
Br
O—CH2CHCH2
CH3
OH
n
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm
7.5
7.0
6.5
ppm
4.2
ppm
2.0
1.5
1.0
ppm
7.19
7.19
7.15
7.11
7.10
7.10
7.09
7.08
7.07
7.05
7.05
7.00
7.00
6.98
6.96
6.94
6.93
6.91
6.91
6.90
6.88
6.86
6.86
6.85
6.84
6.84
6.83
6.83
6.78
6.78
6.77
6.77
6.72
6.70
6.69
6.64
6.64
6.63
6.62
4.28
4.25
2.14
2.04
1.99
1.84
1.16
1.12
1.11
1.07
1.06
1.05
1.01
1.00
0.82
0.81
0.79
0.78

(A) ^{1}HNMR

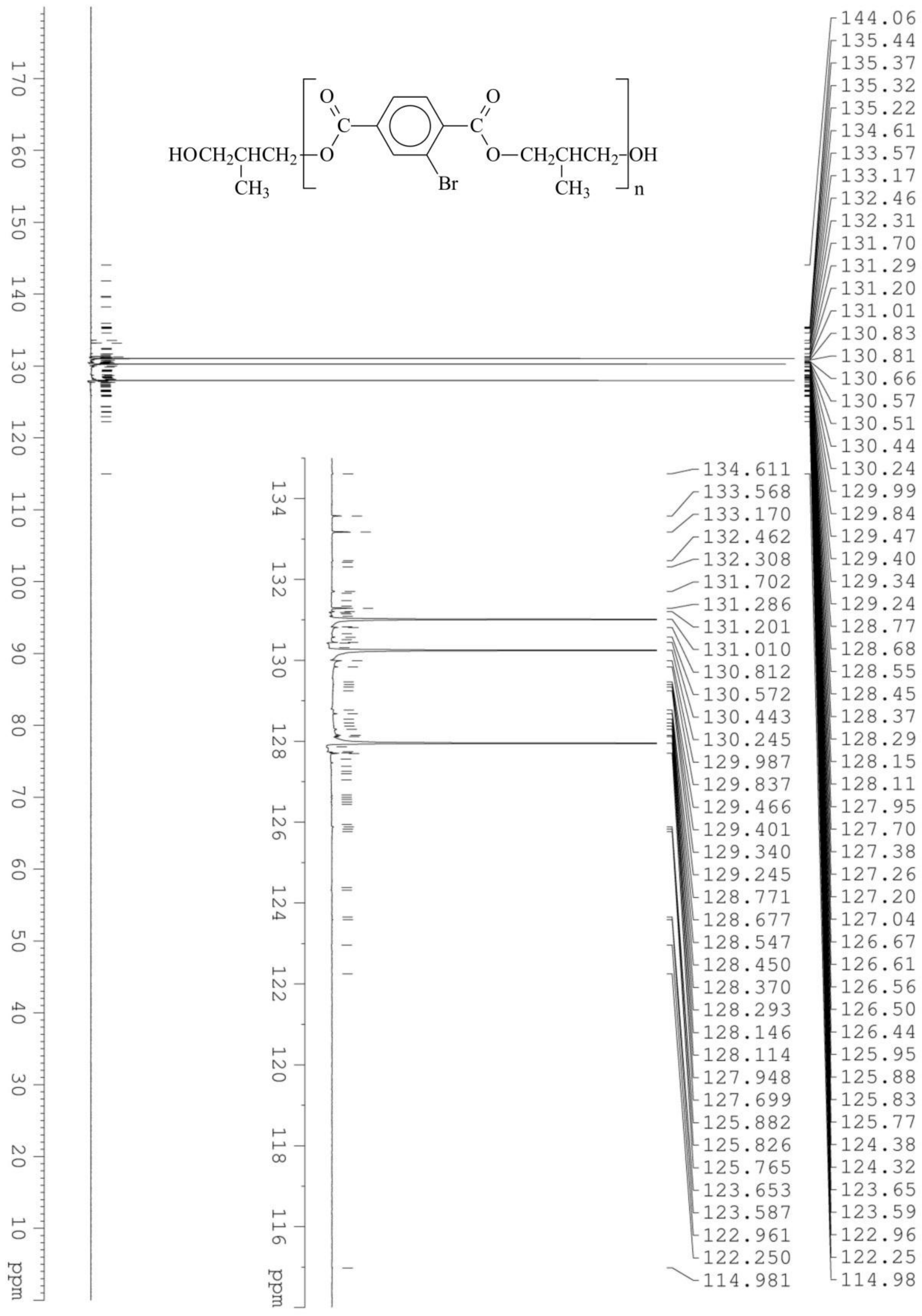

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
135
130
ppm
ppm
68
ppm
30
25
20
ppm
HOCH2CHCH2
CH3
O
C
O
Br
O
C
O
CH2CHCH2
CH3
OH
n

(B) ^{13}CNMR



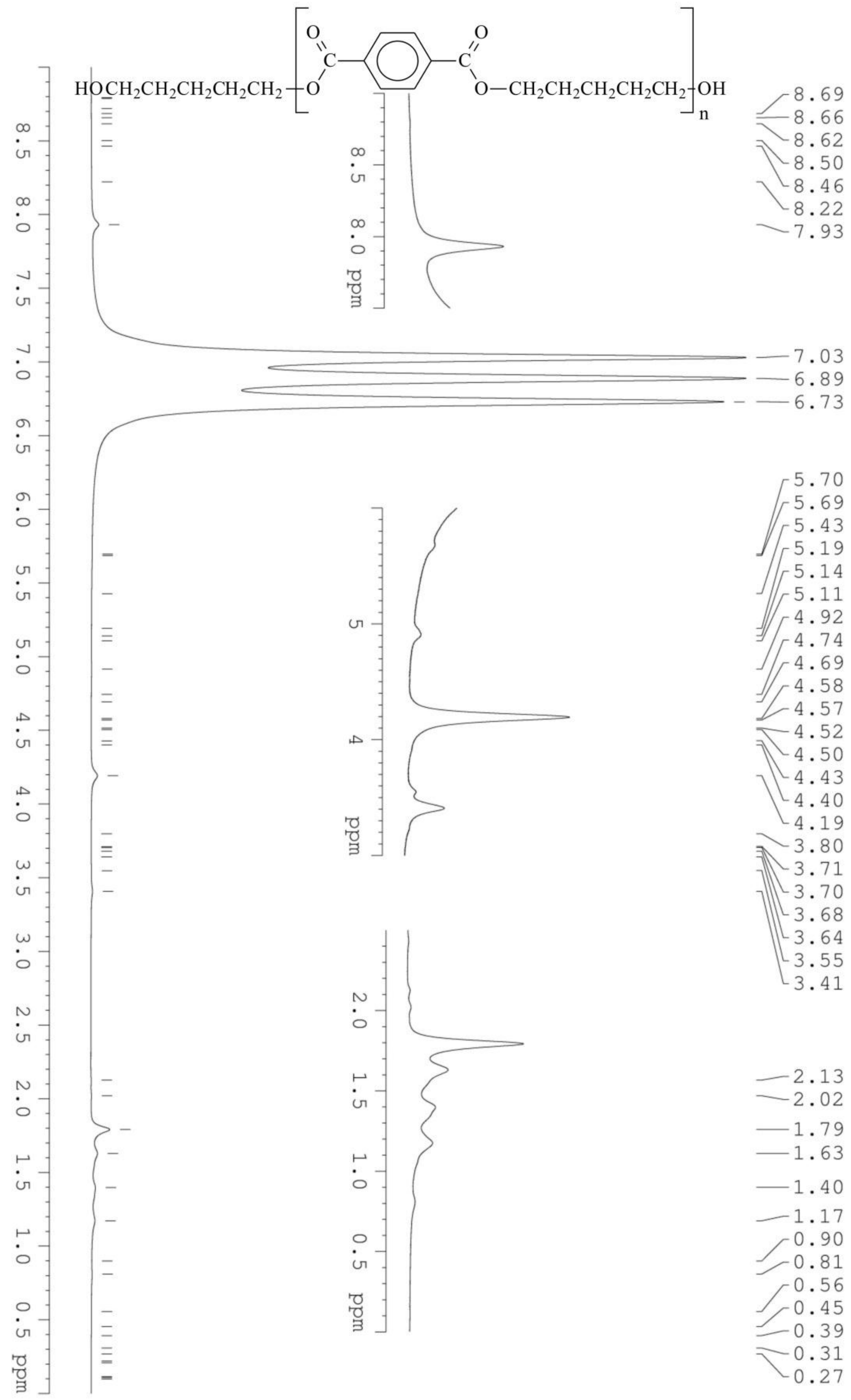
HOCH$_2$CHCH$_2$
CH$_3$
O
C
Br
CH$_2$CHCH$_2$
OH
n
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
134
132
130
128
126
124
122
120
118
116 ppm
134.61
133.57
133.17
132.47
132.31
131.70
131.29
131.20
131.01
130.81
130.57
130.44
130.24
129.99
129.84
129.51
129.41
129.34
129.25
128.78
128.68
128.55
128.45
128.37
128.29
128.15
128.11
127.95
127.70
127.46
126.65
125.88
123.59
120.68
114.98
133.569
133.171
131.703
131.286
131.201
131.010
130.812
130.572
130.443
130.245
129.988
129.836
129.507
129.406
129.340
129.245
128.777
128.677
128.546
128.450
128.370
128.293
128.146
128.114
127.948
127.699
127.465
126.649
125.882
123.588
120.679
114.981

(C) DEPT90

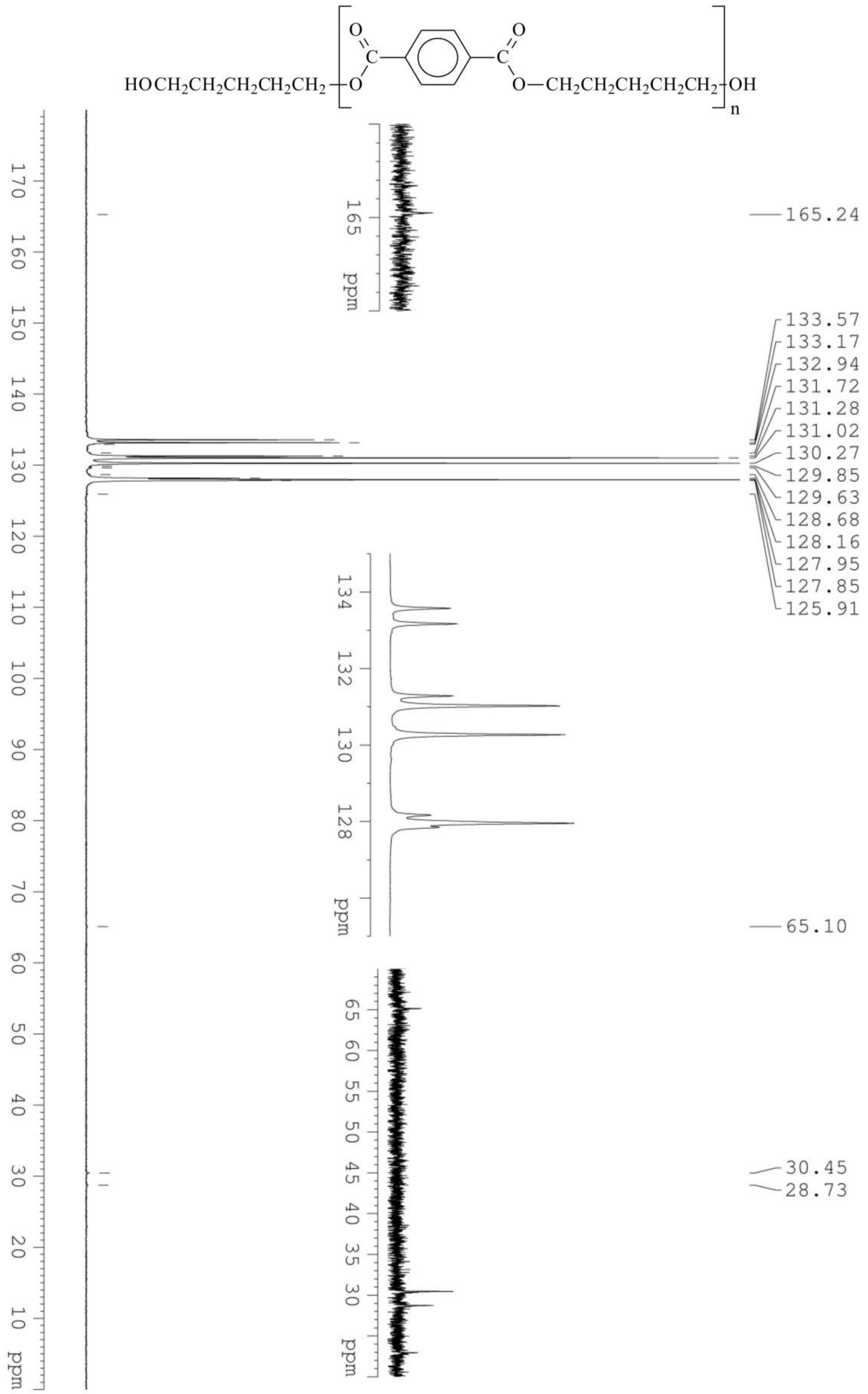


(D) DEPT135

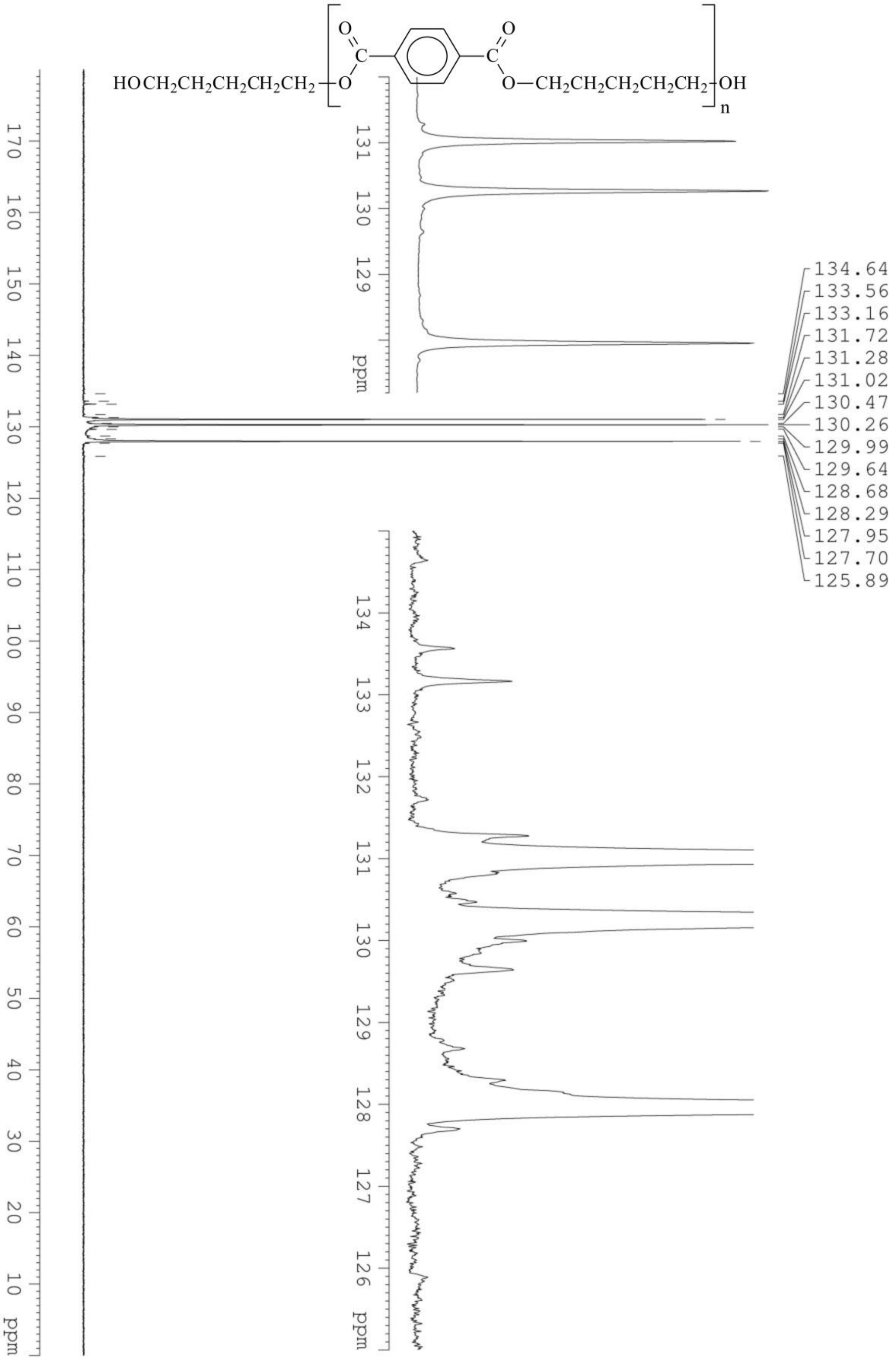
Figure D.16: NMR spectra of Figure 4.12 poly(2-methyl)trimethylene 2-bromoterephthalate


HOCH2CH2CH2CH2CH2CH2–O–C(=O)–C6H4–C(=O)–O–CH2CH2CH2CH2CH2CH2–OH n
8.69
8.66
8.62
8.50
8.46
8.22
7.93
7.03
6.89
6.73
5.70
5.69
5.43
5.19
5.14
5.11
4.92
4.74
4.69
4.58
4.57
4.52
4.50
4.43
4.40
4.19
3.80
3.71
3.70
3.68
3.64
3.55
3.41
2.13
2.02
1.79
1.63
1.40
1.17
0.90
0.81
0.56
0.45
0.39
0.31
0.27
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
8.5 8.0 ppm
5 4 ppm
2.0 1.5 1.0 0.5 ppm

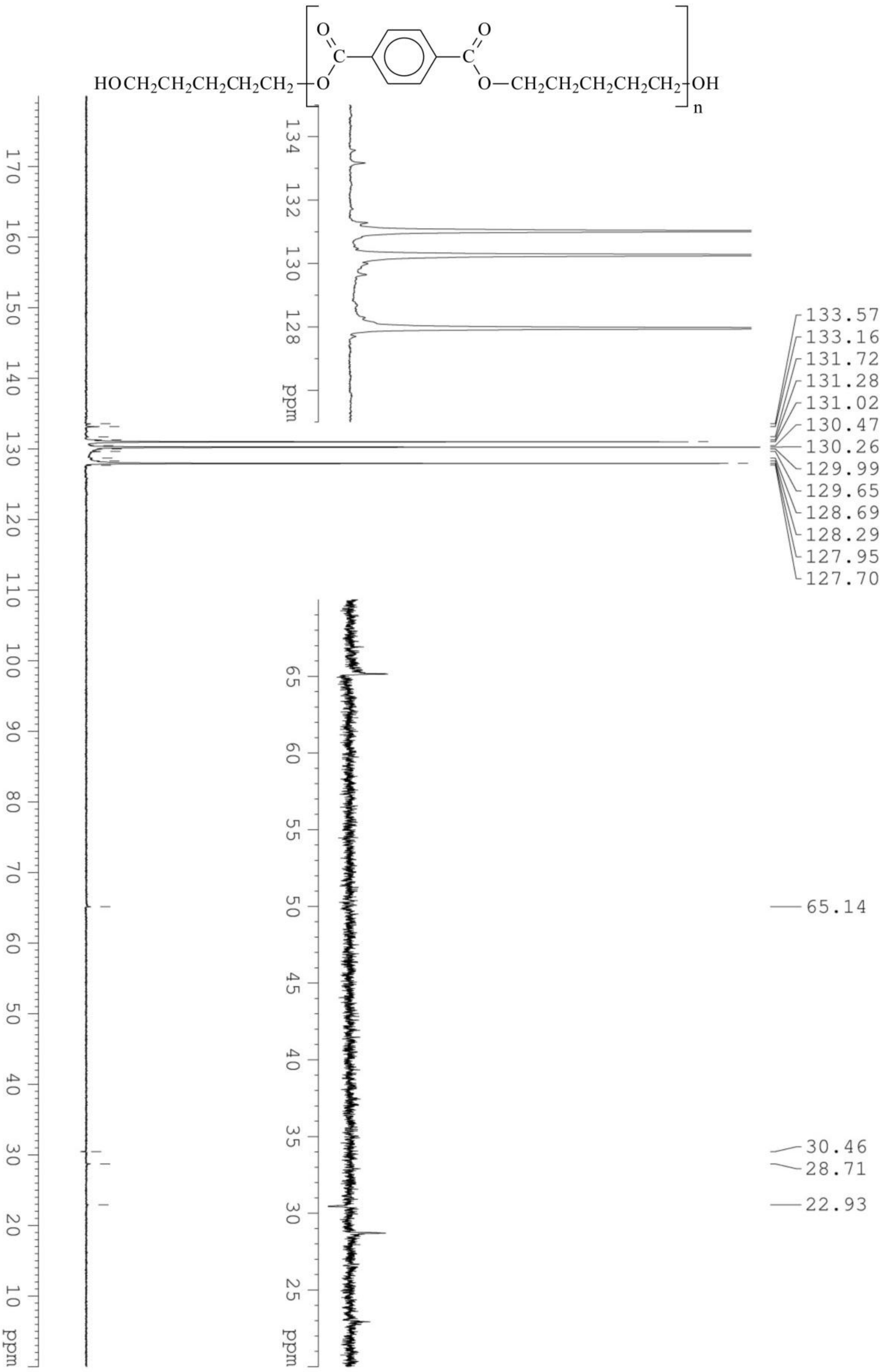
(A) ^{1}HNMR

HOCH2CH2CH2CH2CH2–O
O–CH2CH2CH2CH2CH2–OH
n
165.24
133.57
133.17
132.94
131.72
131.28
131.02
130.27
129.85
129.63
128.68
128.16
127.95
127.85
125.91
65.10
30.45
28.73
ppm

