ALKYLENEDIOXY CONTAINING PEEK POLYMERS CONTAINING META LINKAGES

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science

By

JAMES U. OHAERI
B.S., University of Cincinnati, 2010

2016
Wright State University

WRIGHT STATE UNIVERSITY

GRADUATE SCHOOL

May 13, 2016

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY James Ohaeri ENTITLED Alkylenedioxy Containing PEEK Polymers Containing Meta Linkages. BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

William A. Feld, Ph.D., Director
Department of Chemistry
College of Science and Mathematics

David Grossie, Ph.D., Chair
Department of Chemistry
College of Science and Mathematics

Committee on Final Examination

Eric Fossum, Ph.D.

Kenneth Turnbull, Ph.D.

William A. Feld, Ph.D.

Robert E. W. Fyffe, Ph.D.
Vice President for Research and
Dean of the Graduate School

ABSTRACT

James Ohaeri. M.S., Department of Chemistry, Wright State University, 2016.
Alkylenedioxy Containing PEEK Polymers Containing Meta Linkages Linkages.

The oxyalkylene containing, meta linked monomers 1,2-bis(3-(4-fluorobenzoyl)phenoxy)ethane**,** 1,3-bis(3-(4-fluorobenzoyl)phenoxy)propane**,** 1,4-bis(3-(4-fluorobenzoyl)phenoxy)butane**,** 1,5-bis(3-(4-fluorobenzoyl)phenoxy)pentane can be prepared by a three-step process starting with the dialdehydes (1,2-bis(3-formylphenoxy)ethane, 1,3-bis(3-formylphenoxy)propane, 1,4-bis(3-formylphenoxy)butane and 1,5-bis(3-formylphenoxy)pentane, respectively). Polymerization of the monomers with bisphenol-A gave soluble, thermally stable amorphous poly(ether ether ketone)s. The polymers exhibited molecular weights of (Mw/Mn) (21,841/ 8721) g/mol, (21,195/ 7569) g/mol, (9,107/ 2819) g/mol and (12,990/ 4723) g/mol, respectively. Thermal analyses of the polymers revealed T_gs of 112^o, 106^o, 92^o and 91^o, respectively and 5% weight losses under a nitrogen atmosphere of 389^o, 410^o, 411^o and 414^o, respectively.

TABLE OF CONTENTS

Page

TABLE OF CONTENTS (CONTINUED)

Page

LIST OF FIGURES

Figure Page

LIST OF FIGURES (CONTINUED)

LIST OF FIGURES (CONTINUED)

LIST OF TABLES

ACKNOWLEDGMENTS

I would like to thanks to my advisor, Dr. William Feld, Department of Chemistry, Wright State University, Dayton, Ohio, for his support, tutelage and giving me the opportunity to work in his group. His patience has allowed me the opportunity to grow as a chemist and achieve this milestone. I will always be thankful to him for giving me that chance.

I would also like to acknowledge the faculty, staff, and graduate students of the Wright State Chemistry Department for all I have learned from them and experienced with them as a student. The lessons and experiences I have gained from my interactions with them will never fade.

I would also like to thank Dr. Ken Turnbull and Dr. Eric Fossum for helping me defend this thesis.

DEDICATION

I would like to dedicate this work to my family and friends for their encouragement and support.

INTRODUCTION

Aromatic polymers like polyimides,[1] polyamides,[2] polyquinoxalines,[3] poly(ether ether ketones)[4] and the members of the polybenzazole series[5-7] are used in a variety of applications because of their outstanding thermal properties. They are, however, plagued by processing difficulties due to low solubilities and high processing temperatures. Many approaches have been taken to address both concerns; 1) the introduction of phenyl substituents, 2) the introduction of "kinks," usually meta linkages or tetrahedral centers with minimal non-aromatic content and 3) more radical modifications.

Radical modifications have included the introduction of "alkylenedioxy" (**Figure 1**) subunits in a variety of thermally-stable systems.[8-10] The observed thermal stability of these systems can be attributed to the insertion of an oxygen at the benzylic position which removes an obvious oxidative weak point. Recent work in the Feld group has concentrated on the generation of poly(ether ether ketones) having alkylenedioxy linkages with all para linkages.[11, 12]

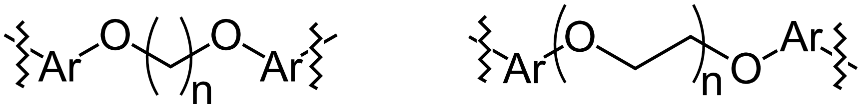


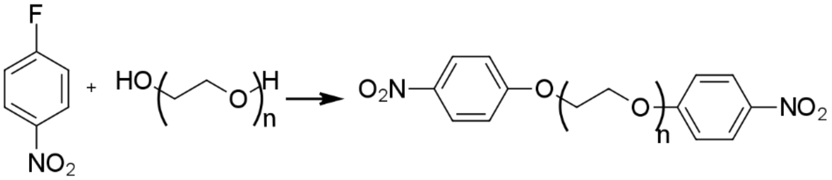
Figure 1. Alkylenedioxy (left) and ethylene glycol (right) related subunits.

The objectives of this research were to 1) generate a series of poly(ether ether ketones containing alkylenedioxy subunits AND meta linkages and 2) characterize all new monomers and polymers and 3) compare the thermal properties of the new polymers to existing alkylenedioxy all para linked poly(ether ether ketones).

HISTORICAL

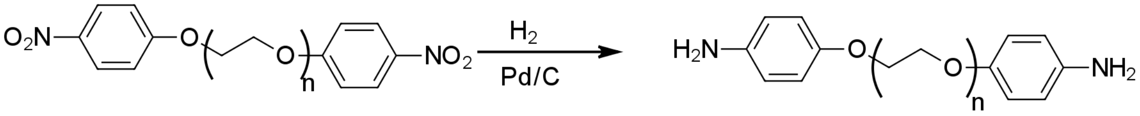
Polymers Containing Alkylenedioxy Linkages

In 1981, Ramalingam, et al.[8] reported the first incorporation of oxyalkylene units in a thermally stable polymer. It involved Williamson ether synthesis of dinitro compounds **6-9** by the reaction of 1-fluoro-4-nitrobenzene **1** with the appropriate glycol derivative **2-5** and potassium carbonate used as base.



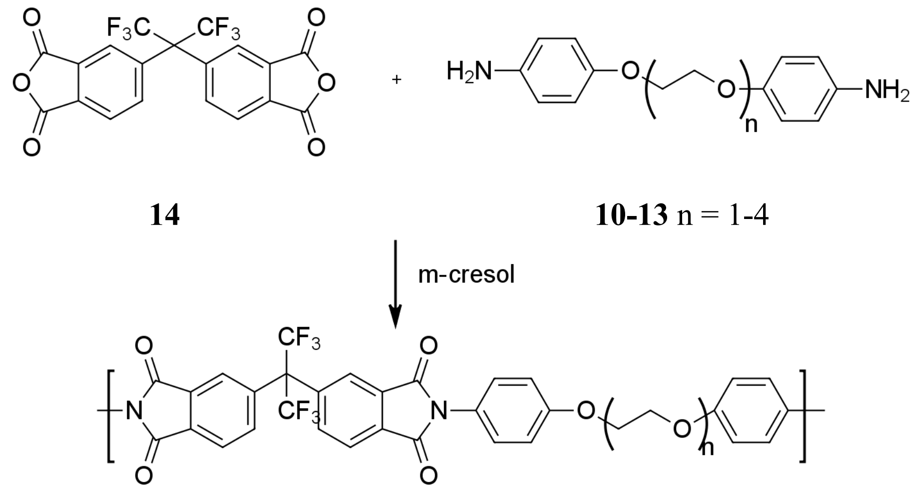
1 **2-5** n = 1-4 **6-9** n = 1-4

Compounds **6-9** were subsequently reduced to diamines **10-13** using hydrazine-hydrate and Pd/C as a catalyst in ethanol solution. The diamines were obtained quantitatively.



6-9 n = 1-4 **10-13** n = 1-4

Polymerization involved reaction of compounds **10-13** with 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride **14** in m-cresol containing isoquinoline at 165-180° to form fluorinated polyimides **15-18.** Toluene was utilized as an azeotrope to take out the water formed during the cyclization of the intermediate polyamic acid.



14 **10-13** n = 1-4

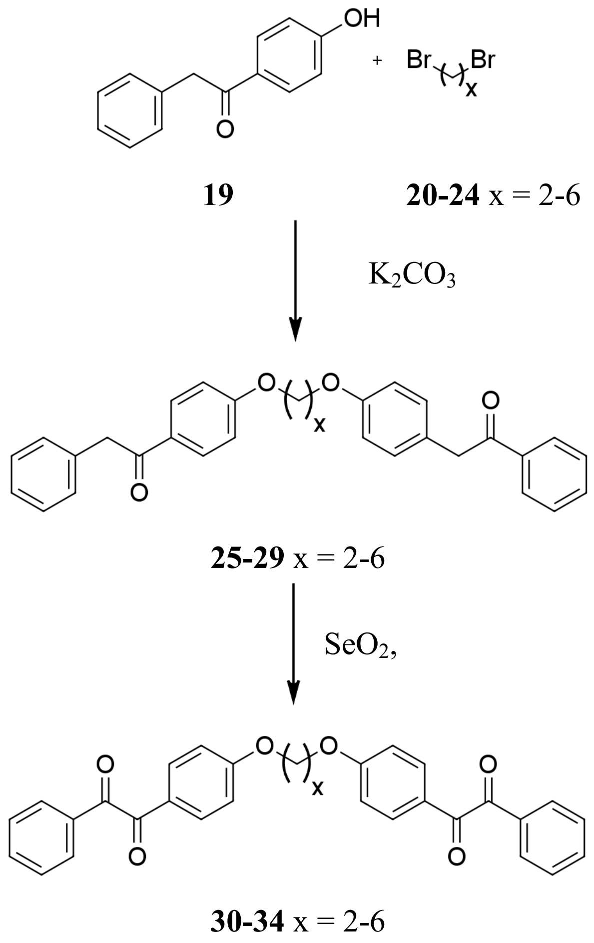
15-18 n = 1-4

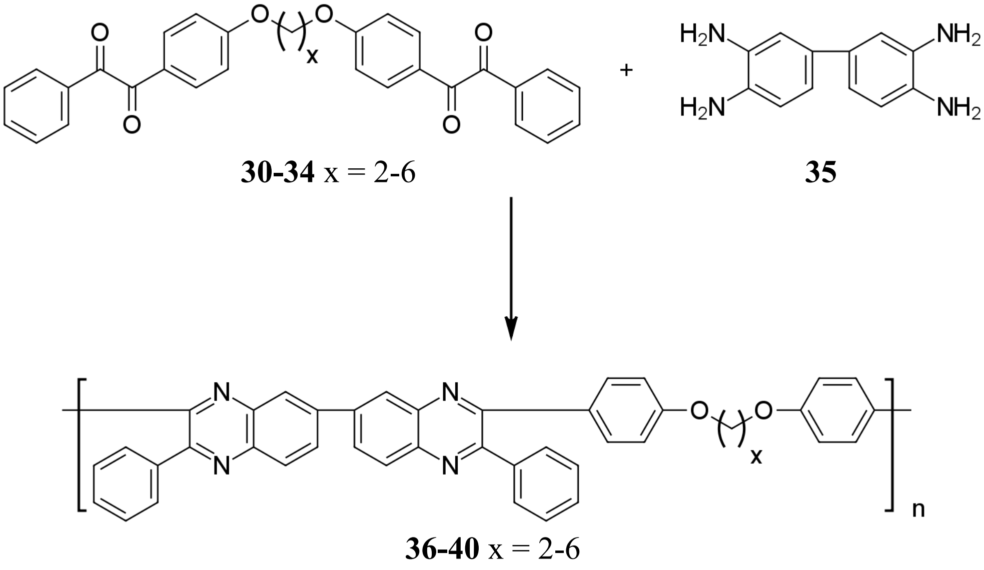
For this series of polyimides, it was observed that as the chain flexibility increased, due to longer oxyethylene units, the glass transition temperature decreased **(Table 1).** However, the thermal stability, as judged by the 5% weight loss, is still in the 400° range. The polymers formed films and exhibited good thermal properties.