(B) ^{13}CNMR

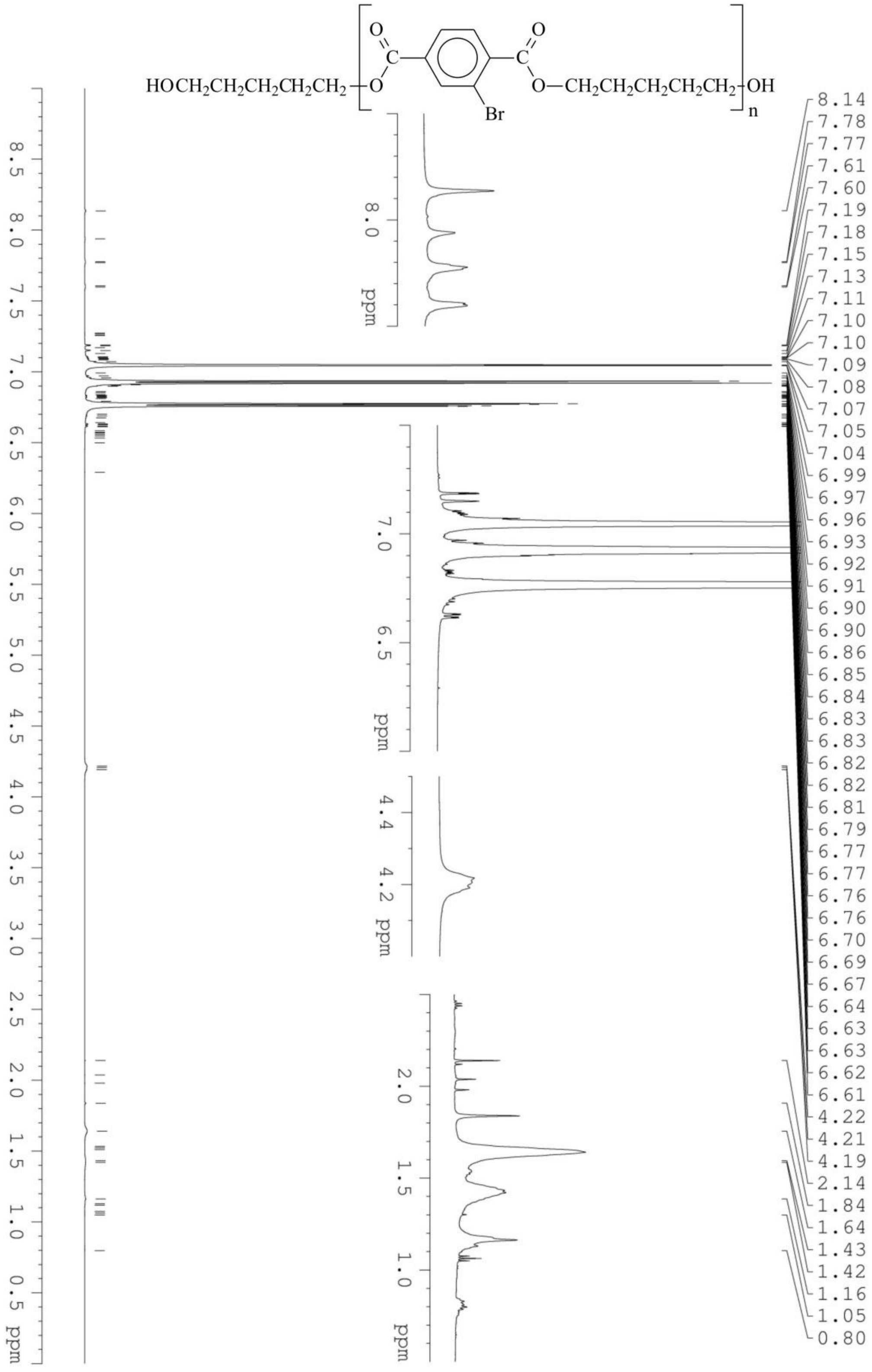

HOCH2CH2CH2CH2CH2 O C O C O O C O CH2CH2CH2CH2CH2 OH n
134.64
133.56
133.16
131.72
131.28
131.02
130.47
130.26
129.99
129.64
128.68
128.29
127.95
127.70
125.89
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
131
130
129
ppm
134
133
132
131
130
129
128
127
126
ppm

(C) DEPT90

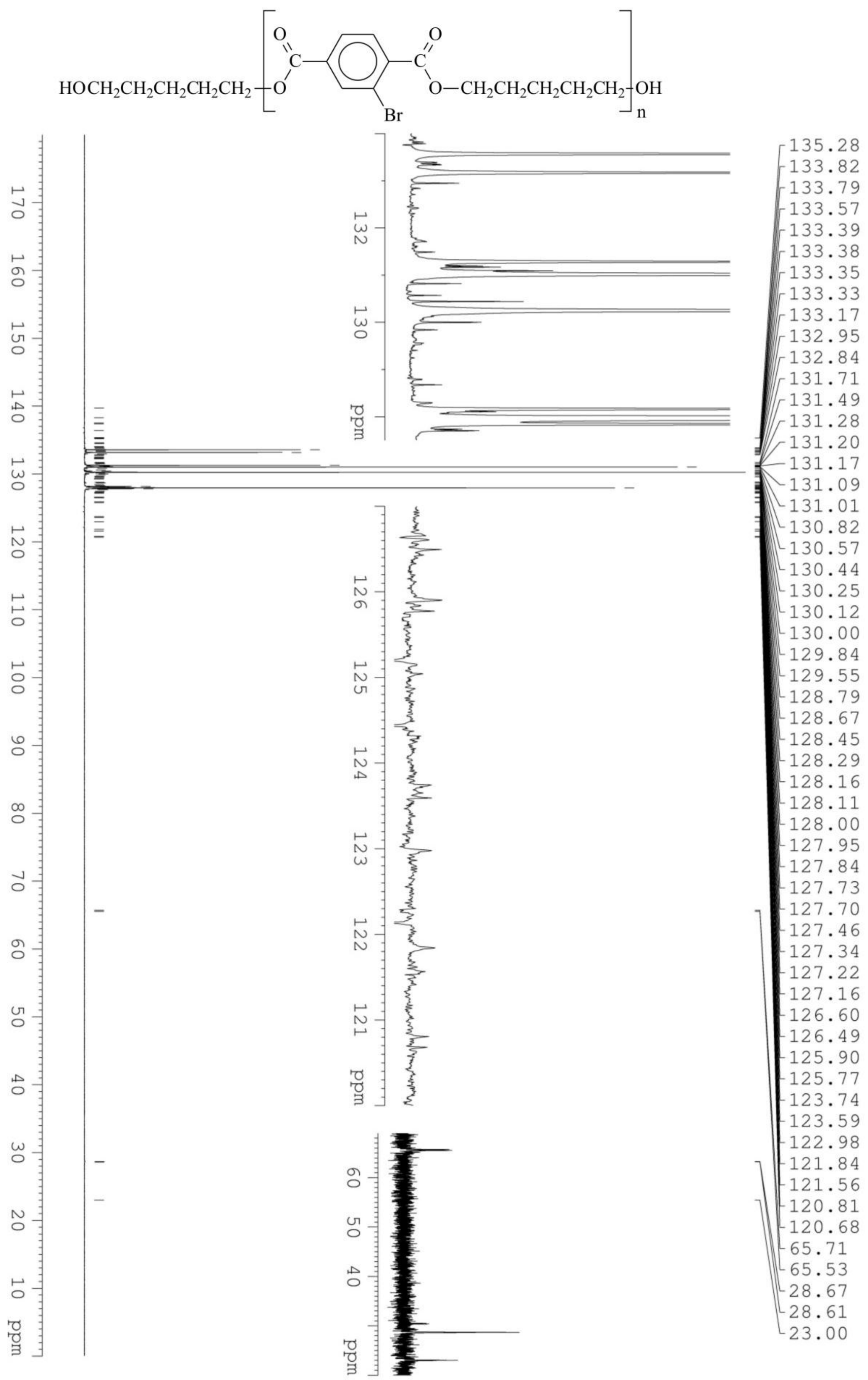


(D) DEPT135

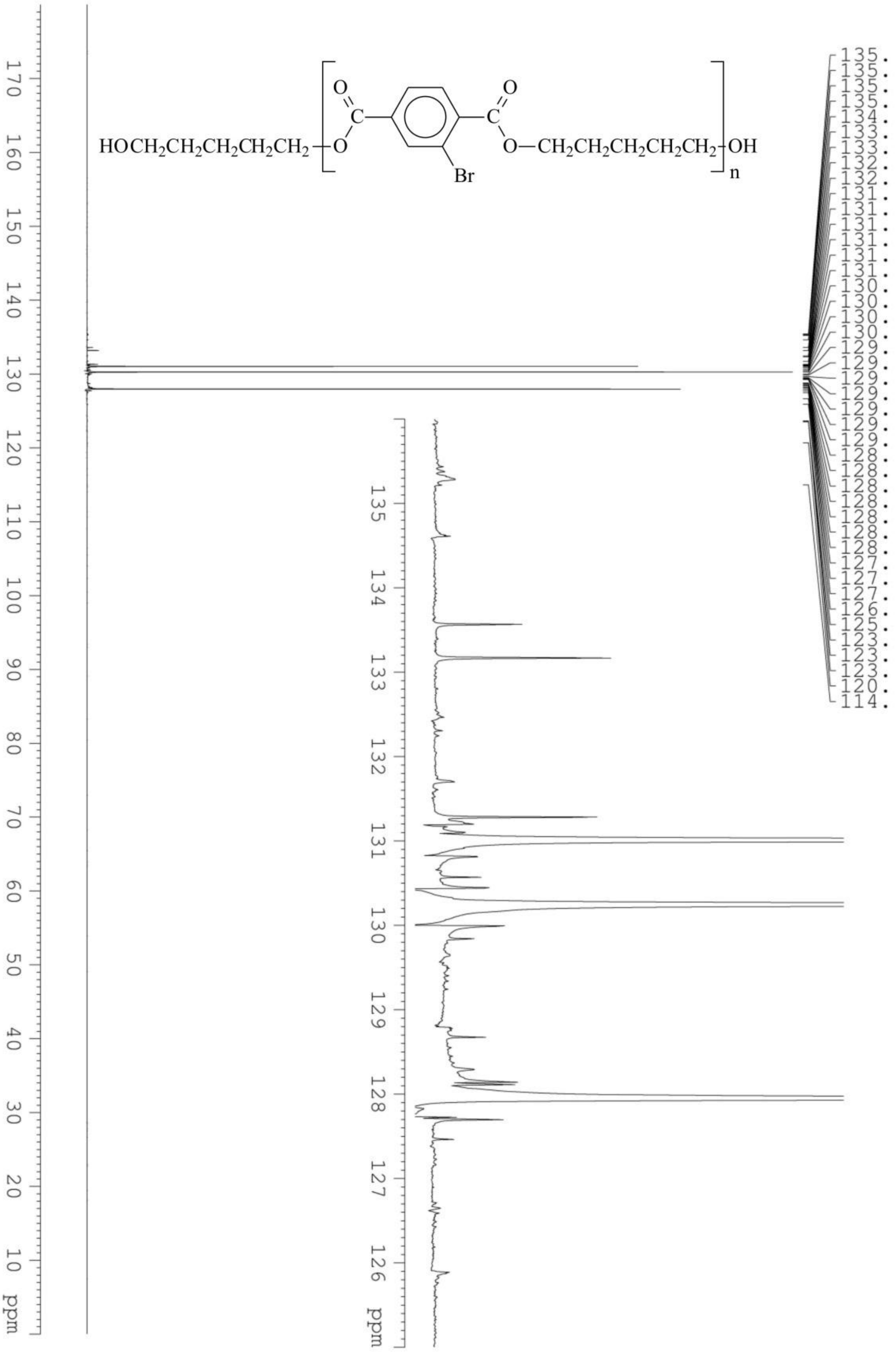
Figure D.17: NMR spectra of Figure 4.13 polypentamethylene terephthalate


HOCH₂CH₂CH₂CH₂CH₂–O–C(=O)–C₆H₃(Br)–C(=O)–O–CH₂CH₂CH₂CH₂CH₂–OH
n
8.14
7.78
7.77
7.61
7.60
7.19
7.18
7.15
7.13
7.11
7.10
7.10
7.09
7.08
7.07
7.05
7.04
6.99
6.97
6.96
6.93
6.92
6.91
6.90
6.90
6.86
6.85
6.84
6.83
6.83
6.82
6.82
6.81
6.79
6.77
6.77
6.76
6.76
6.70
6.69
6.67
6.64
6.63
6.63
6.62
6.61
4.22
4.21
4.19
2.14
1.84
1.64
1.43
1.42
1.16
1.05
0.80
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

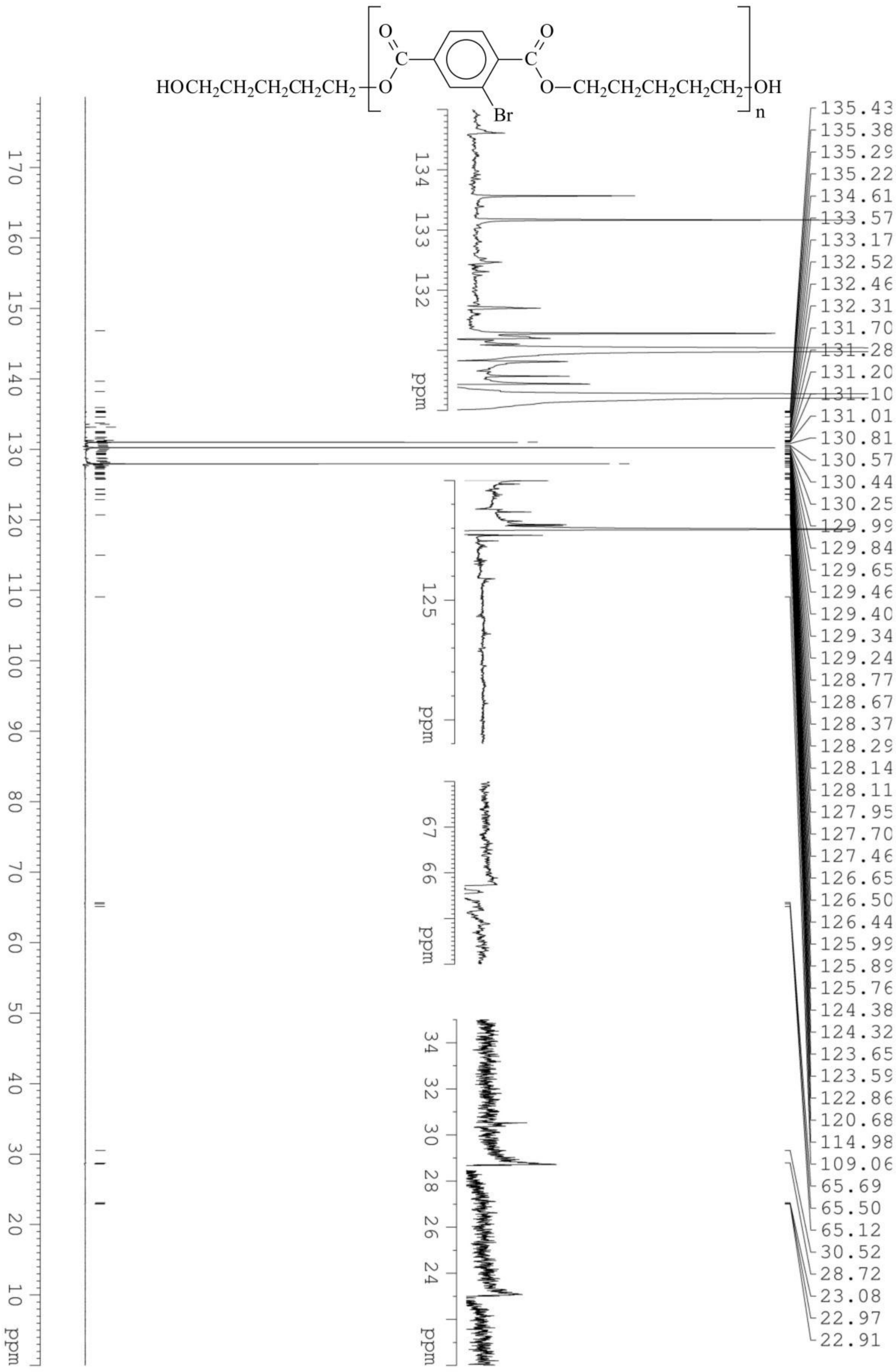
(A) ^{1}HNMR


HOCH2CH2CH2CH2CH2
O
C
O
Br
C
O
O—CH2CH2CH2CH2CH2
OH
n
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
132
130
ppm
126
125
124
123
122
121
ppm
60
50
40
ppm
135.28
133.82
133.79
133.57
133.39
133.38
133.35
133.33
133.17
132.95
132.84
131.71
131.49
131.28
131.20
131.17
131.09
131.01
130.82
130.57
130.44
130.25
130.12
130.00
129.84
129.55
128.79
128.67
128.45
128.29
128.16
128.11
128.00
127.95
127.84
127.73
127.70
127.46
127.34
127.22
127.16
126.60
126.49
125.90
125.77
123.74
123.59
122.98
121.84
121.56
120.81
120.68
65.71
65.53
28.67
28.61
23.00