Table 1. Melting Points of Dinitro and Diamine Derivatives Along with the T_g and $T_{d5\%}$ of the Fluorinated Polyimides.

n	Dinitro (mp)	Diamine (mp)	T_g	$T_{d5\%}$
1	148-49	179-80	254-55	460
2	55-56	59-60	175-180	425
3	96-97	93-95	170-175	425
4	62-64	-	135-140	385

Work done by Havens et al.[9] incorporated alkylenedioxy groups into polyphenylquinoxalines. The monomer synthesis involved a reaction between benzyl 4-hydroxyphenyl ketone **19** with the appropriate dibromoalkanes **20-24** in the presence of potassium carbonate to produce a series of bis(4-phenylacetylphenoxy)alkanes **25-29**. Subsequent oxidation by selenium dioxide in glacial acetic acid yielded bis(4-phenylglyoxylylphenoxy)alkanes **30-34**, which served as the monomers.


OH
+
Br
Br
x
O
19
20-24 x = 2-6
K2CO3
25-29 x = 2-6
SeO2,
30-34 x = 2-6

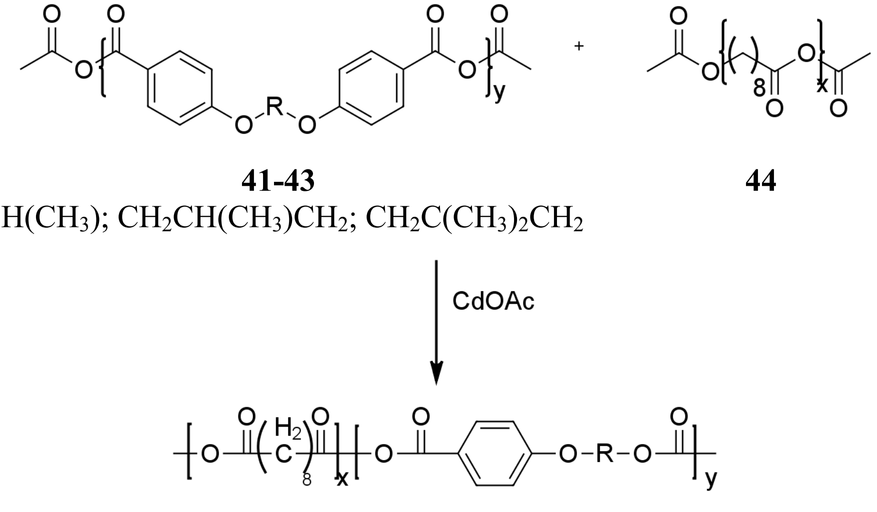

30-34 x = 2-6
+
H2N
NH2
H2N
NH2
35
N
O
x
n
36-40 x = 2-6

Polymerization of the tetraketone monomers **30-34** with 3,3-diaminobenzidine **35** in m-cresol under a nitrogen atmosphere yielded the polyphenylquinoxalines (PPQ) **36-40**. The polymers formed thick transparent yellow films with thermal stability above 400º. The Tg decreased with increasing chain flexibility as depicted in the **Table 2**.

Table 2. Tg of PPQ.

x	Tg (ºC)
2	241
3	238
4	220
5	212
6	203

The incorporation of alkylenedioxy units into polymers was further investigated in polyanhydrides. The project objective was to improve the processability of polyanhydrides. Polyanhydrides and their degradation products are biocompatible and they also undergo surface erosion making them suitable in drug delivery systems. Sanders et al. [10] synthesized polyanhydrides **45-47** by copolymerization of aromatic dianhydrides **41-43** and sebacic anhydride **44**. Variation of the ratio of diacid monomers



41-43

44

R = $CH_2CH(CH_3)$; $CH_2CH(CH_3)CH_2$; $CH_2C(CH_3)_2CH_2$

45-47

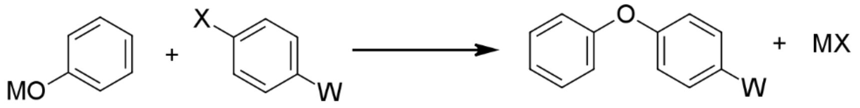
R = $CH_2CH(CH_3)$; $CH_2CH(CH_3)CH_2$; $CH_2C(CH_3)_2CH_2$

in the copolymer allowed control of the hydrolytic degradation rates to suit specific patient requirements.

The incorporation of oxyalkylene units into thermally stable polymers like polyimides, offers an avenue to study thermal, and possibly other physical, trends in these polymers. In addition to improving flexibility of the polymer backbone, it does not significantly degrade the thermal properties, when compared to derivatives without the alkylenedioxy linkages. For example, Hergenrother et al.[13] showed that polyquinoxalines (PQ) with phenyl links exhibited a 5% weight loss of 500° while PQ with aliphatic links had a 5% weight loss of 425°[10]. This is advantageous because it permits the design of polymers with good overall properties to suit various applications.

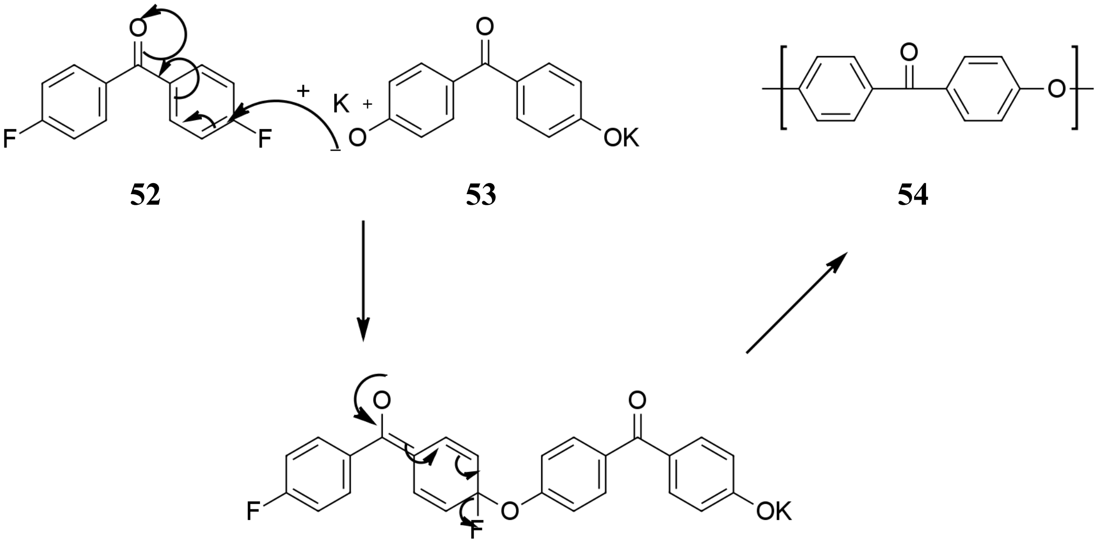
Poly(aryl ether ketone)s History and Selected Modifications

Poly(aryl ether ketone)s are considered high-performance polymers owing to their excellent thermal, physical and mechanical properties. The potential to regulate their morphology by varying their thermal history makes them useful in researching structure/property relationships.[14] A higher proportion of ketone linkage in the backbone increases the stiffness as well as the crystal binding energy. A higher proportion of ether linkage increases the flexibility and solubility.[15] Some of the most studied polymers in this class are poly(ether ether ketone)s, PEEK, they are usually crystalline in nature and exhibit a Tg of about 146°.[16] They are commercially made via nucleophilic aromatic substitution using a similar synthetic strategy developed by Bunnett et al.[17] that proved that alkali metal phenates **48** and activated aromatic halides **49** react, via a Meisenheimer complex, under suitable conditions to produce aryl ethers **50.** The nature and position of the activating group in the aryl halide are important factors in determining the course of the reaction. The activating group must be electron withdrawing and be positioned either ortho or para to the halogen being displaced.



48 M = Na, K **49** X = ortho or para
W = $-NO_2$, $-SO_2R$
50 **51**

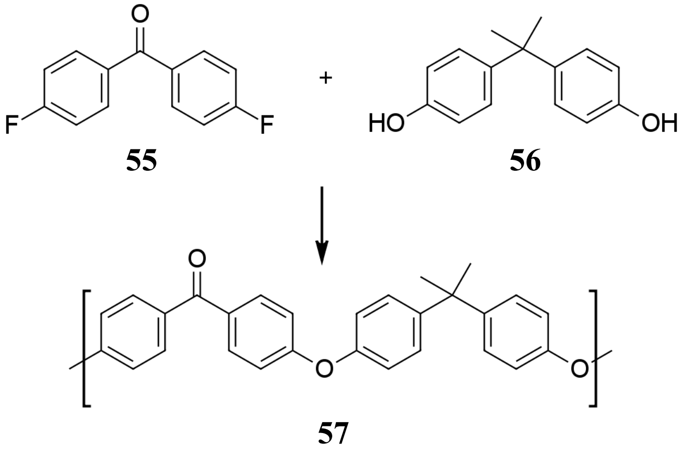
In 1981, Attwood et al.[4] developed the first synthetic method for making high molecular weight poly(ether ketone) **54** quantitatively. The synthesis involved a reaction between bis(4-fluorophenyl) ketone **52** and potassium hydroxyphenyl ketone bisphenate **53** in diphenyl sulfone at 355° for 2-3h. An inherent viscosity greater than 1 was reported for the polymer.