(B) ^{13}CNMR

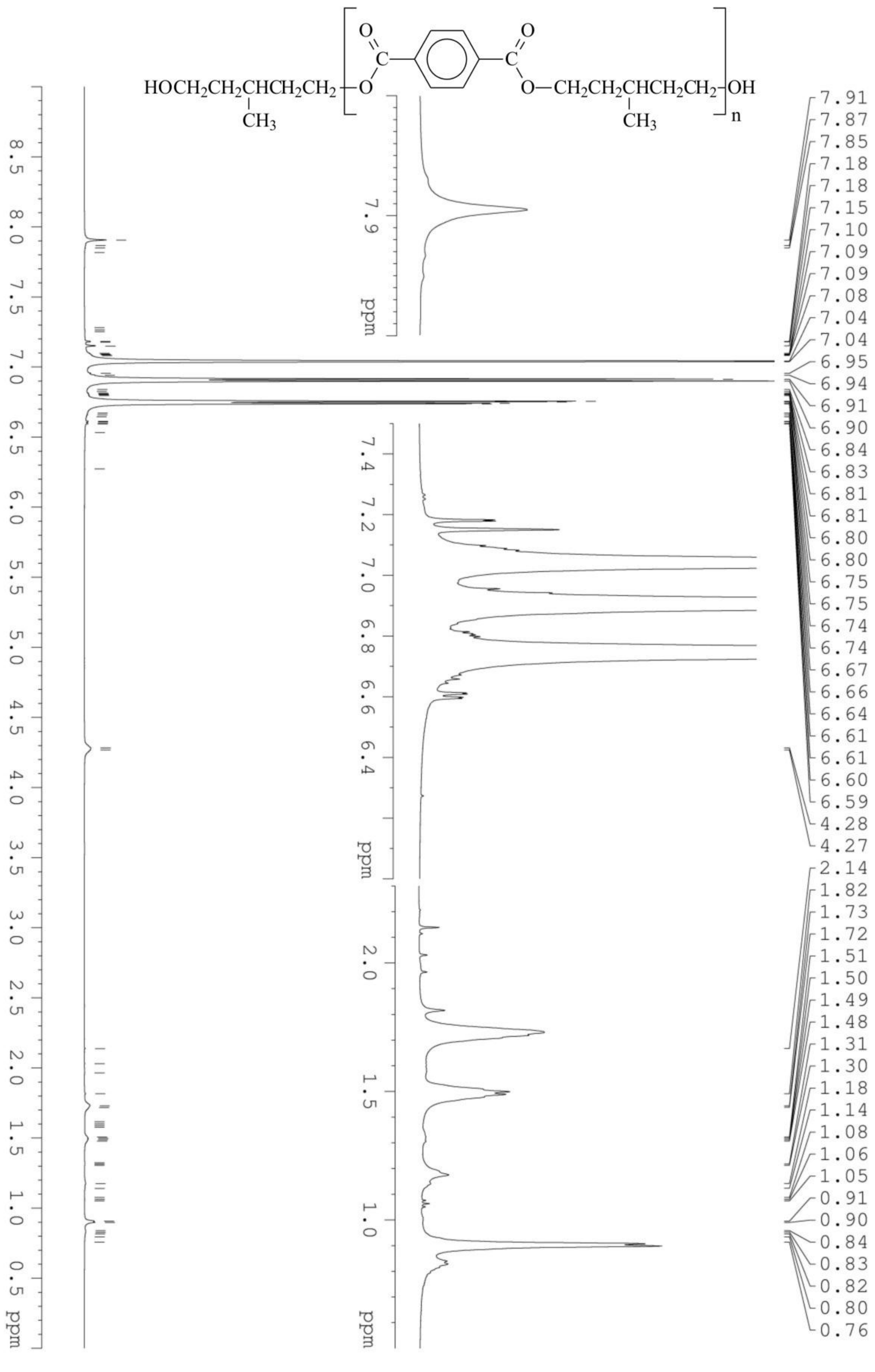

HOCH2CH2CH2CH2CH2
O
C
O
Br
O
C
O
CH2CH2CH2CH2CH2
OH
n
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
135
134
133
132
131
130
129
128
127
126
ppm

(C) DEPT90

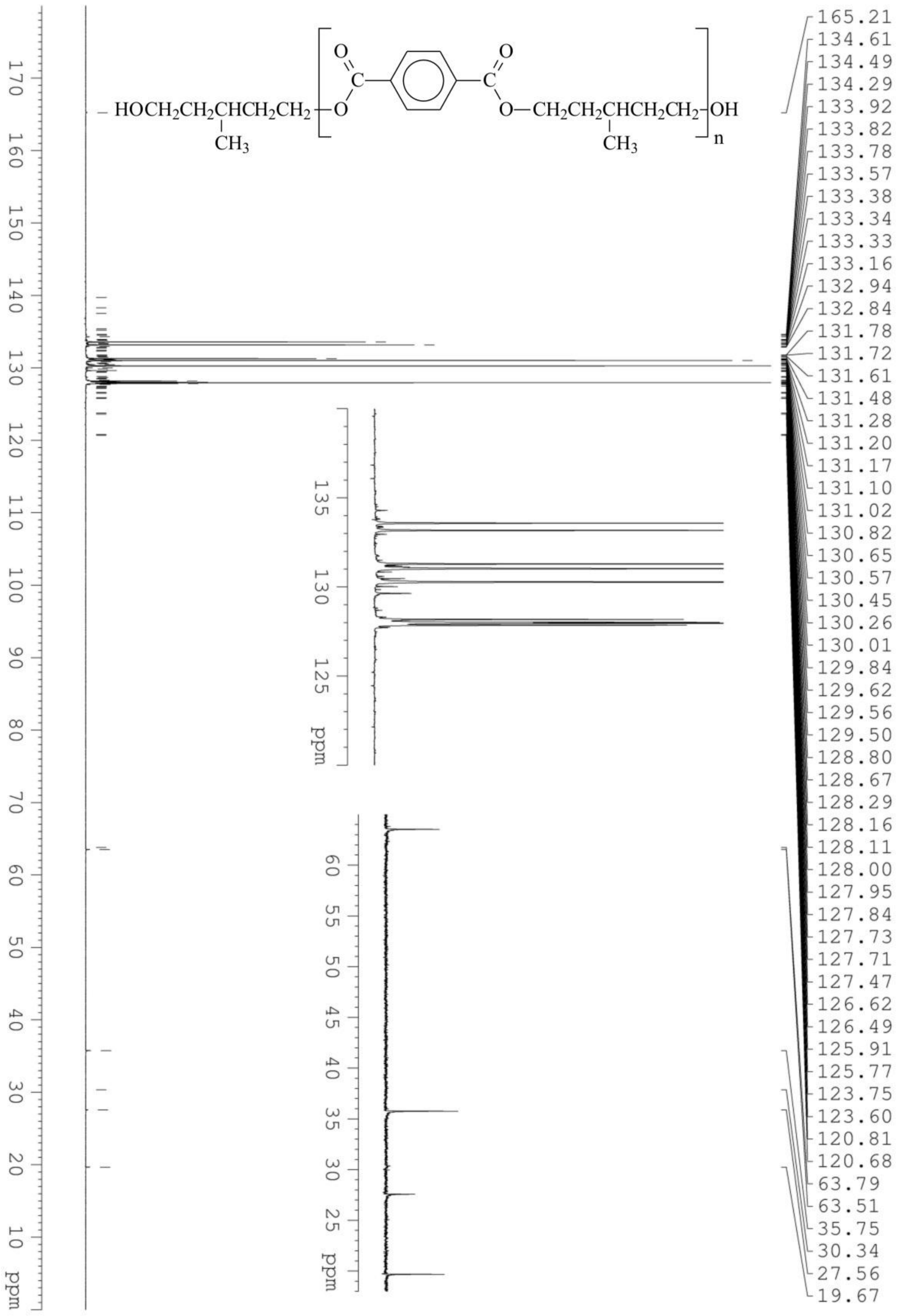


(D) DEPT135

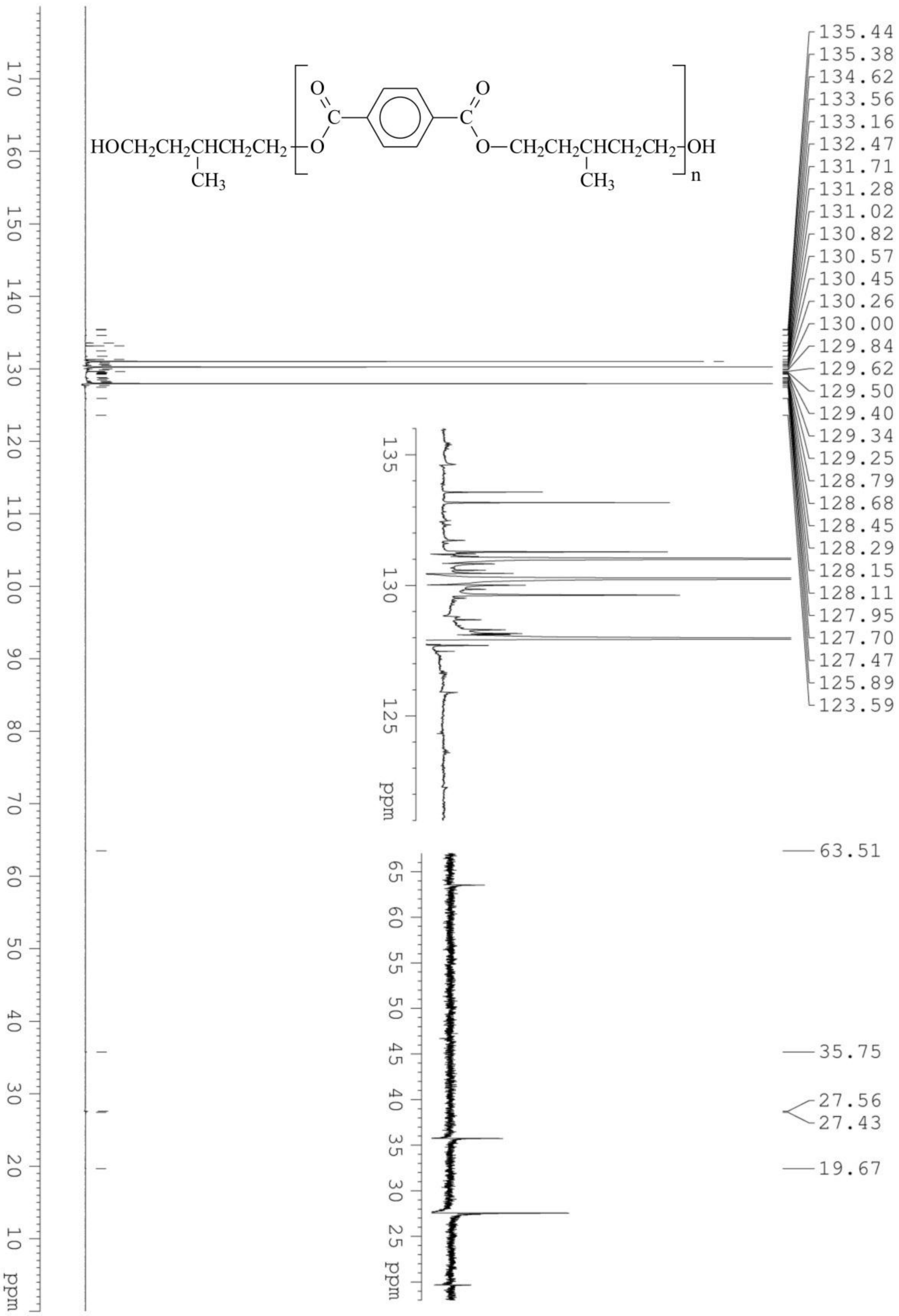
Figure D.18: NMR spectra of Figure 4.14 polypentamethylene 2-bromoterephthalate


HOCH2CH2CHCH2CH2 O C O C O O O CH2CH2CHCH2CH2 OH
CH3
CH3
n
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm
7.9
ppm
7.4
7.2
7.0
6.8
6.6
6.4
ppm
2.0
1.5
1.0
ppm
7.91
7.87
7.85
7.18
7.18
7.15
7.10
7.09
7.09
7.08
7.04
7.04
6.95
6.94
6.91
6.90
6.84
6.83
6.81
6.81
6.80
6.80
6.75
6.75
6.74
6.74
6.67
6.66
6.64
6.61
6.61
6.60
6.59
4.28
4.27
2.14
1.82
1.73
1.72
1.51
1.50
1.49
1.48
1.31
1.30
1.18
1.14
1.08
1.06
1.05
0.91
0.90
0.84
0.83
0.82
0.80
0.76

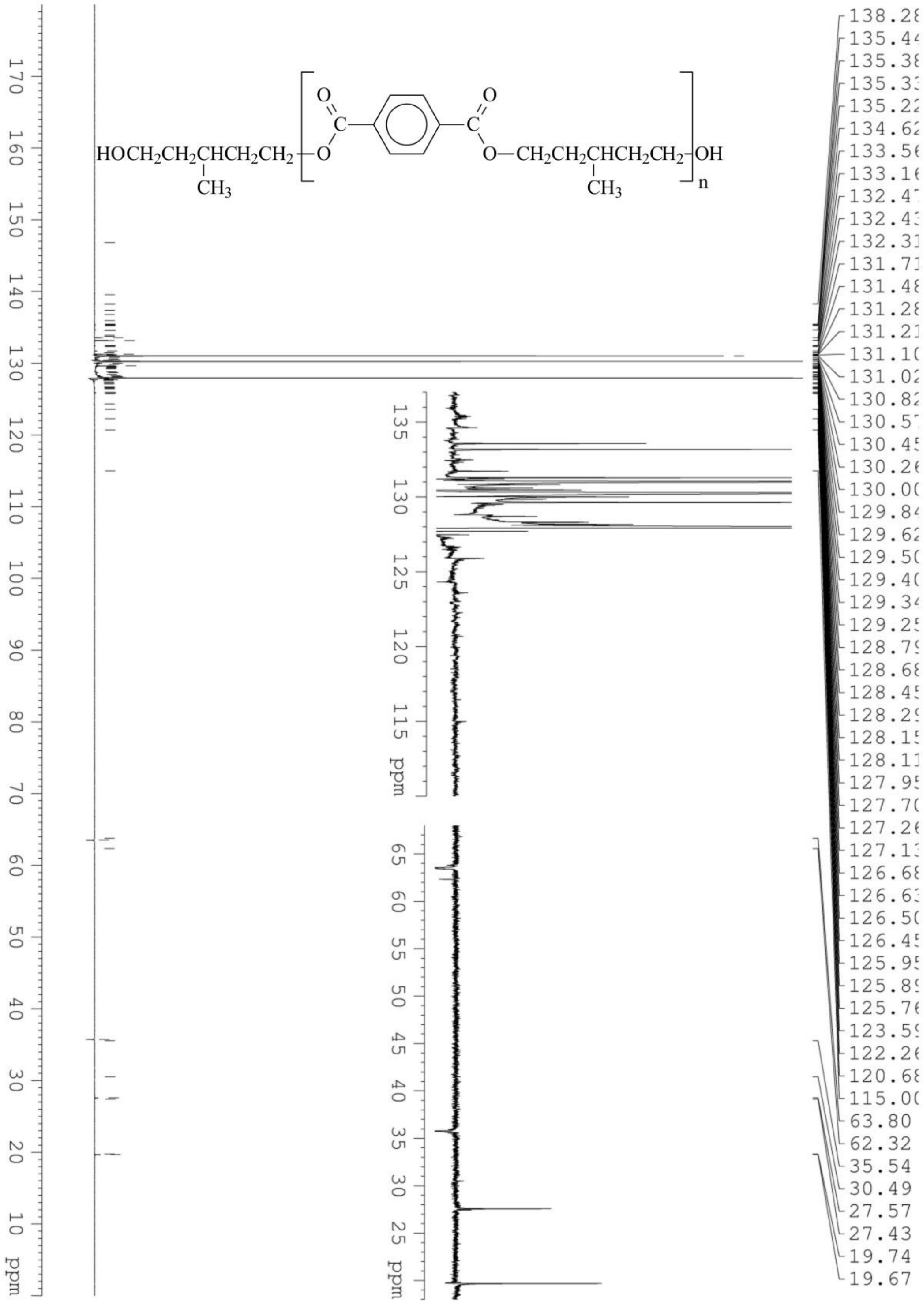
(A) ^{1}HNMR


HOCH2CH2CHCH2CH2 O C O C O O CH2CH2CHCH2CH2 OH
CH3
CH3
n
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
135
130
125
ppm
60
55
50
45
40
35
30
25
ppm
165.21
134.61
134.49
134.29
133.92
133.82
133.78
133.57
133.38
133.34
133.33
133.16
132.94
132.84
131.78
131.72
131.61
131.48
131.28
131.20
131.17
131.10
131.02
130.82
130.65
130.57
130.45
130.26
130.01
129.84
129.62
129.56
129.50
128.80
128.67
128.29
128.16
128.11
128.00
127.95
127.84
127.73
127.71
127.47
126.62
126.49
125.91
125.77
123.75
123.60
120.81
120.68
63.79
63.51
35.75
30.34
27.56
19.67

(B) ^{13}CNMR

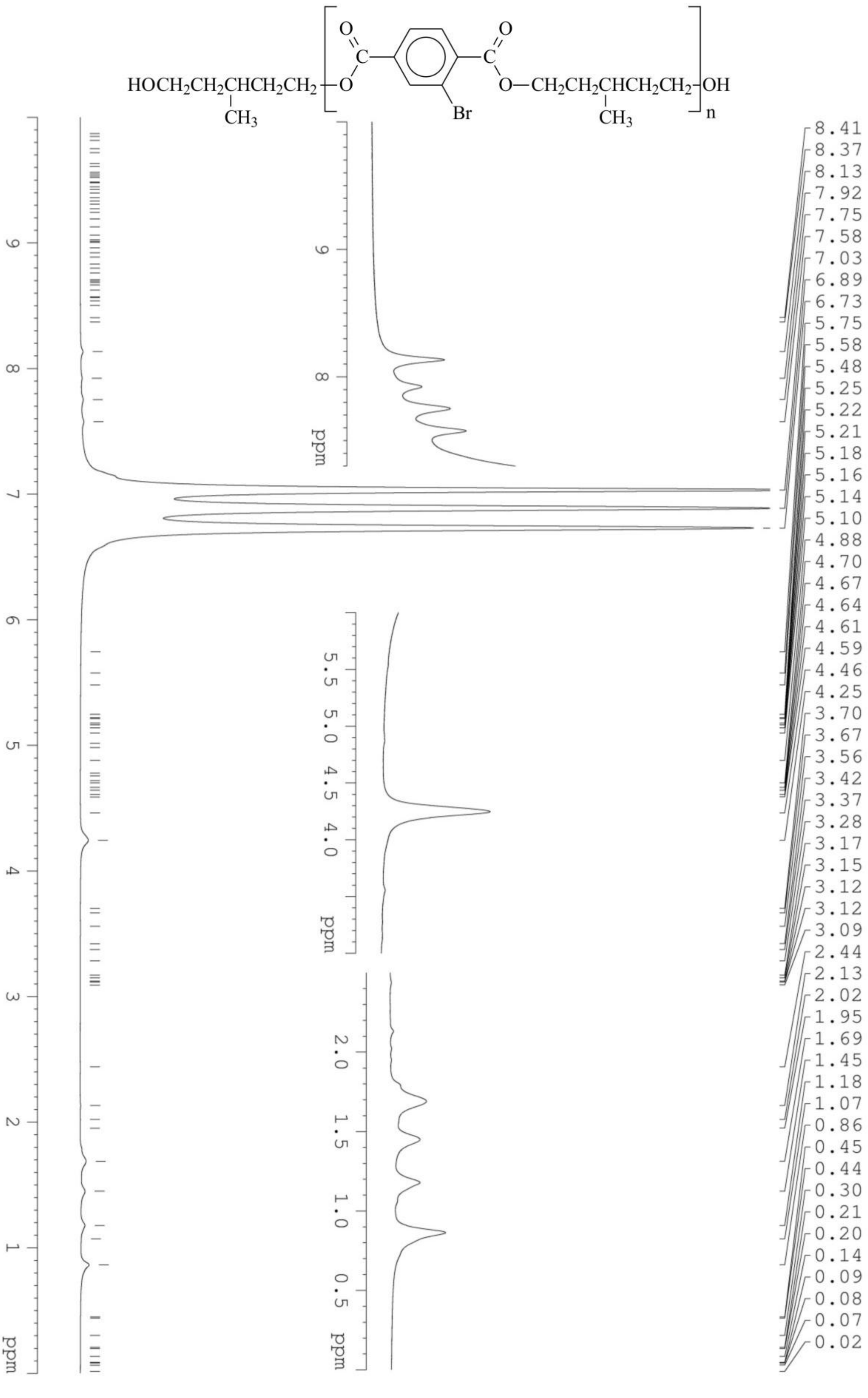

HOCH₂CH₂CHCH₂CH₂ O C O C O O—CH₂CH₂CHCH₂CH₂ OH
CH₃
CH₃
n
135.44
135.38
134.62
133.56
133.16
132.47
131.71
131.28
131.02
130.82
130.57
130.45
130.26
130.00
129.84
129.62
129.50
129.40
129.34
129.25
128.79
128.68
128.45
128.29
128.15
128.11
127.95
127.70
127.47
125.89
123.59
63.51
35.75
27.56
27.43
19.67
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
135
130
125
ppm
65
60
55
50
45
40
35
30
25
ppm

(C) DEPT90

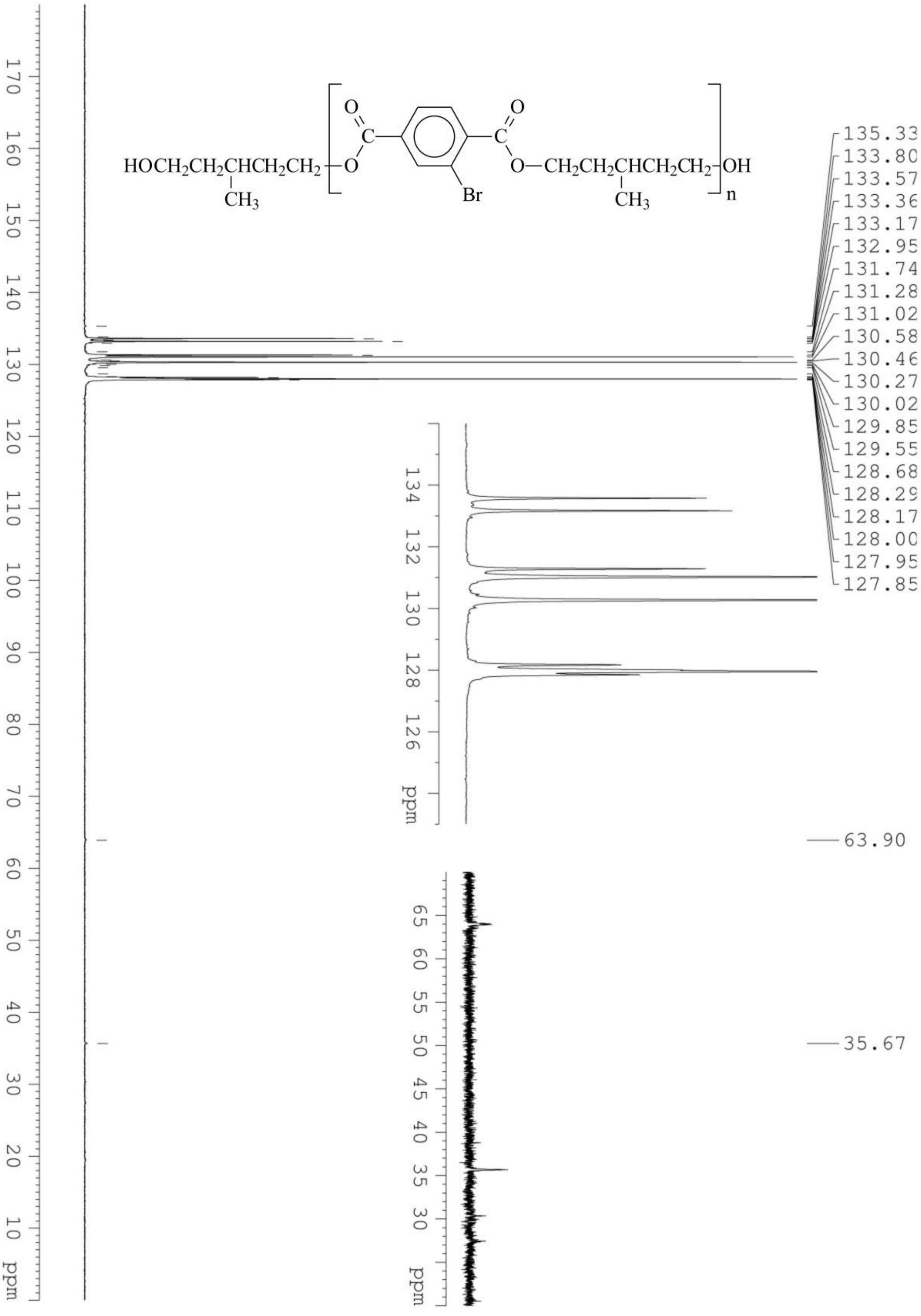


(D) DEPT135

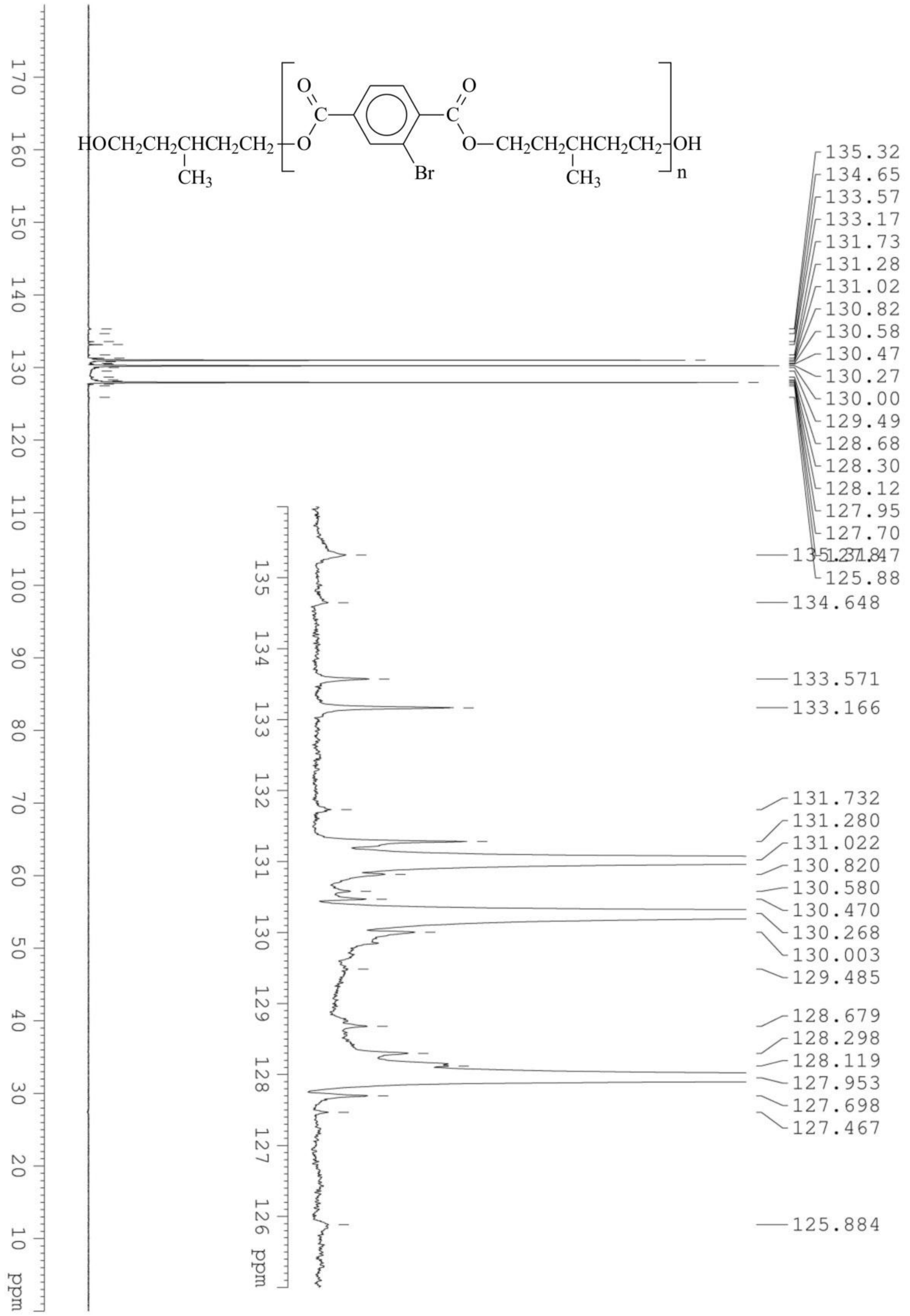
Figure D.19: NMR spectra of Figure 4.15 poly(3-methyl)pentamethylene terephthalate


HOCH₂CH₂CHCH₂CH₂
CH₃
O
C
O
Br
O—CH₂CH₂CHCH₂CH₂
OH
n
ppm
8.41
8.37
8.13
7.92
7.75
7.58
7.03
6.89
6.73
5.75
5.58
5.48
5.25
5.22
5.21
5.18
5.16
5.14
5.10
4.88
4.70
4.67
4.64
4.61
4.59
4.46
4.25
3.70
3.67
3.56
3.42
3.37
3.28
3.17
3.15
3.12
3.12
3.09
2.44
2.13
2.02
1.95
1.69
1.45
1.18
1.07
0.86
0.45
0.44
0.30
0.21
0.20
0.14
0.09
0.08
0.07
0.02

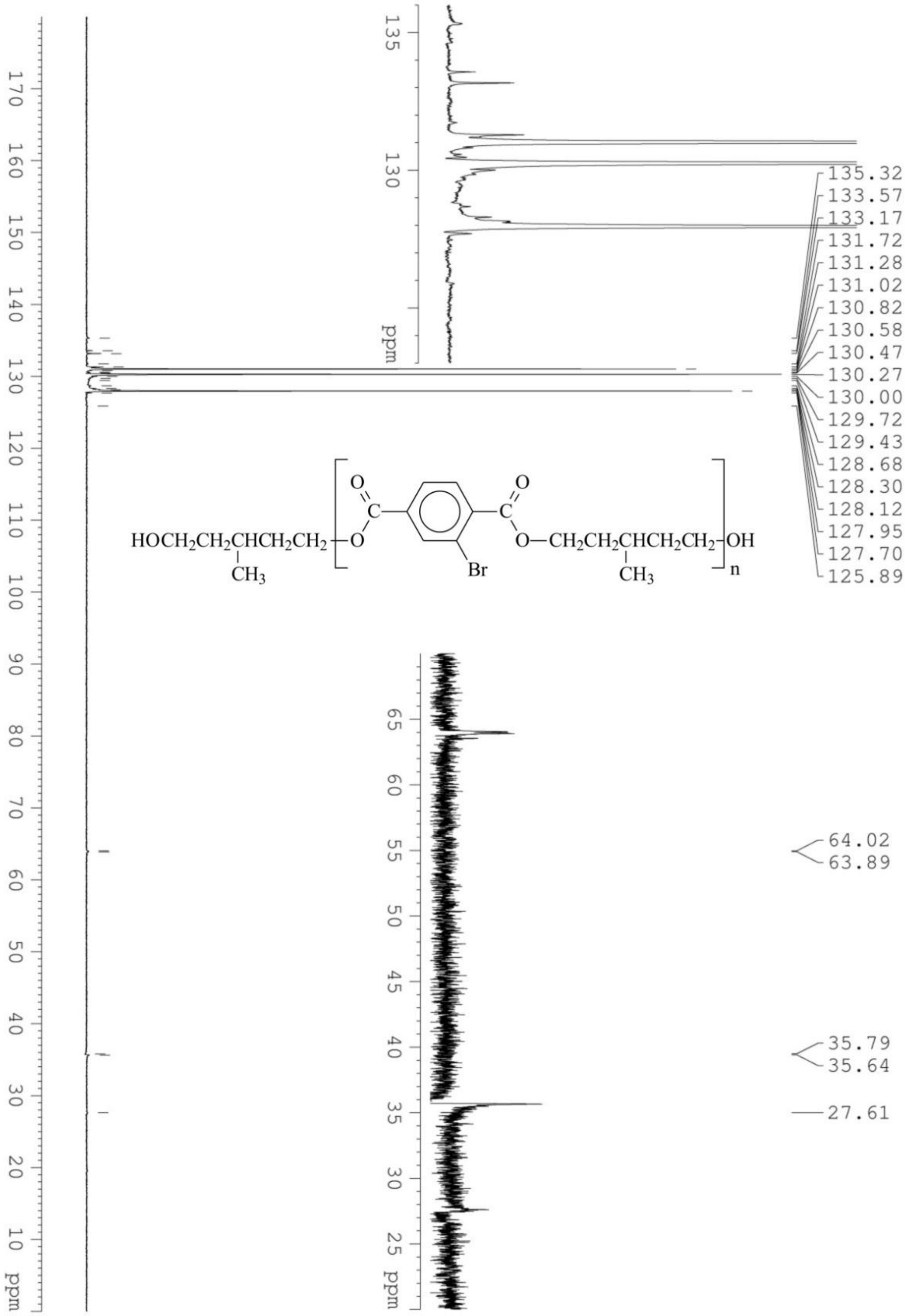
(A) ^{1}HNMR


HOCH2CH2CHCH2CH2 O C O C O Br O C O CH2CH2CHCH2CH2 OH n CH3 CH3
135.33
133.80
133.57
133.36
133.17
132.95
131.74
131.28
131.02
130.58
130.46
130.27
130.02
129.85
129.55
128.68
128.29
128.17
128.00
127.95
127.85
63.90
35.67
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
134 132 130 128 126 ppm
65 60 55 50 45 40 35 30 ppm

(B) ^{13}CNMR


HOCH₂CH₂CHCH₂CH₂–O–C(=O)–C₆H₃(Br)–C(=O)–O–CH₂CH₂CHCH₂CH₂–OH
CH₃
CH₃
Br
n
135.32
134.65
133.57
133.17
131.73
131.28
131.02
130.82
130.58
130.47
130.27
130.00
129.49
128.68
128.30
128.12
127.95
127.70
127.47
125.88
135.318
134.648
133.571
133.166
131.732
131.280
131.022
130.820
130.580
130.470
130.268
130.003
129.485
128.679
128.298
128.119
127.953
127.698
127.467
125.884
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
135
134
133
132
131
130
129
128
127
126
ppm

(C) DEPT90



(D) DEPT135

Figure D.20: NMR spectra of Figure 4.16 poly(3-methyl)pentamethylene 2-bromoterephthalate

Appendix E: TGA /DTG

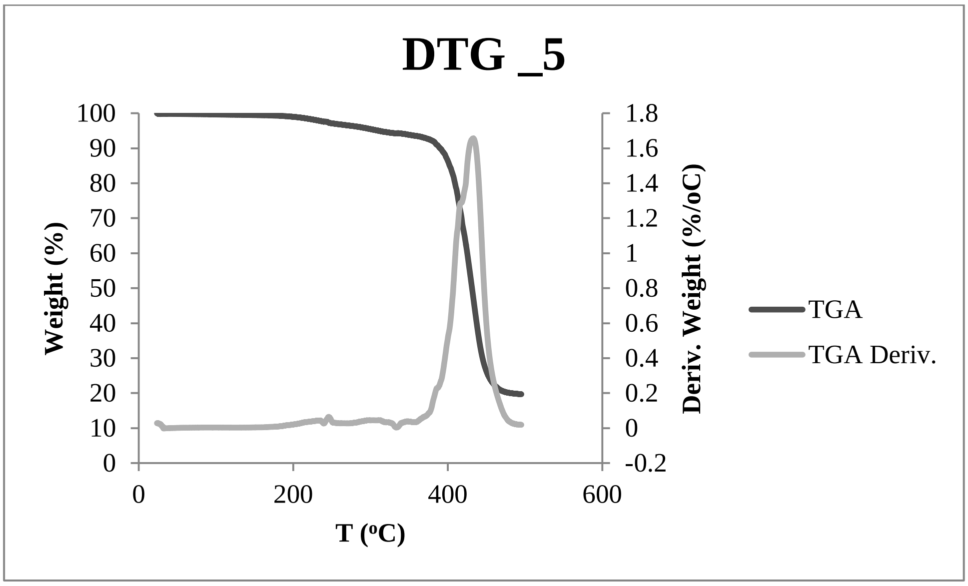


Figure E.1: DTG thermogram of Figure 4.5 polyethylene terephthalate

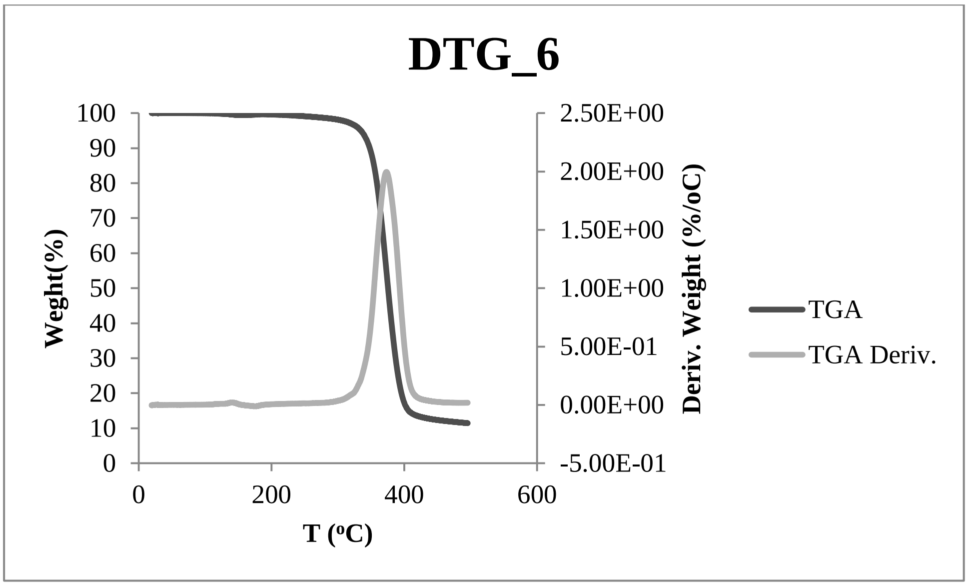


Figure E.2: DTG thermogram of Figure 4.6 poly(1,2-propanediol) terephthalate

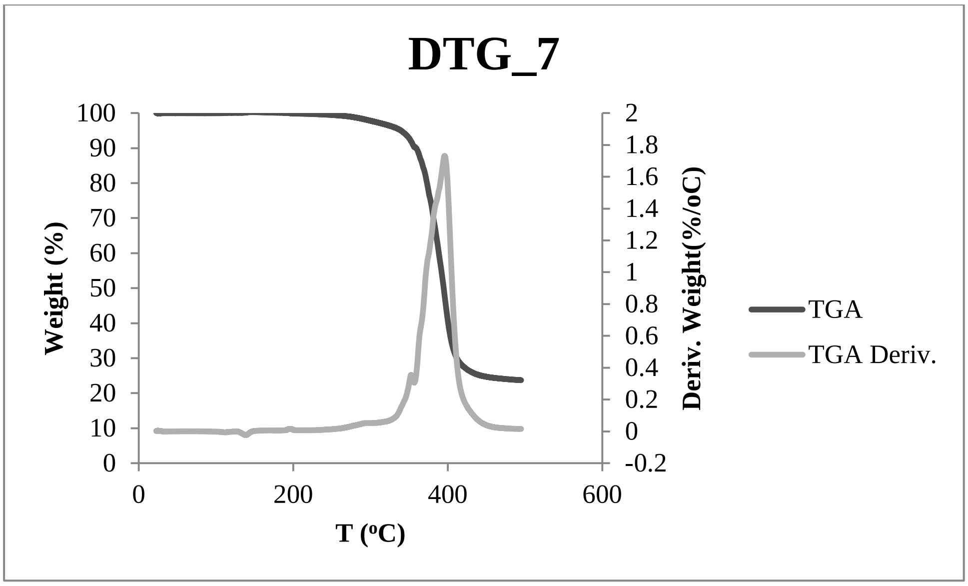


Figure E.3: DTG thermogram of Figure 4.7 polyethylene 2-bromoterephthalate

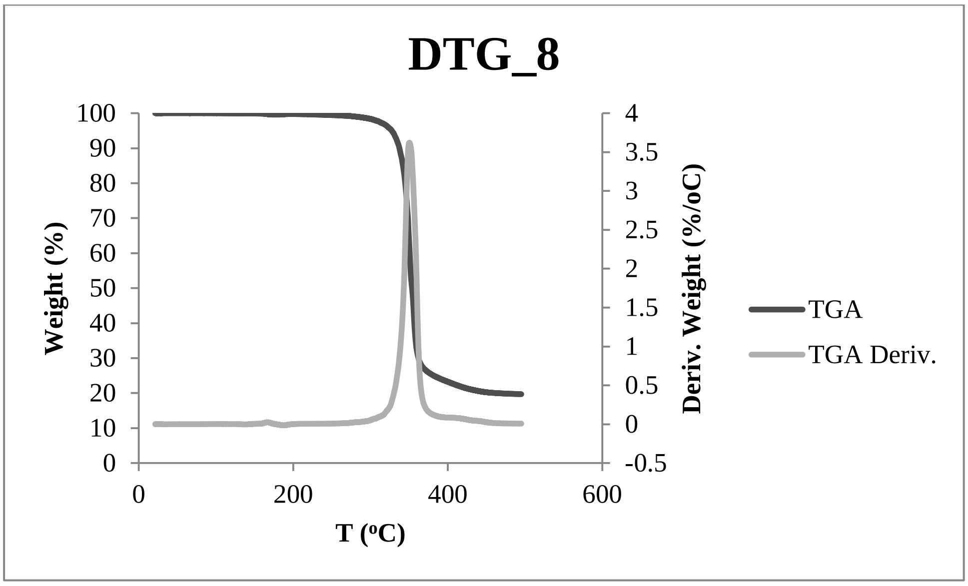


Figure E.4: DTG thermogram of Figure 4.8 poly(1,2-propanediol) 2-bromoterephthalate