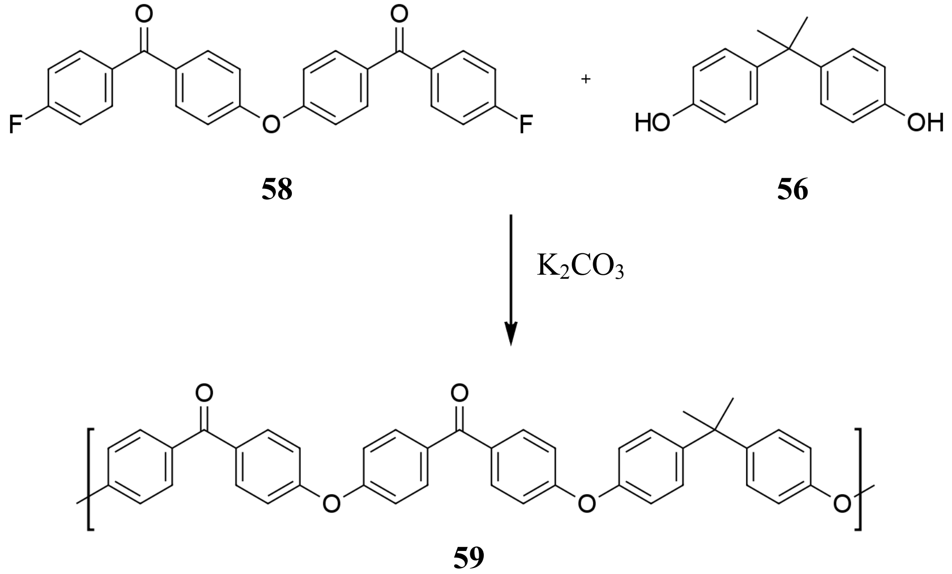


52 **53** **54**

In 1988, Hergenrother, Jensen and Havens[18] synthesized several poly(ether ketone)s via nucleophilic displacement on bis(fluorophenyl) monomers. The synthetic strategy was similar to Attwood[4] except that a different solvent system comprising a dimethylacetamide/K_2CO_3 solution at just 155° was used. The reaction of bis(fluorophenyl)ketone (FPK) **58** and bisphenol-A **56** provided polymer **57** that had a T_g

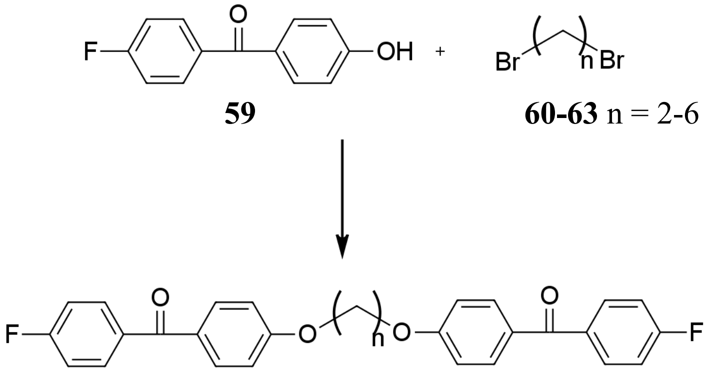
of 162º. Similarly, the reaction of bis(4-fluorobenzoylphenyl) ether (FBDE) **55** with bisphenol-A **56** provided polymer **59** that had a T_g of 155º.





In 1991, B. Patel[11] incorporated oxymethylene units into poly(ether ether ketone)s, PEEK. The project aimed to improve the solubility of PEEK while maintaining its good thermal properties. Monomer synthesis involved a Williamson ether synthesis comprising a reaction between 4-fluoro-4’-hydroxybenzophenone **59** with various dibromoalkanes

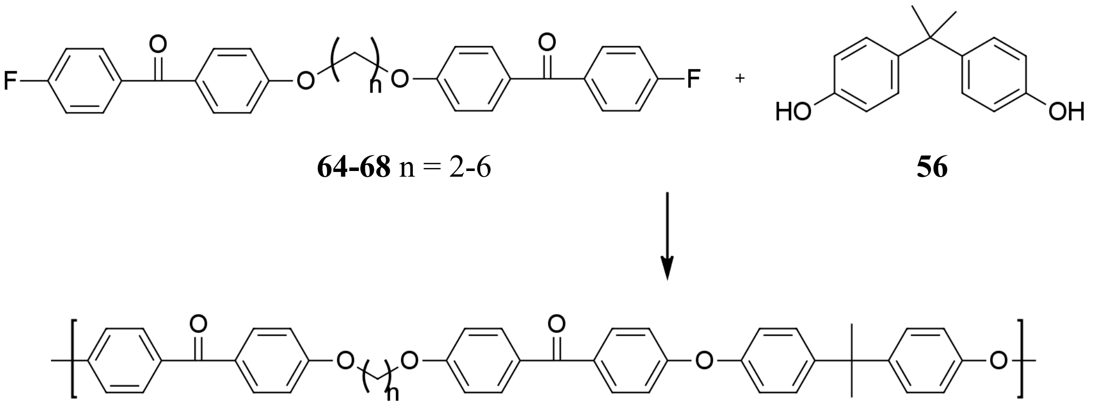
60-63, in ethanol, and potassium hydroxide used as base, to form thebis(fluorobenzophenone) derivatives **64-68**.



59 **60-63** n = 2-6

64-68 n = 2-6

Compounds **64-68** were subsequently polymerized in NMP/toluene with potassium carbonate used as a base and bisphenol-A **56** produced the poly(ether ether ketone)s **69-73**. Toluene was used as an azeotroping agent in the preparation of the dipotassium salt of bisphenol-A. The bisphenol-A disrupts the crystallinity of PEEK due to its non-coplanar structure, which affects the stacking of the individual polymeric chains.[19] This makes PEEK become amorphous and readily soluble in various organic solvents.