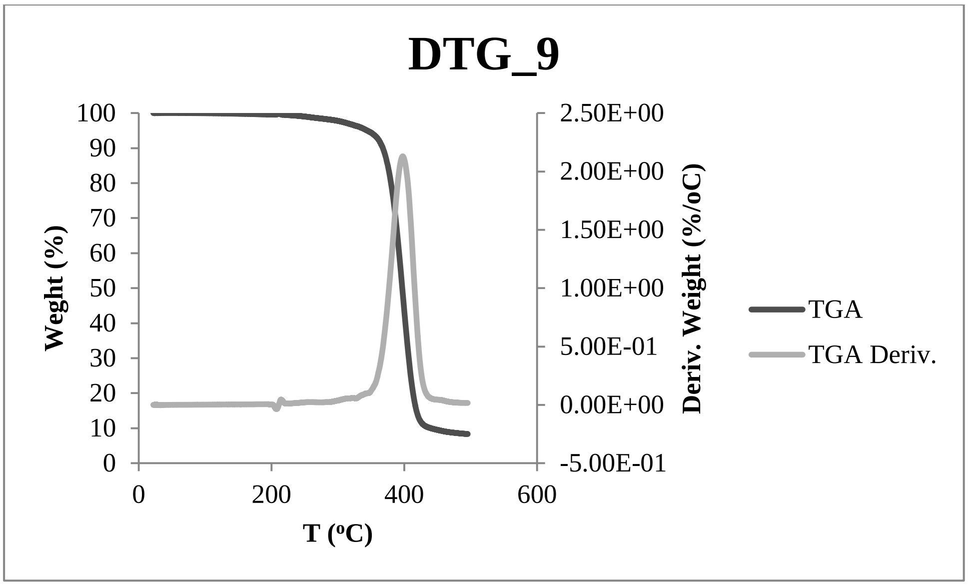


Figure E.5: DTG thermogram of Figure 4.9 polypropylene terephthalate

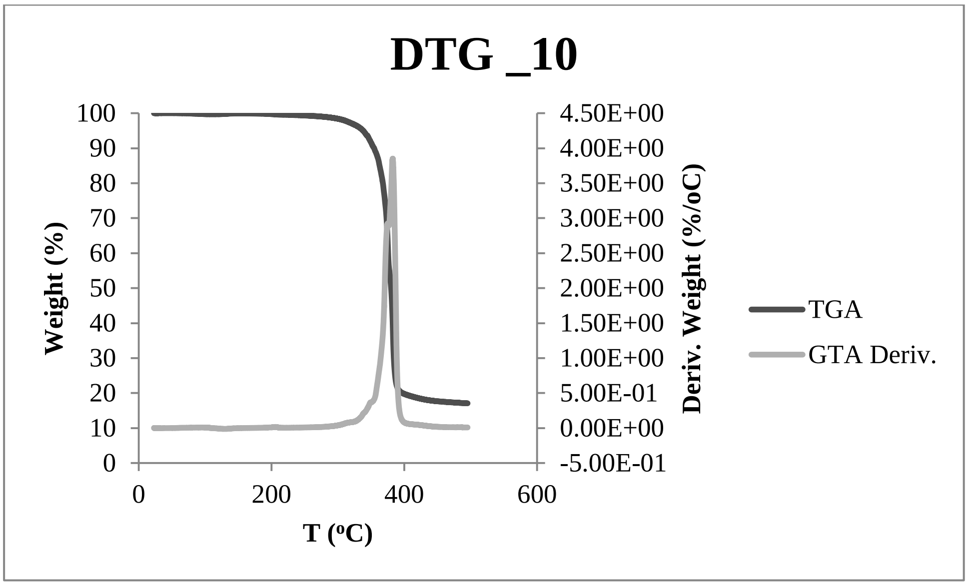


Figure E.6: DTG thermogram of Figure 4.10 polypropylene 2-bromoterephthalate

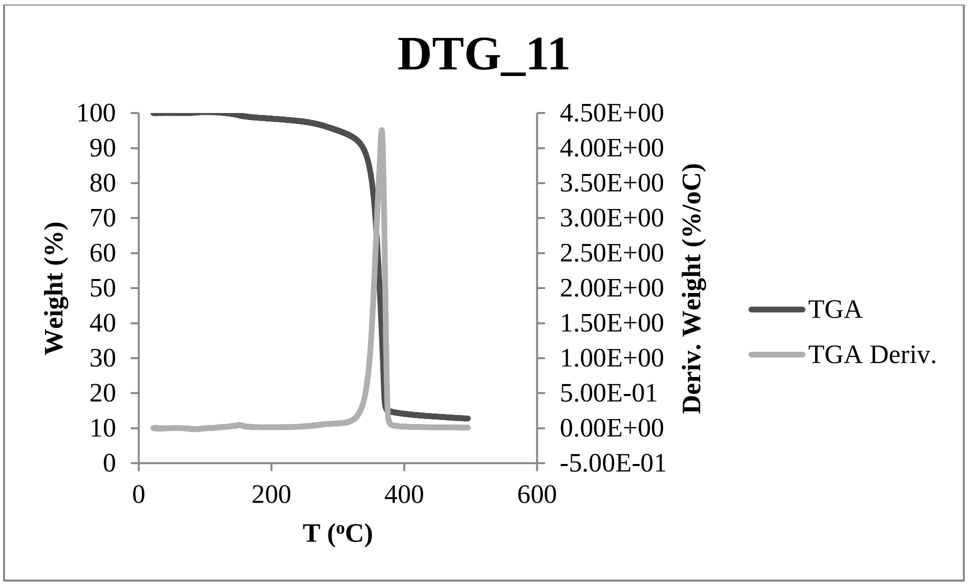


Figure E.7: DTG thermogram of Figure 4.11 poly(2-methyl)trimethylene terephthalate

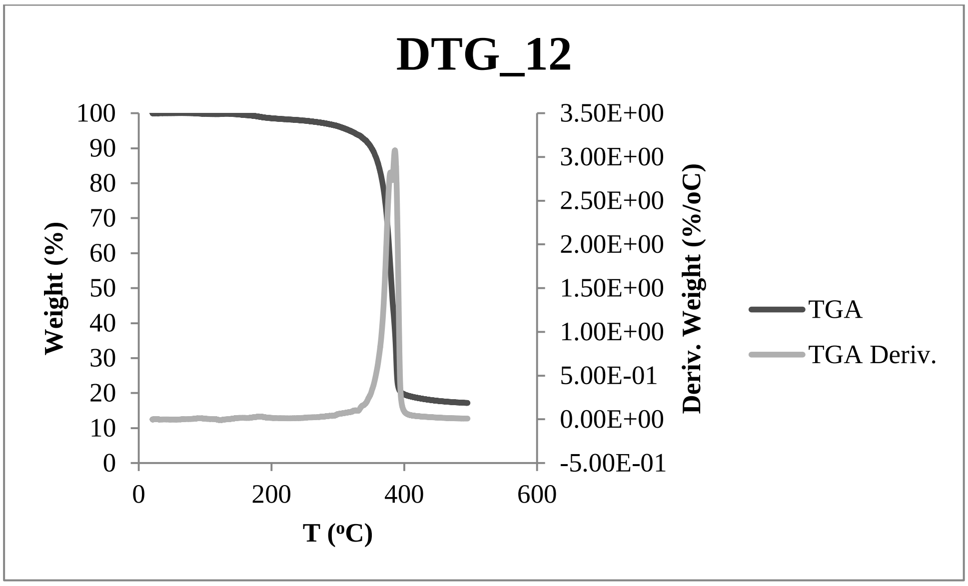


Figure E.8: DTG thermogram of Figure 4.12 poly(2-methyl)trimethylene 2-bromoterephthalate

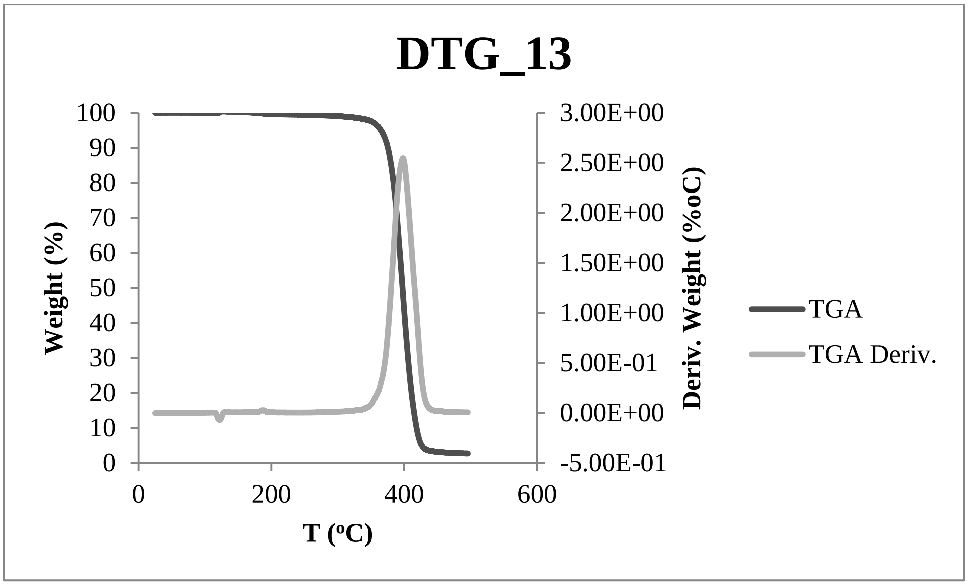


Figure E.9: DTG thermogram of Figure 4.13 polypentamethylene terephthalate

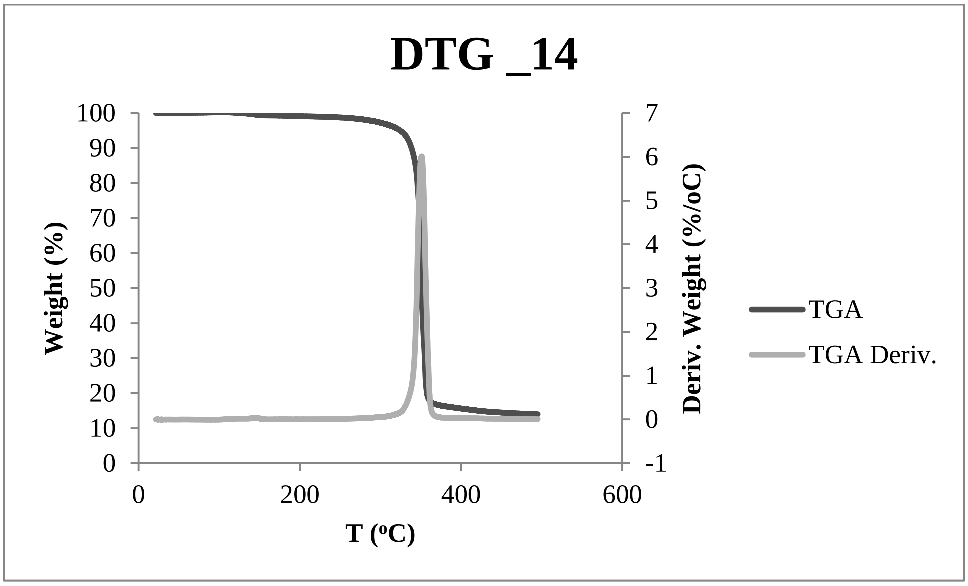


Figure E.10: DTG thermogram of Figure 4.14 polypentamethylene 2-bromoterephthalate

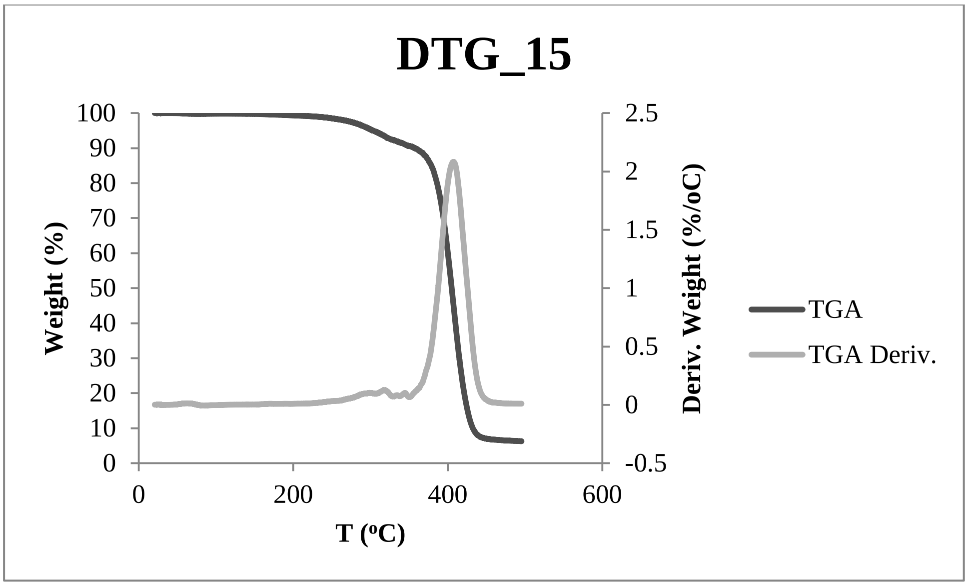


Figure E.11: DTG thermogram of Figure 4.15 poly(3-methyl)pentamethylene terephthalate

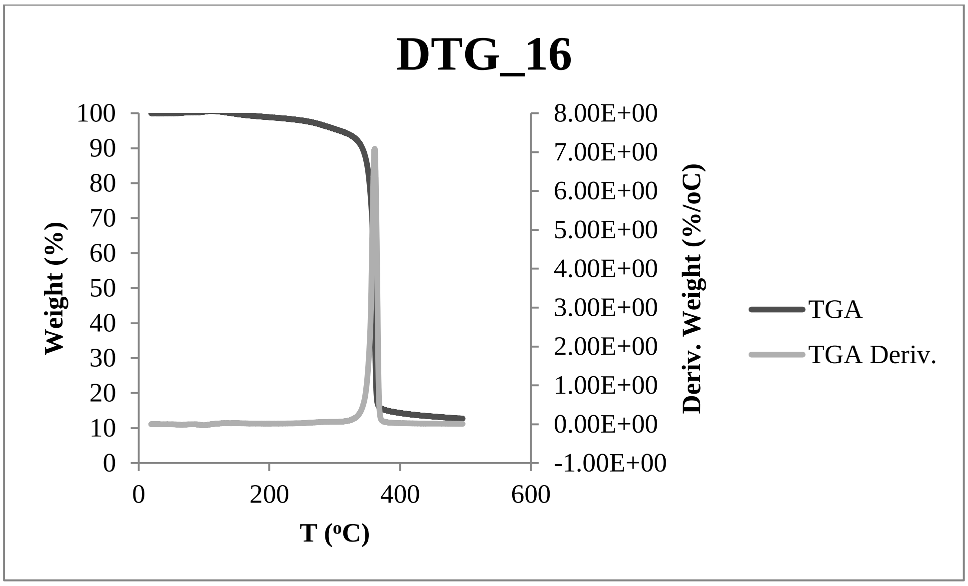


Figure E.12: DTG thermogram of Figure 4.16 poly(3-methyl)pentamethylene 2-bromoterephthalate

Appendix F: DSC

Please note (Exo up)