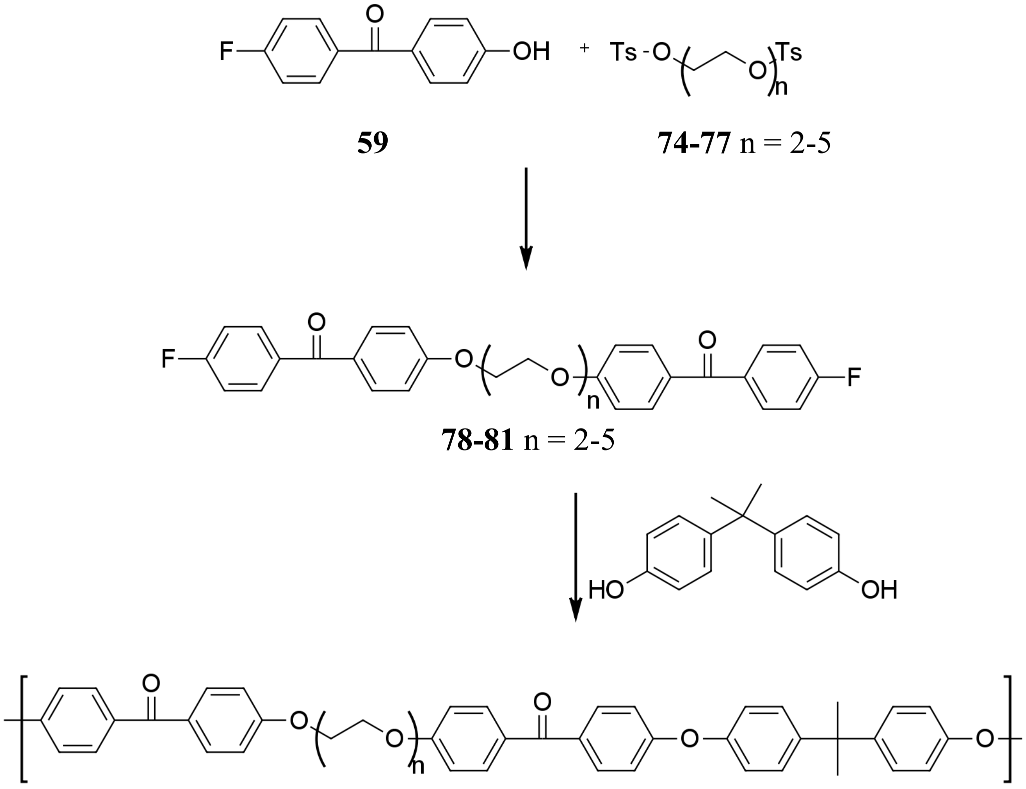


64-68 n = 2-6 **56**

69-73 n = 2-6

The glass transition temperatures decreased as the number of units increased and the polymers exhibited a 5% weight loss above 450º. The polymers were soluble in NMP and chlorinated solvents and they formed flexible, transparent and colorless films.

In a similar study,[12] PEEK with oxyethylene units were synthesized to observe the physical properties differ from the methylene derivatives.



59 **74-77** n = 2-5

78-81 n = 2-5

82-85 n = 2-6

The polymers formed flexible, colorless, transparent films, and were soluble in NMP and chlorinated solvents. The trend of the glass transition temperatures was inversely proportional to the length of the oxyethylene units but the thermal stability of the polymer was not lowered significantly. The properties of the oxymethylene and oxyethylene linked polymers are presented in **Table 3**.

Table 3. Thermal Properties of Monomers and Polymers of PEEK Containing Oxyalkylene links.

n	M.p of monomers (ºC)		Tg (ºC)		$T_{d5\%}$ (N_2)	
	O.M	O.E	O.M	O.E	O.M	O.E
2	228-230	153-155	136	104	500	430
3	145-146	115-116	125	87	490	430
4	198-200	67-69	114	73	460	400
5	151-152	63-64	108	63.8	480	400
6	176-177	X	91	X	460	X

O.M – Oxymethylene; O.E - Oxyethylene

The melting points of the oxymethylene linked monomers are higher than those of the oxyethylene derivatives. This is due to the presence of the oxygen in place of the –CH_2- group, which makes the chain more flexible hence lowering the melting point. The glass transition temperatures (T_g) of both polymers decrease with increasing chain length however, this does not have an adverse effect on the thermal stability of the polymers.

In 2011, Wu et al.[19] synthesized poly(ether ether ketone) copolymers (Co-PEEK) **(Figure 2)** with pendant phenyl groups, and bisphenol-A, for application in ion exchange membranes. Co-PEEK with low BPA content (0.2) was semi-crystalline and only soluble in 98% sulfuric acid, derivatives with higher BPA (0.4-1) were amorphous and soluble in common organic solvents including NMP, THF and chloroform. The soluble derivatives all formed tough, transparent films.

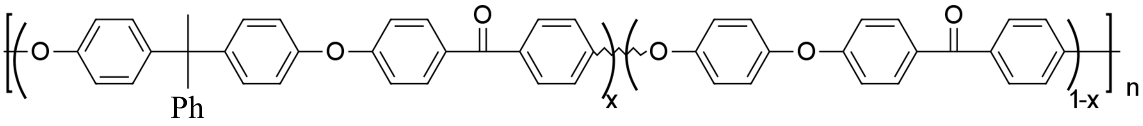
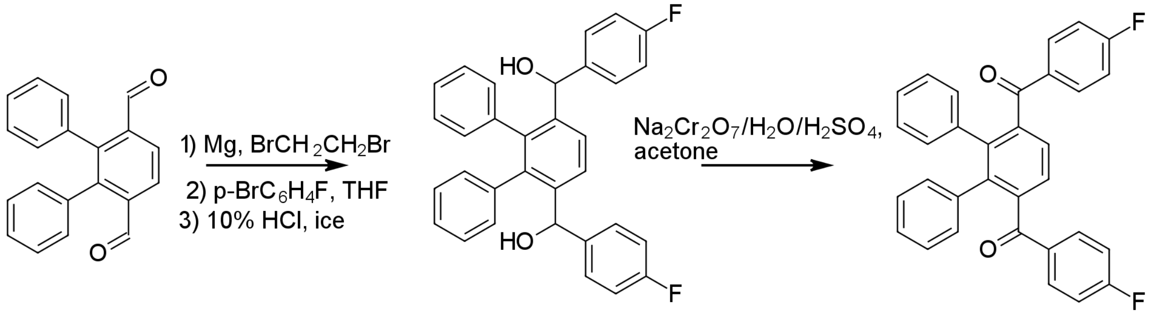


Figure 2. CoPEEK with varying BPA content.

It can be concluded from the above research that 1) the addition of oxyalkylene units in thermally stable polymers, improves the flexibility of the chain, lowers the Tg but does not adversely affect the thermal properties. 2) The incorporation of bisphenol-A disrupts the crystallinity of poly(ether ether ketone)s making them amorphous and readily soluble in common organic solvents.

Dialdehydes as Precursors to Bis(fluorophenyl)ketones

Many bis(fluorobenzophenone) monomers are made by Friedel-Crafts acylation, however, Dancevic[20] showed that they could be prepared via a Grignard reaction. The synthesis involved a two-step process. The first step involved a Grignard reaction of 2,3-diphenylterephthaldehyde **86** with p-bromofluorobenzene in THF to give a diol intermediate **87**. The second step involved the Jones oxidation of the diol intermediate in acetone to yield 2,3 diphenyl-1,4-bis(fluorobenzoyl)benzene **88.**



86 **87** **88**

The effects of paraoxyalkylene links in thermally stable polymers have been well documented but the effects of meta oxyalkylene links have yet to be explored. Exploring this provides an avenue to study the trend in structure-property relationships in poly(ether ether ketone)s and other thermally stable polymers, which could be useful in commercial applications.

The objectives of this research were to 1) generate a series of poly(ether ether ketones containing alkylenedioxy subunits AND meta linkages and 2) characterize all new monomers and polymers and 3) compare the thermal properties of the new polymers to existing alkylenedioxy all para linked poly(ether ether ketones).

Experimental

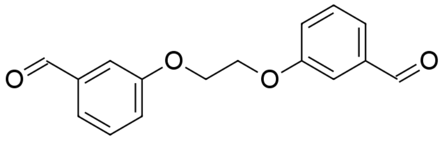
Instrumentation and Chemicals.

Nuclear Magnetic Resonance (NMR) spectra were acquired using a Bruker Avance 300 NMR Spectrometer (^1H and ^{13}C) using $CDCl_3$ and Acetone-d_6 as a solvent. All NMR data manipulations were carried out using Bruker Topspin 3.2. Melting points were obtained with a DigiMelt MPA-160 apparatus. Elemental analyses were performed by Midwest Micro Laboratories, Indianapolis, Indiana. Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) spectra were obtained with a TA TGA Q 500 and a TA DSC Q 200 both employing air or N_2 atmospheres. Infrared (IR) spectra were recorded as thin films (KBr) with a Nicolet 6700 FT-IR spectrometer. The number-average molecular weights (M_n) and weight-average molecular weight (M_w) of polymers were determined with a Viscotek Triple Detector Array (TDA) Model 300 Gel Permeation Chromatograph (GPC) calibrated with polystyrene standards. Starting materials were obtained from Sigma-Aldrich Chemical Company and used without further purification.

General Procedure for the Synthesis of Dialdehydes

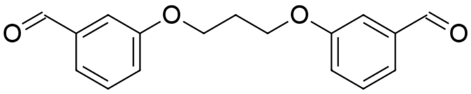
Into a Q-Tube™ equipped with a magnetic stir bar, potassium hydroxide (KOH) (6.74 g, 0.12 mol) and 3-hydroxybenzaldehyde (14.66 g, 0.12 mol) were dissolved in 65 mL of ethanol. The appropriate dibromoalkane was added to the solution and the mixture was heated at reflux (90º) for 12h. The reaction was cooled to room temperature and precipitated in 600 mL of water and stirred for 5h. The crude product was isolated via vacuum filtration and air dried. The resulting solid was recrystallized from methanol/water to afford a tan solid.

1,2-Bis(3-formylphenoxy)ethane 94



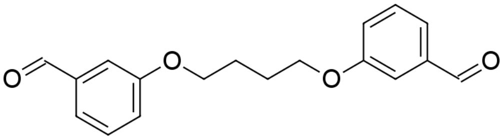
The compound was obtained using 1,2-dibromoethane in yield of 40%; mp 52-53°; (lit.[13,14] mp 54-55°); IR (KBr) cm^{-1} 3066 2935, 1685, 1581;^{1}H NMR ($CDCl_3$) δ 9.98 (s, 2H, CHO), 7.19- 7.23 (m, 2H, Ar), 7.43-7.48 (m, 6H, Ar), 4.46 (s, 4H, CH_2); ^{13}C NMR ($CDCl_3$) ppm 192.06 (C=O), 159.38 (Ar, C), 137.83 (Ar, C), 130.09 (Ar, CH), 123.65 (Ar, CH), 121.92 (Ar, CH), 112.72 (Ar, CH), 67.53 (CH_2).

1,3-Bis(3-formylphenoxy)propane 95



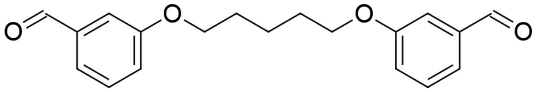
The compound was obtained using 1,2-dibromopropane in a yield of 88%; mp 52-53° (lit.[13,14] mp 48-50°); IR (KBr) cm^{-1} 2944, 2724, 1681, 1581;^{1}H NMR ($CDCl_3$) δ 9.98 (s, 2H, CHO), 7.19- 7.23 (m, 2H, Ar), 7.43-7.48 (m, 6H, Ar), 4.26 (t, 4H, CH_2), 2.34 (q, 2H, CH_2); ^{13}C NMR ($CDCl_3$) ppm 192.06 (C=O), 159.38 (Ar, C), 137.83 (Ar, C), 130.09 (Ar, CH), 123.65 (Ar, CH), 121.92 (Ar, CH), 112.72 (Ar, CH), 64.53 (CH_2), 29.07 (CH_2).