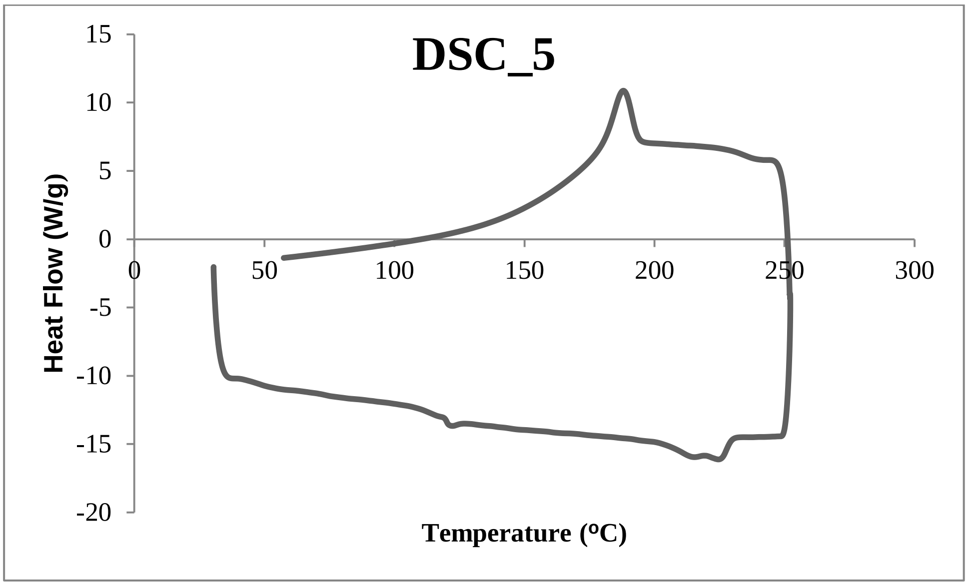


Figure F.1: DSC thermogram of Figure 4.5 polyethylene terephthalate

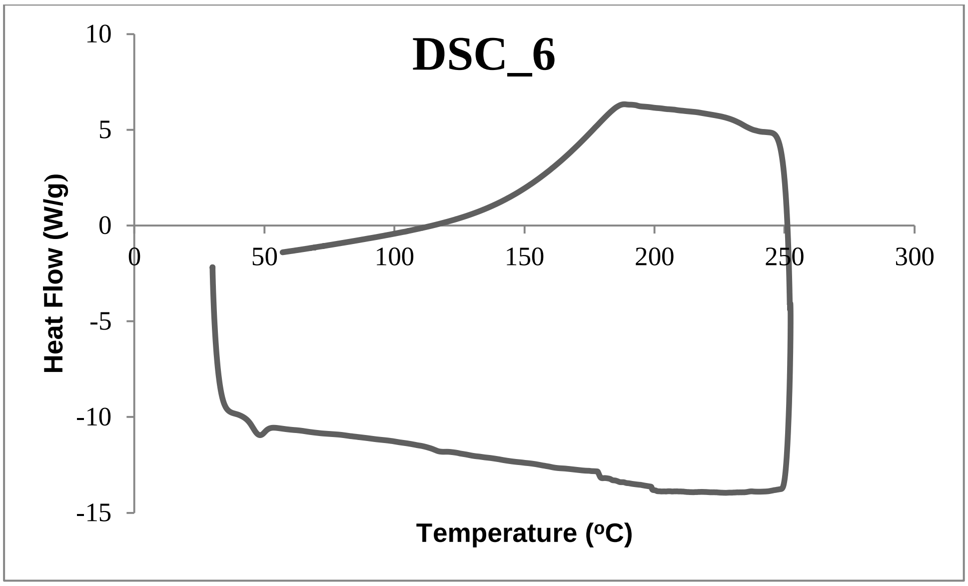


Figure F.2: DSC thermogram of Figure 4.6 poly(1,2-propanediol) terephthalate

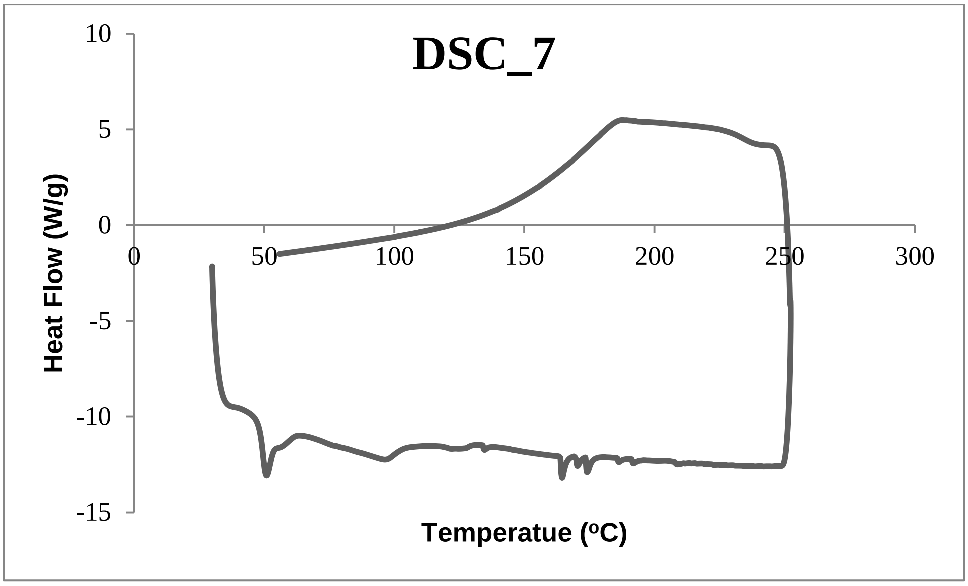


Figure F.3: DSC thermogram of Figure 4.7 polyethylene 2-bromoterephthalate

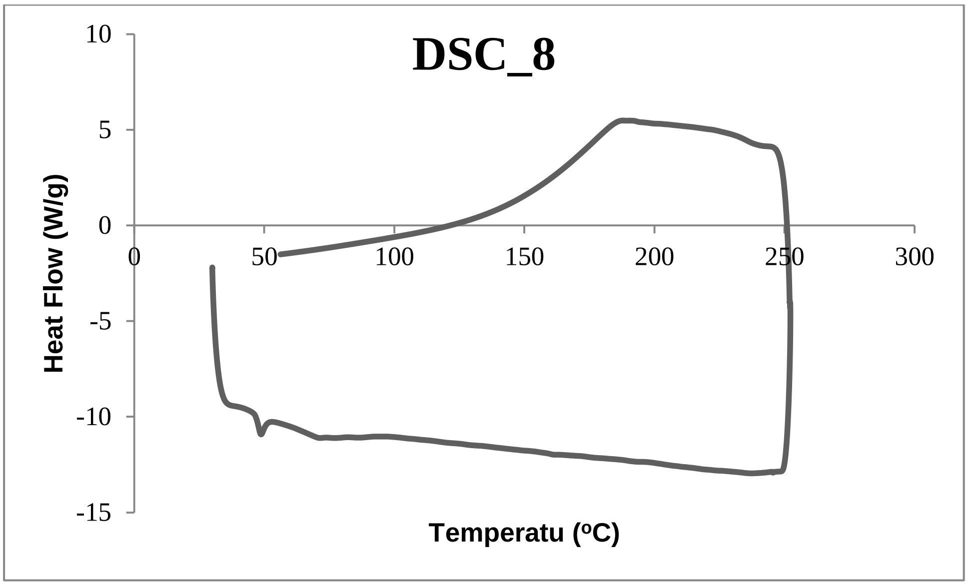


Figure F.4: DSC thermogram of Figure 4.8 poly(1,2-propanediol) 2-bromoterephthalate

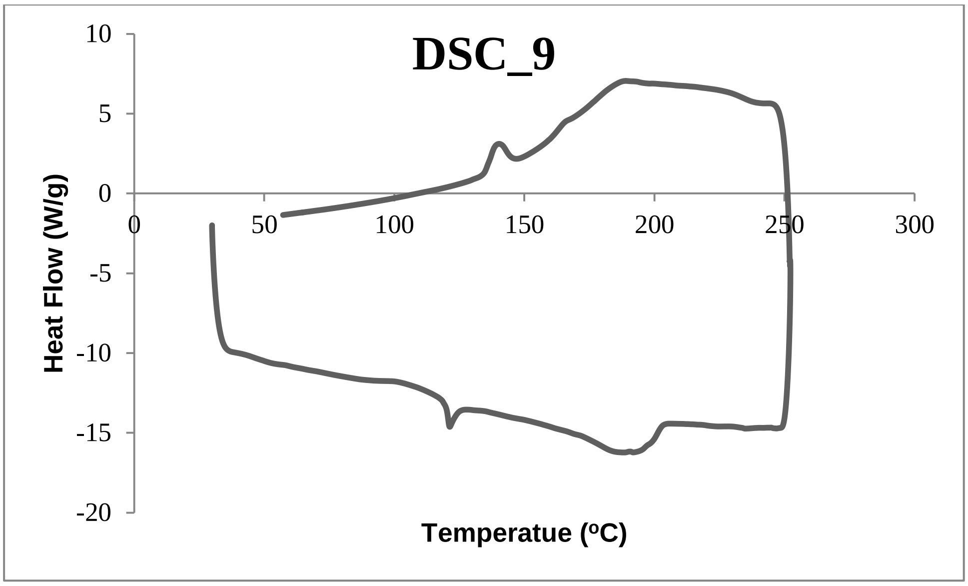


Figure F.5: DSC thermogram of Figure 4.9 polypropylene terephthalate

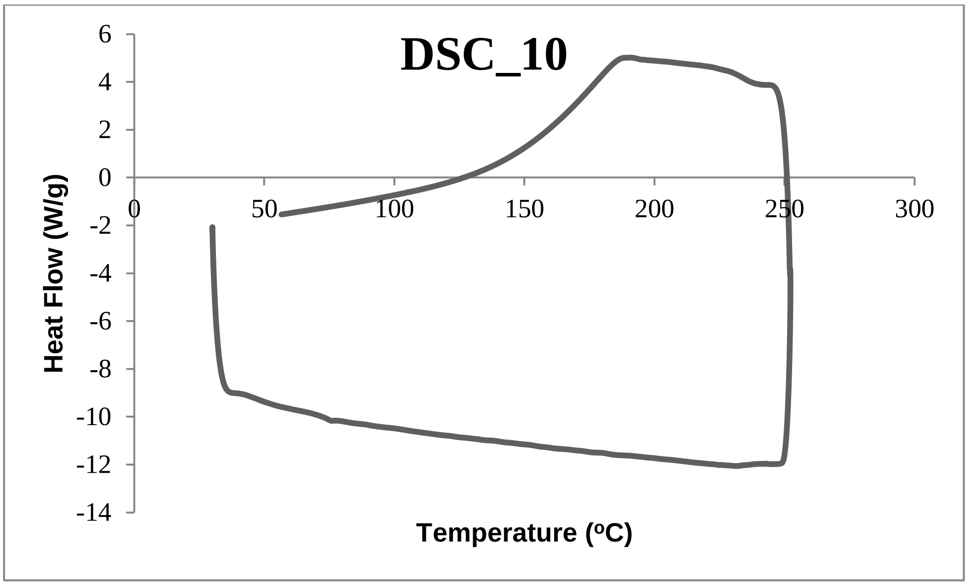


Figure F.6: DSC thermogram of Figure 4.10 polypropylene 2-bromoterephthalate

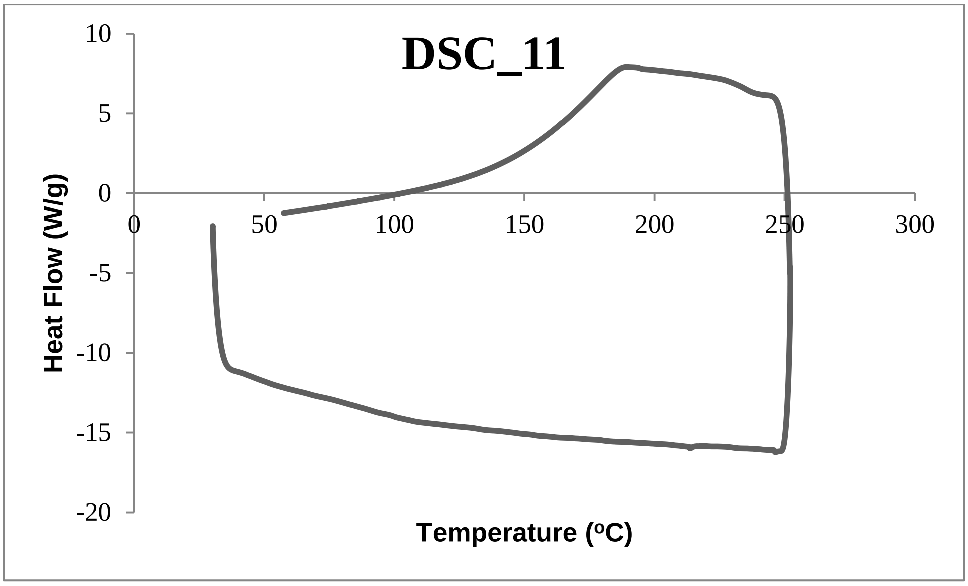


Figure F.7: DSC thermogram of Figure 4.11 poly(2-methyl)trimethylene terephthalate

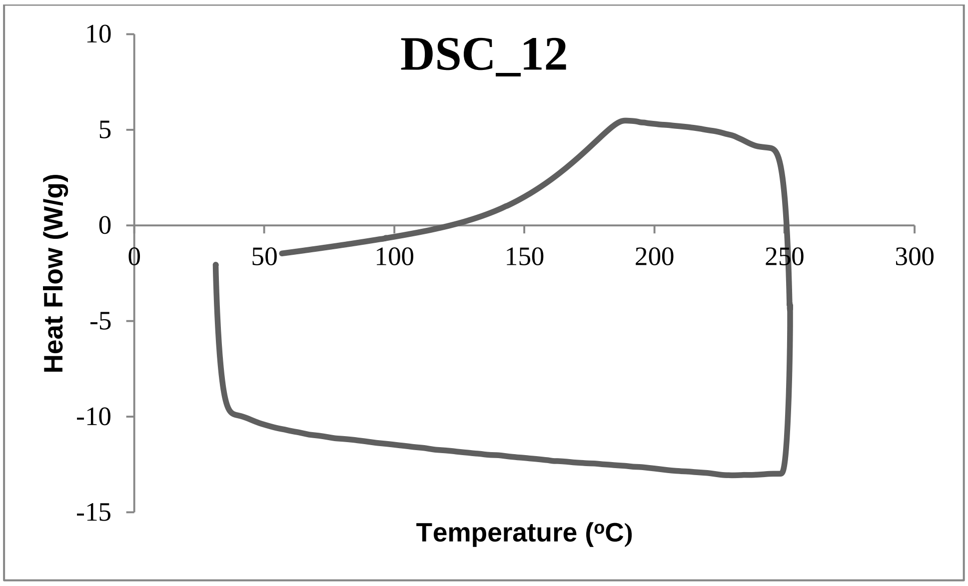


Figure F.8: DSC thermogram of Figure 4.12 poly(2-methyl)trimethylene 2-bromoterephthalate

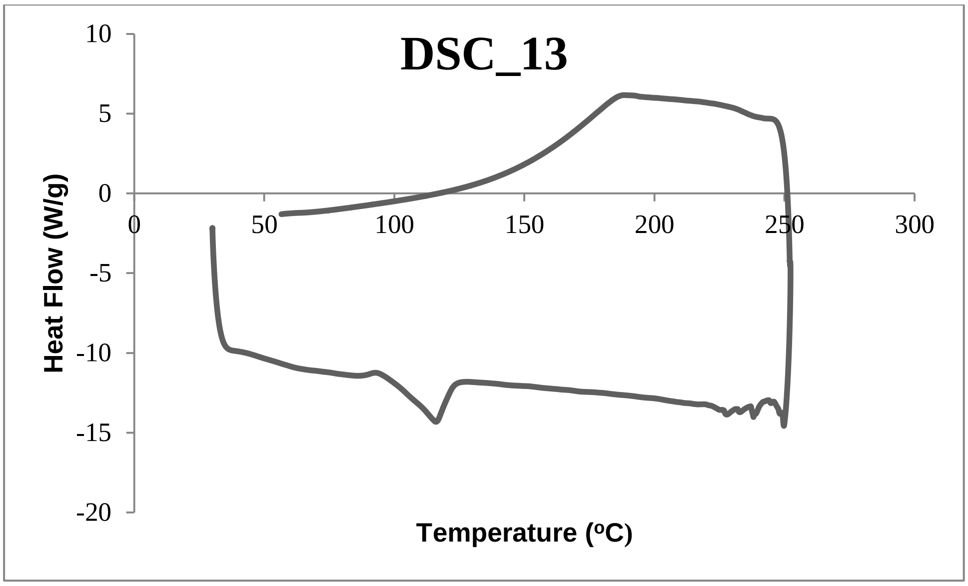


Figure F.9: DSC thermogram of Figure 4.13 polypentamethylene terephthalate

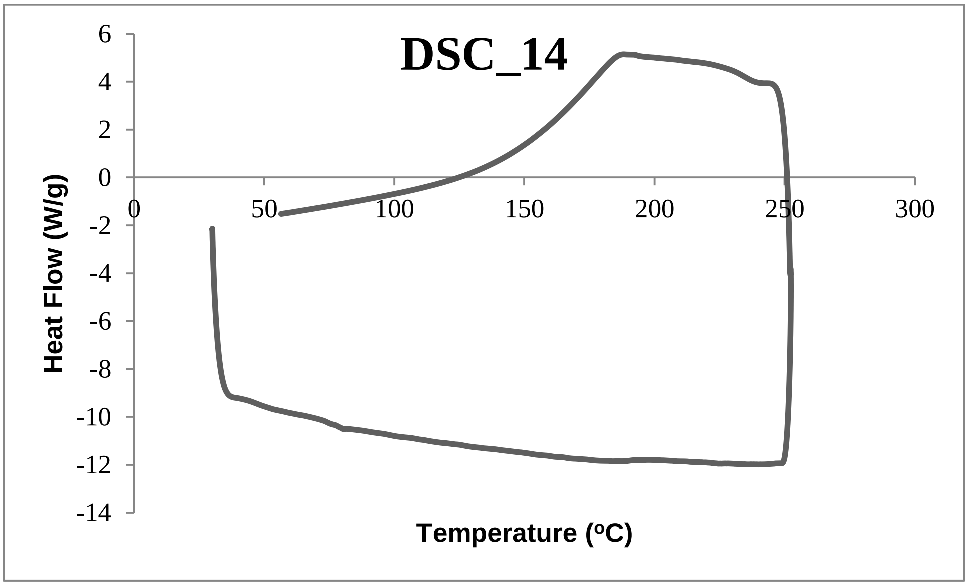


Figure F.10: DSC thermogram of Figure 4.14 polypentamethylene 2-bromoterephthalate

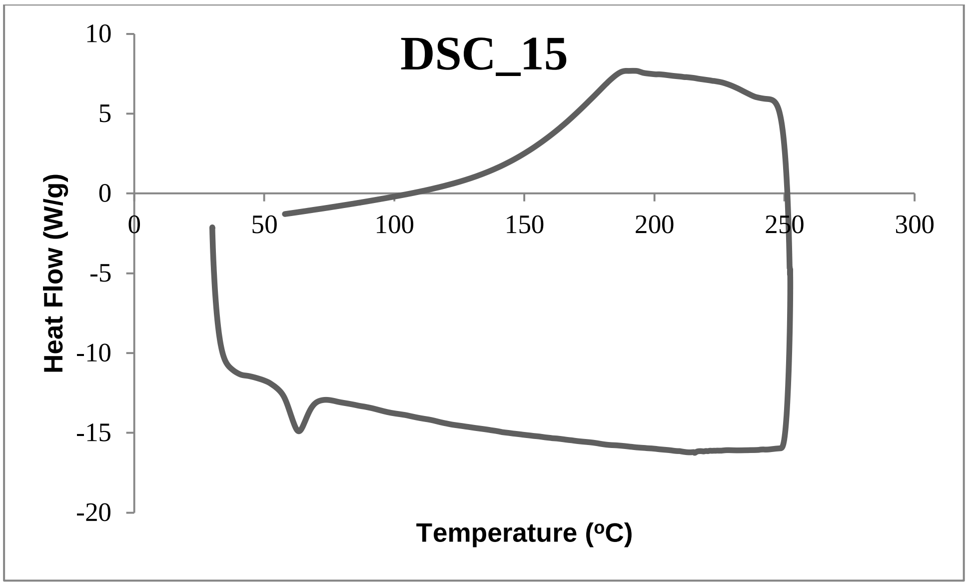


Figure F.11: DSC thermogram of Figure 4.15 poly(3-methyl)pentamethylene terephthalate

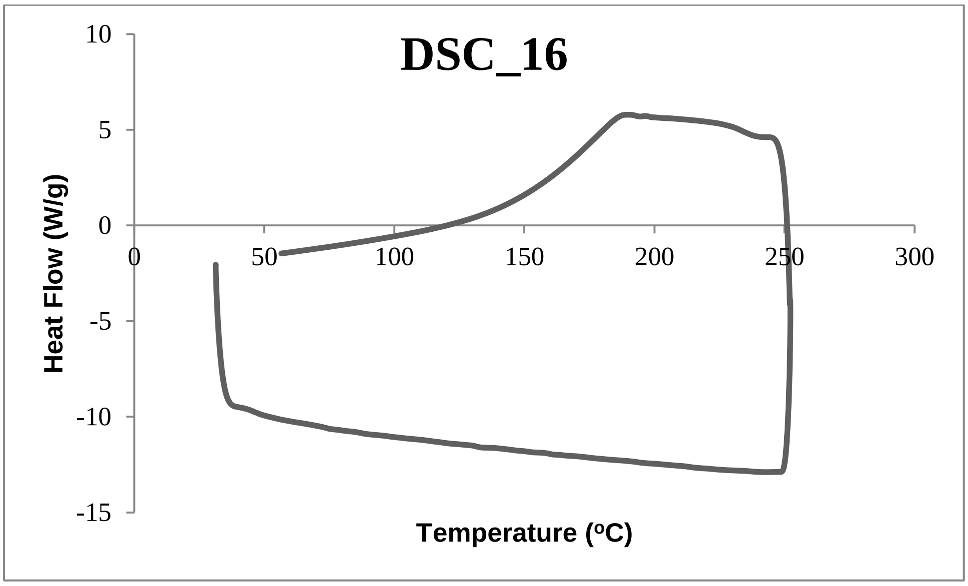


Figure F.12: DSC thermogram of Figure 4.16 poly(3-methyl)pentamethylene 2-bromoterephthalate

Appendix G: XRD

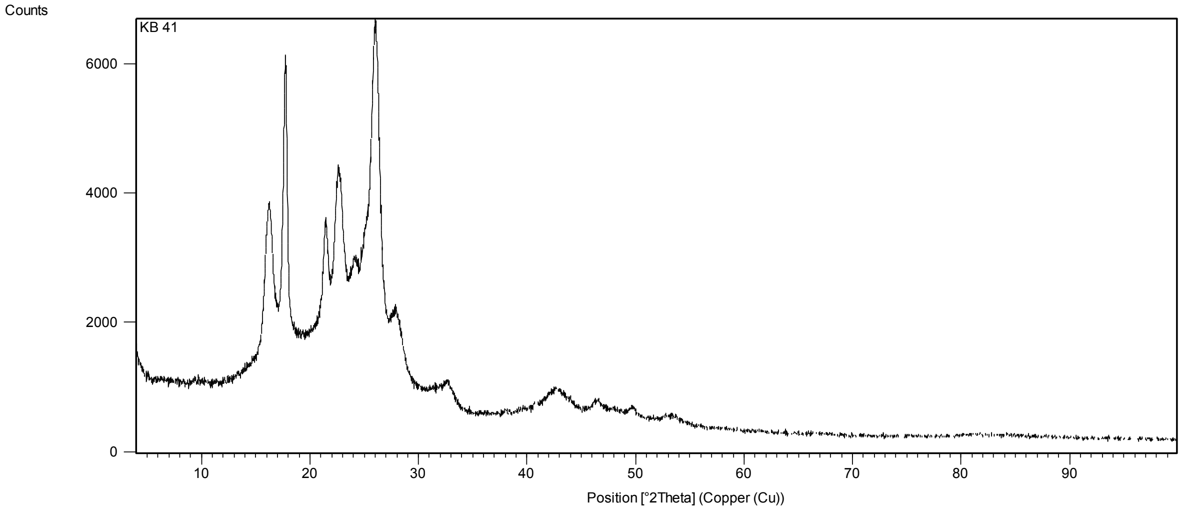


Figure G.1: XRD spectrum of Figure 4.5 polyethylene terephthalate

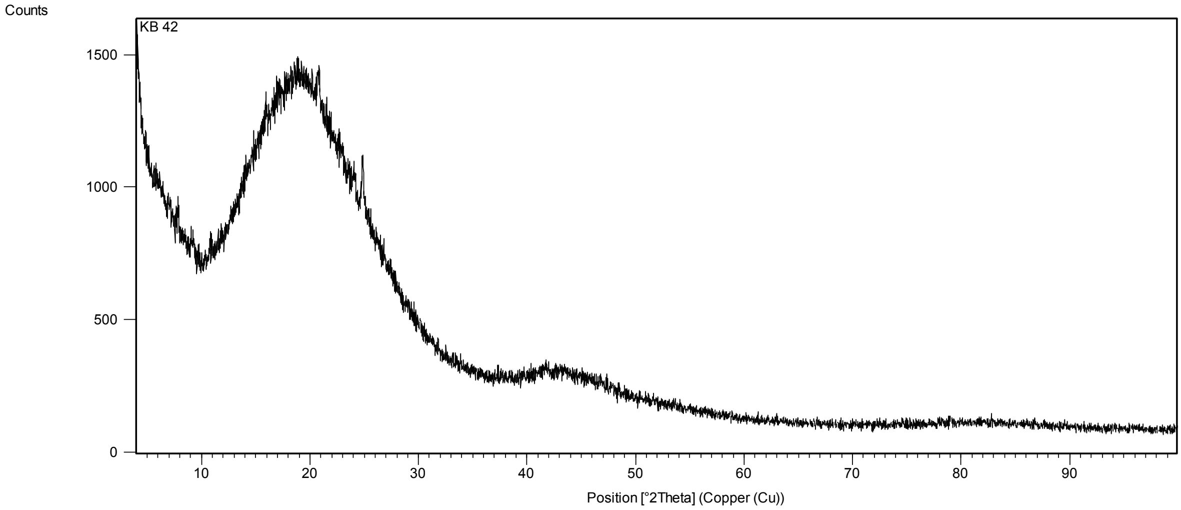


Figure G.2: XRD spectrum of Figure 4.6 poly(1,2-propanediol) terephthalate

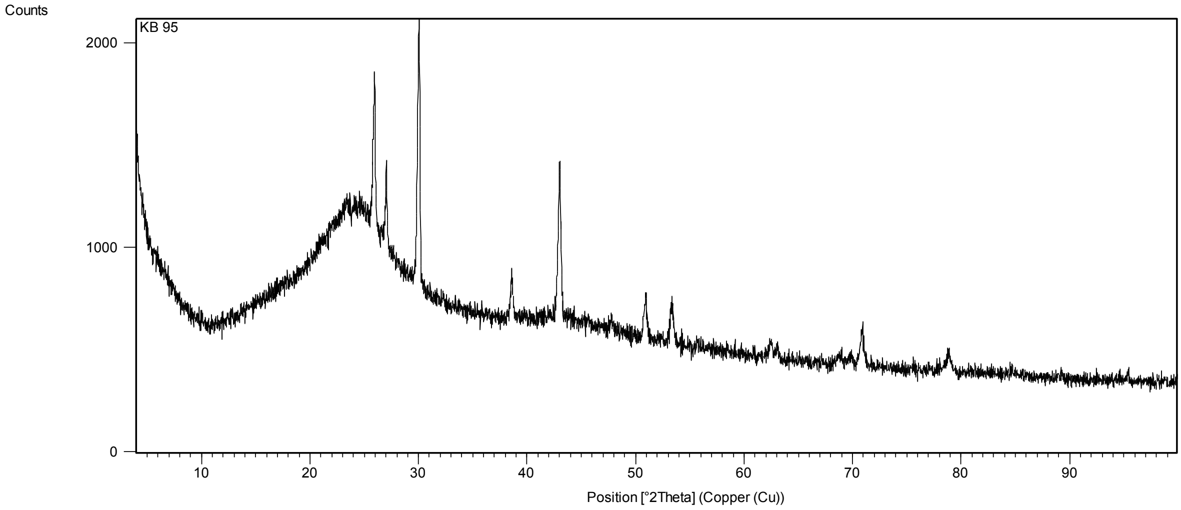


Figure G.3: XRD spectrum of Figure 4.7 polyethylene 2-bromoterephthalate

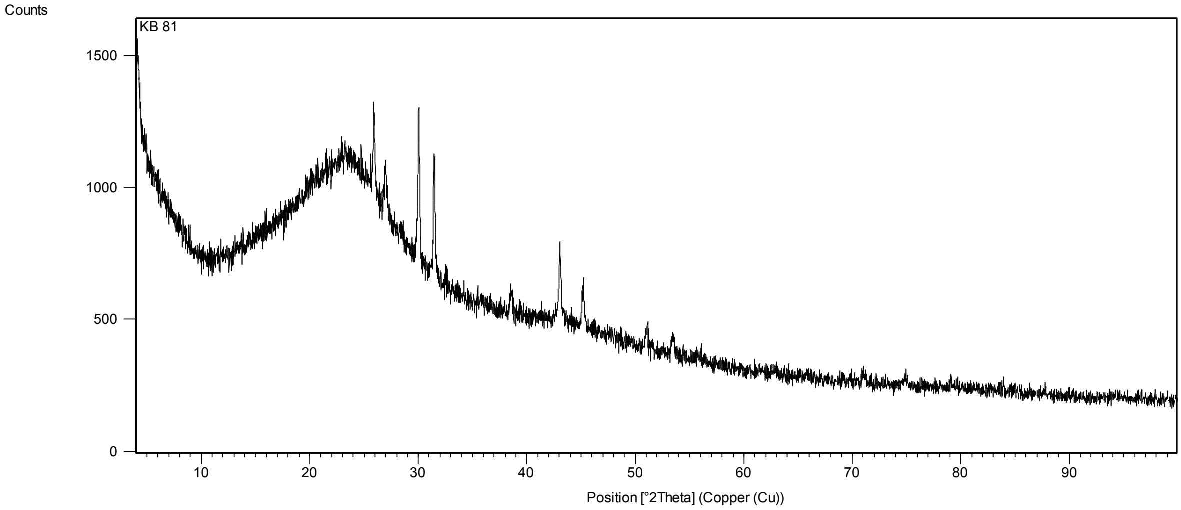


Figure G.4: XRD spectrum of Figure 4.8 poly(1,2-propanediol) 2-bromoterephthalate

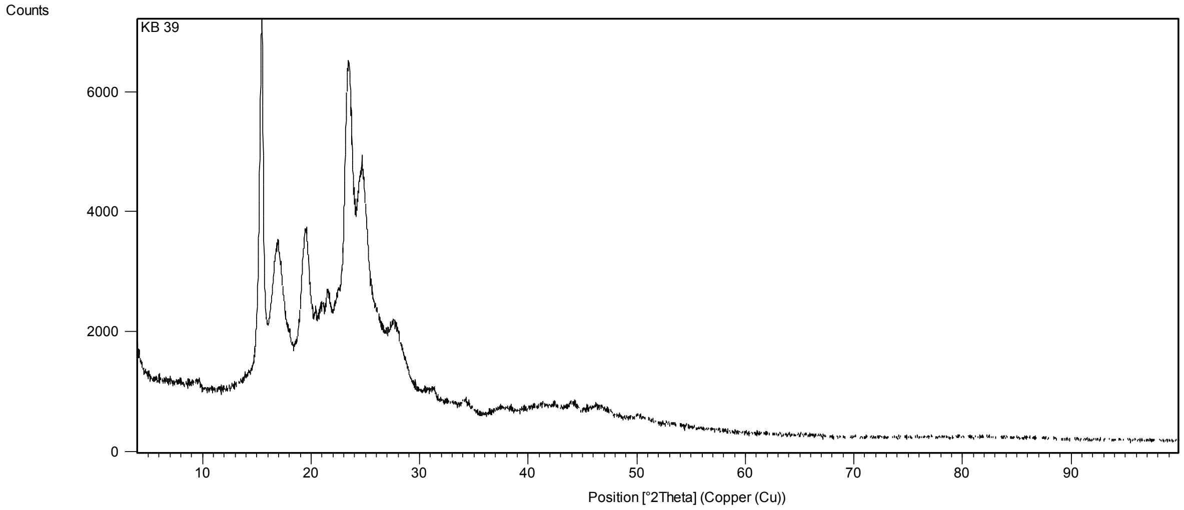


Figure G.5: XRD spectrum of Figure 4.9 polypropylene terephthalate

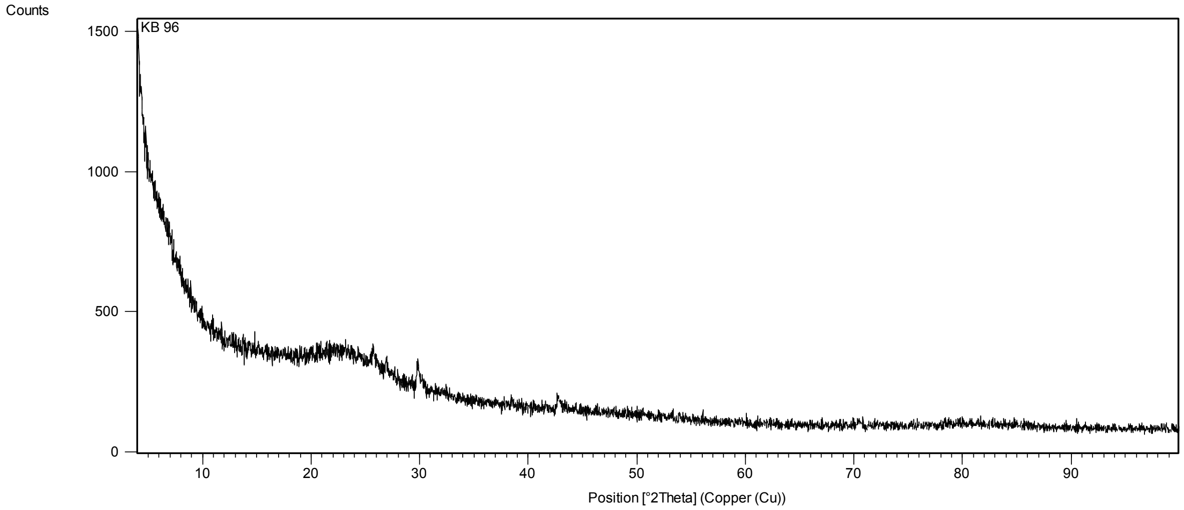


Figure G.6: XRD spectrum of Figure 4.10 polypropylene 2-bromoterephthalate

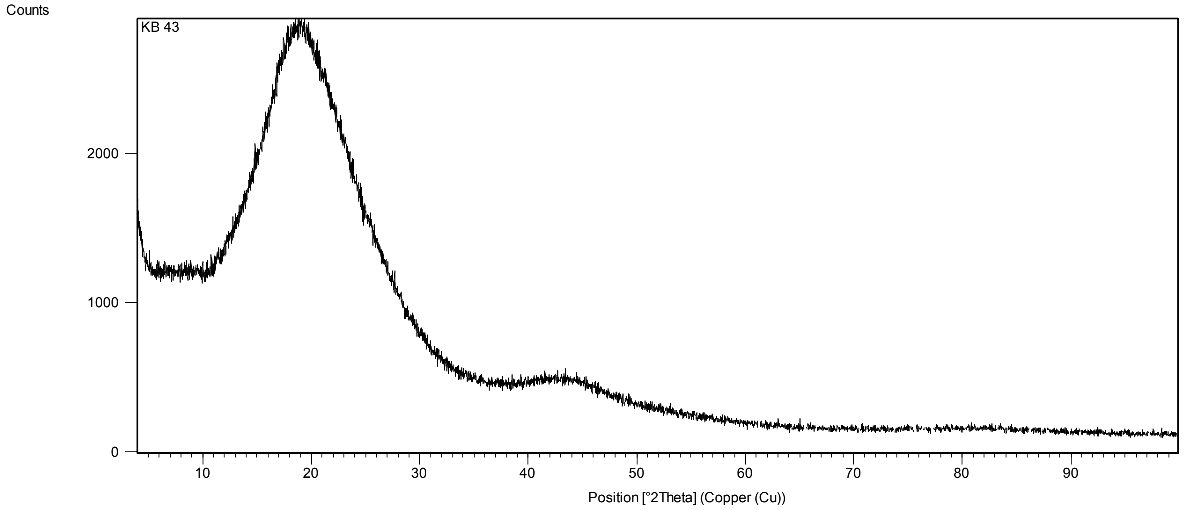


Figure G.7: XRD spectrum of Figure 4.11 poly(2-methyl)trimethylene terephthalate

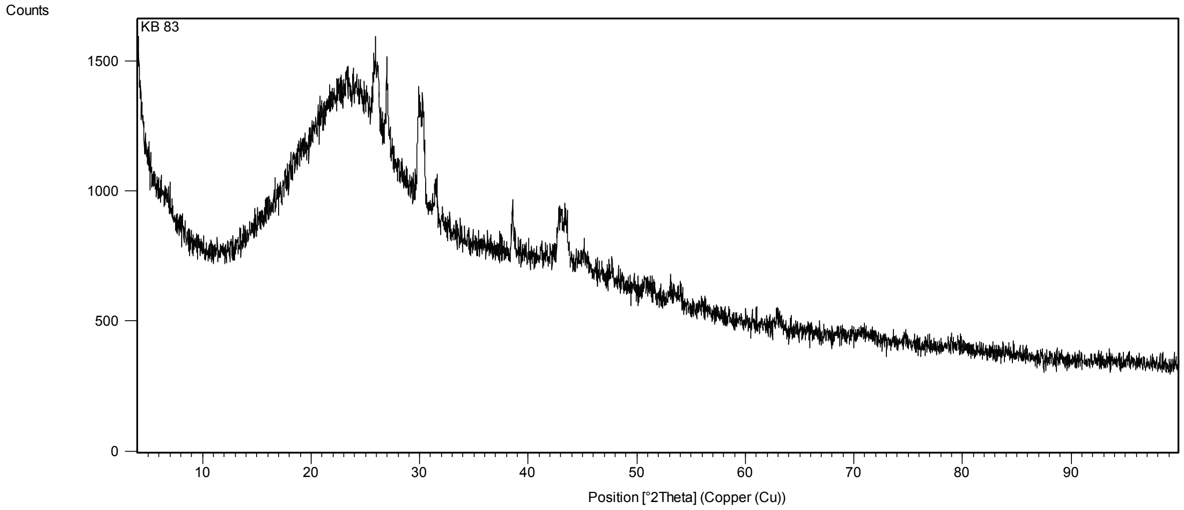


Figure G.8: XRD of Figure 4.12 poly(2-methyl)trimethylene 2-bromoterephthalate

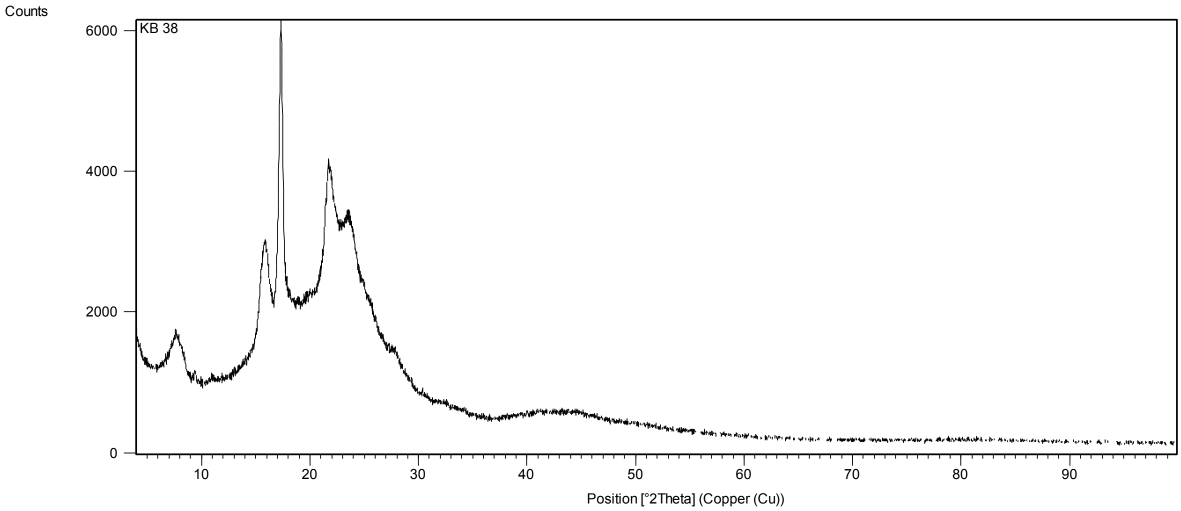


Figure G.9: XRD spectrum of Figure 4.13 polypentamethylene terephthalate

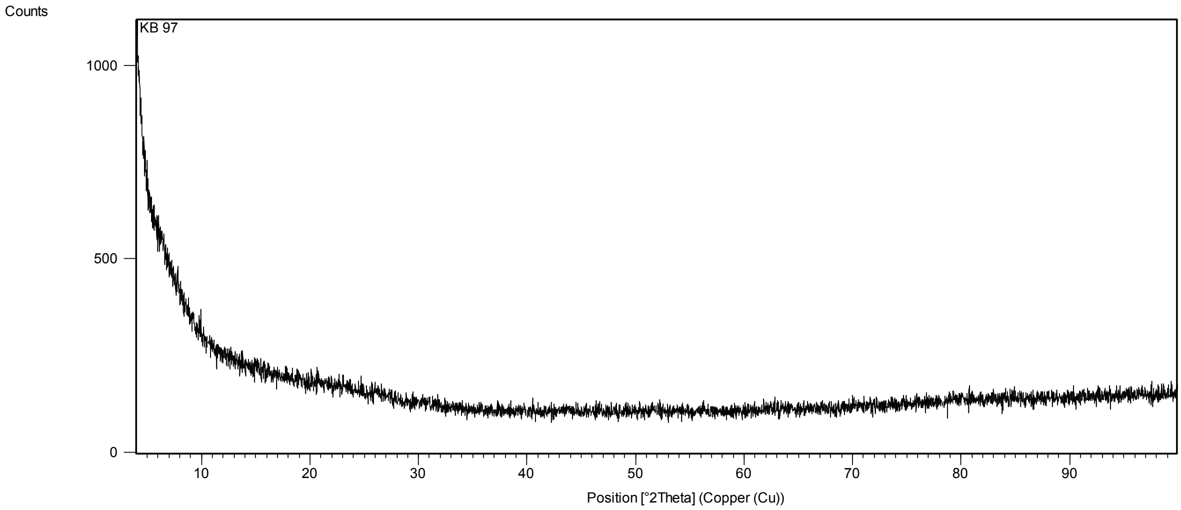


Figure G.10: XRD spectrum of Figure 4.14 polypentamethylene 2-bromoterephthalate

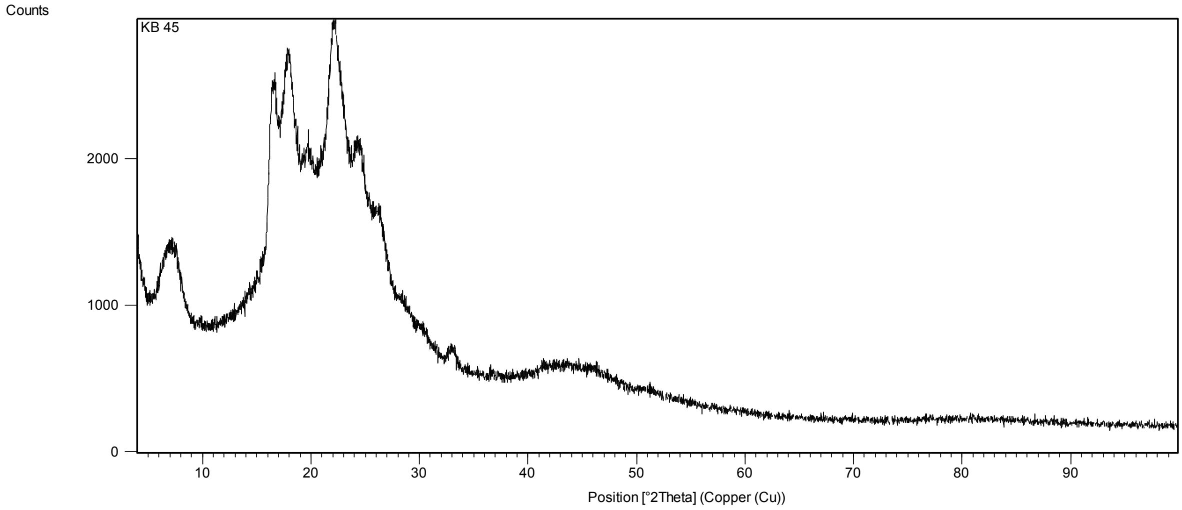


Figure G.11: XRD spectrum of Figure 4.15 poly(3-methyl)pentamethylene terephthalate

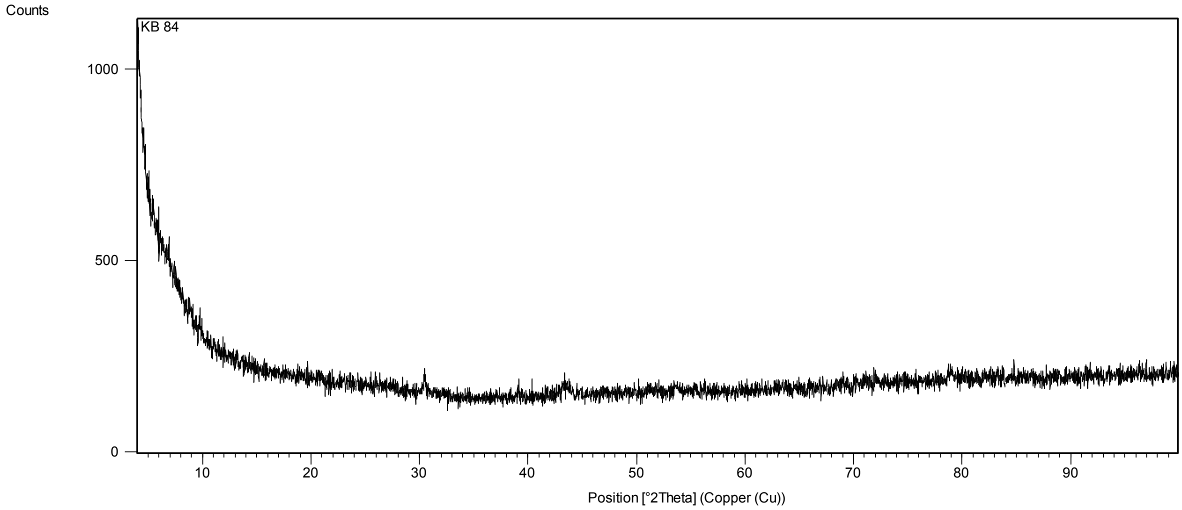


Figure G.12: XRD spectrum of Figure 4.16 poly(3-methyl)pentamethylene 2-bromoterephthalate

Appendix H: SEM

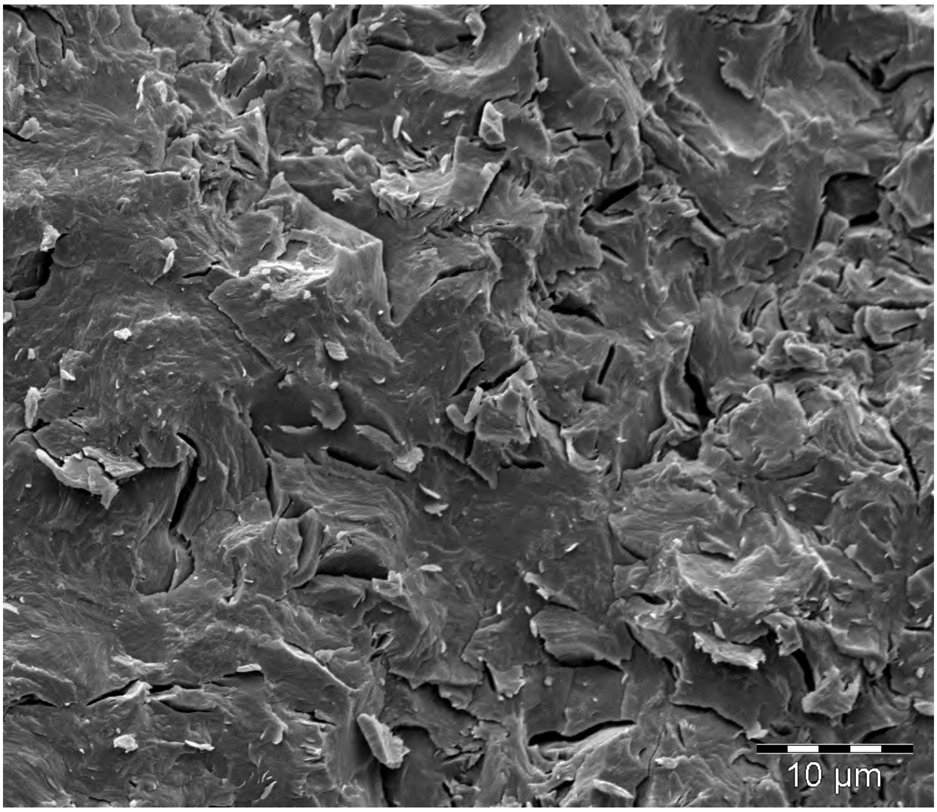


Figure H.1: SEM scan of Figure 4.5 polyethylene terephthalate

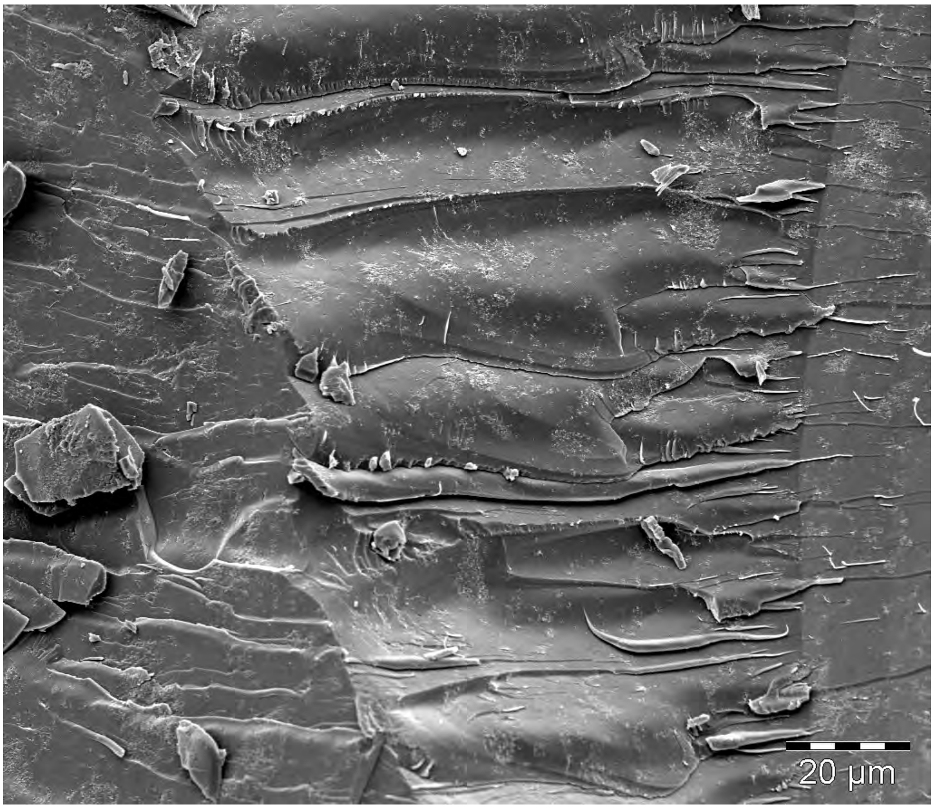


Figure H.2: SEM scan of Figure 4.6 poly(1,2-propanediol) terephthalate

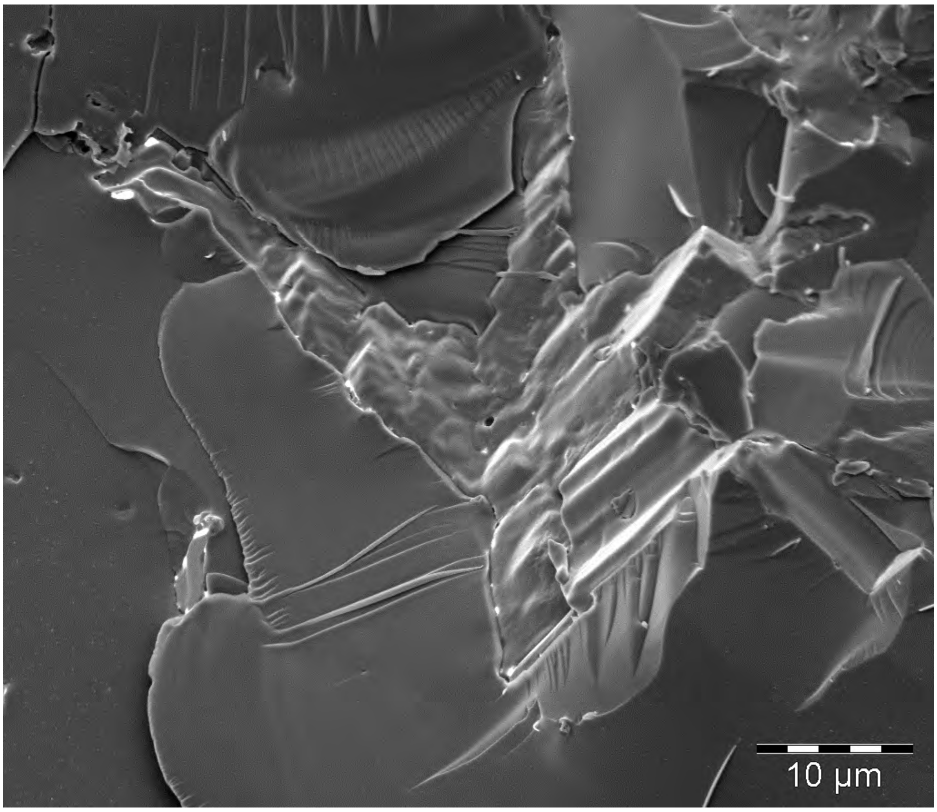


Figure H.3: SEM scan of Figure 4.7 polyethylene 2-bromoterephthalate

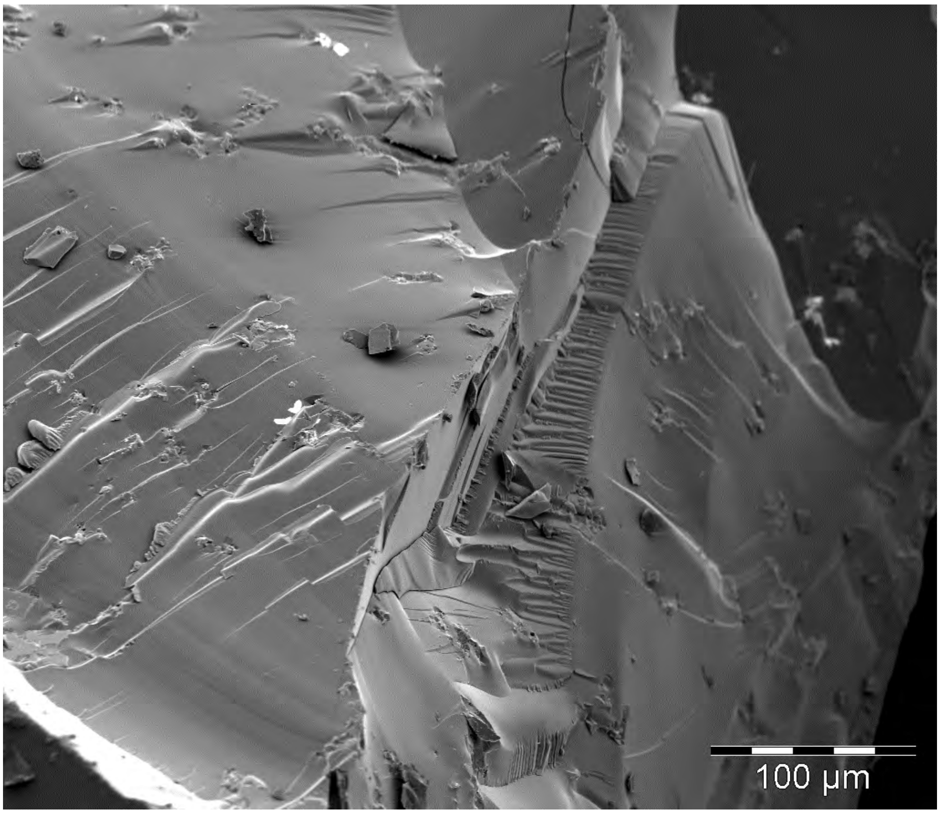


Figure H.4: SEM scan of Figure 4.8 poly(1,2-propanediol) 2-bromoterephthalate

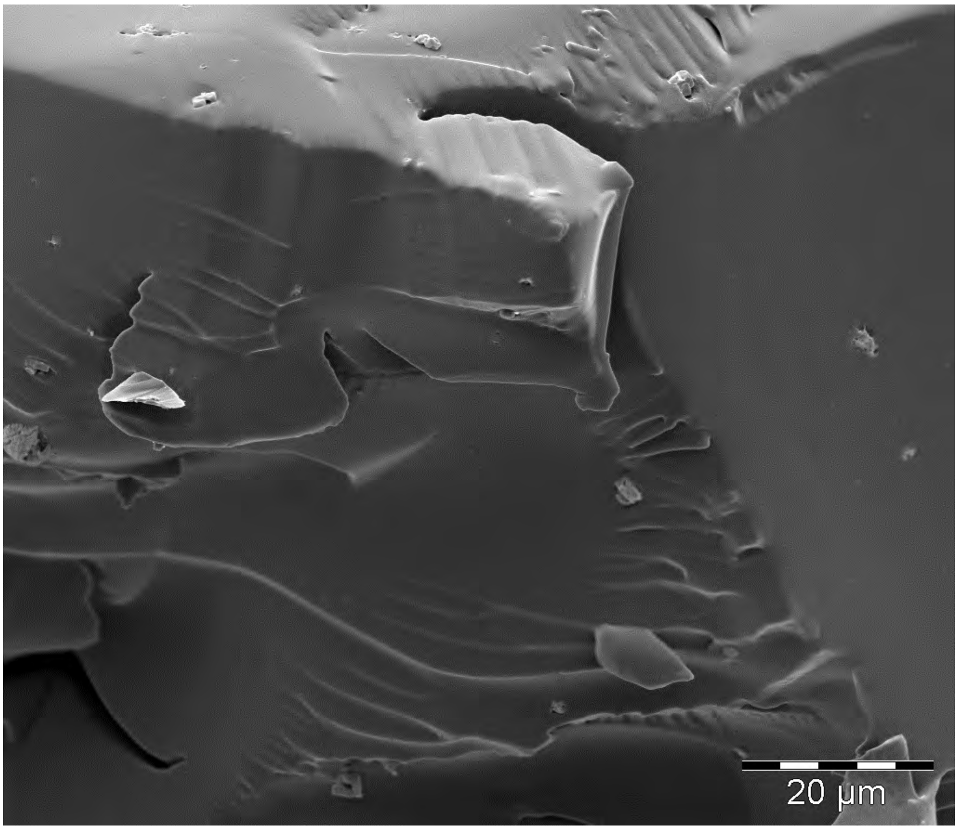


Figure H.5: SEM scan of Figure 4.10 polypropylene 2-bromoterephthalate

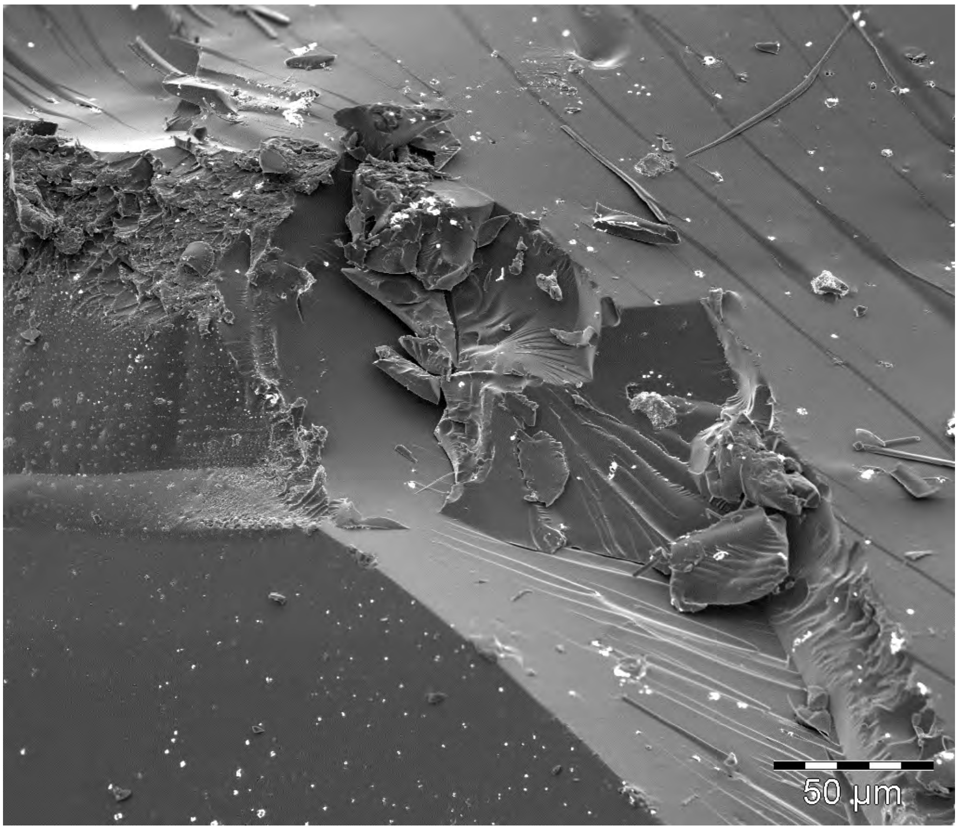


Figure H.6: SEM scan of Figure 4.12 poly(2-methyl)trimethylene 2-bromoterephthalate