1,4-Bis(3-formylphenoxy)butane 96



The compound was obtained using 1,2-dibromobutane in a yield of 88% mp 55-57° (lit.[14] mp 49-50°); IR (KBr) cm^{-1} 2944, 2724, 1681, 1581;^{1}H NMR ($CDCl_3$) δ 9.99 (s, 2H, CHO), 7.17-7.21 (m, 2H, Ar), 7.41-7.48 (m, 6H, Ar), 4.13 (t, 4H, CH_2), 2.05 (q, 4H, CH_2); ^{13}C NMR ($CDCl_3$) ppm 192.14 (C=O), 159.52 (Ar, C), 137.82 (Ar, C), 130.07 (Ar, CH), 123.55 (Ar, CH), 121.93 (Ar, CH), 112.69 (Ar, CH), 67.71 (CH_2), 25.87 (CH_2).

1,5-Bis(3-formylphenoxy)pentane 97

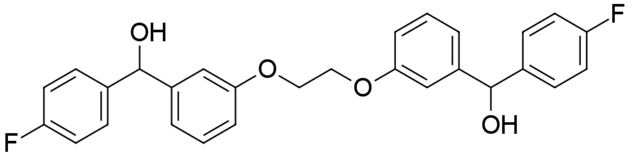


The compound was obtained using 1,2-dibromopentane in a yield of 77%; m.p 51-53° (lit.[2] 55-57°); IR (KBr) 2944, 2724, 1681, 1581 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.98 (s, 2H, CHO), 7.17-7.21 (m, 2H, Ar), 7.40-7.47 (m, 6H, Ar), 4.08 (t, 4H, CH_2), 1.92 (q, 4H, CH_2), 1.70 (q, 2H, CH_2); ^{13}C NMR ($CDCl_3$) ppm 192.17 (C=O), 159.61 (Ar, C), 137.80 (Ar, C), 130.04 (Ar, C), 123.48 (Ar, C), 121.95 (Ar, C), 112.69 (Ar, C), 68.00 (CH_2), 28.87 (CH_2).

General Procedure for the Synthesis of Diols

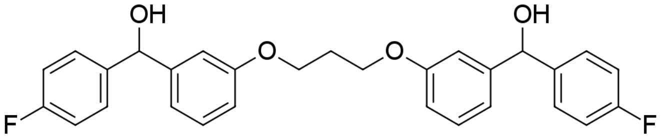
Magnesium (1.08 g, 0.045 mol) was added to a flame-dried, three-necked, 250 mL, round-bottomed flask equipped with a magnetic stir bar. A 25 mL portion of anhydrous tetrahydrofuran (THF) and three drops of dibromoethane were added. The flask was then fitted with a nitrogen inlet and the contents allowed to stir for 15 min. Using an addition funnel, 1-bromo-4-fluorobenzene (7.91 g , 0.045 mol) was added over a period of 15 min after which the appropriate dialdehyde (0.015 mol) dissolved in 30 mL of anhydrous THF, was added dropwise to the reaction flask. The flask was fitted with a condenser and a drying tube and heated to 70° for 2h. The reaction was allowed to cool to 40°, cooled in an ice bath, and acidified with 10% sulfuric acid. The product was extracted using ethyl acetate. The product obtained by evaporation of the ethyl acetate was used in the next step without further purification.

1,2-Bis(3-[(4-fluorophenyl)hydroxymethyl]phenoxy)ethane 99



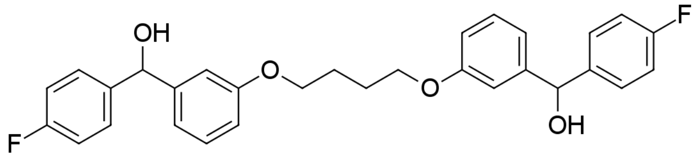
An off-white solid was obtained in 84% yield: IR (KBr) cm^{-1} 3383, 3058, 2972, 1621; ^{1}H NMR (Acetone-d$_6$) δ 7.47 (dd, 4H, $^4J_{HF}$ = 5.5 Hz , $^3J_{HH}$ = 8.4 Hz), 7.24 (dd, 2H, $^3J_{HH}$ = 8.0 Hz), 7.06 (dd, 6H, $^3J_{HF}$ = 8.9 Hz, $^3J_{HH}$ = 8.9 Hz), 7.02 (dd, 2H, $^3J_{HH}$ = 7.9 Hz), 6.86 (dd, 2H, $^3J_{HH}$ = 8.4 Hz), 5.76 (d, 2H, CH), 4.92 (d, 2H, OH), 4.35 (s, 4H, CH$_2$); ^{13}C NMR (Acetone-d$_6$) ppm 162.61 (Ar. CF, d $^1J_{CF}$ = 245.5 Hz), 159.09 (Ar, C), 147.99 (Ar, C) 142.49 (Ar, C, d, $^4J_{CF}$ = 3.1 Hz),134.13 (Ar, CH), 130.14 (Ar, CH), 129.17 (Ar, CH, d, $^2J_{CF}$ = 8.1 Hz), 119.81 (Ar, CH) 115.53 (Ar, CH, d $^2J_{CF}$ = 21.8 Hz) 113.61 (Ar, CH), 112.67 (Ar, CH), 75.27 (CHOH), 67.37 (CH$_2$).

1,3-Bis(3-[(4-fluorophenyl)hydroxymethyl]phenoxy)propane 100



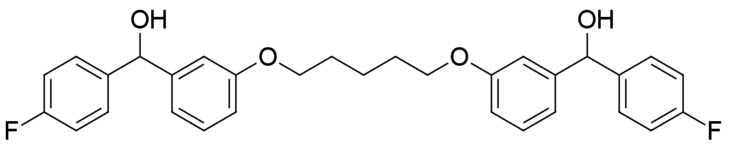
A light brown oil, was obtained in 87% yield: IR (KBr) cm^{-1} 3371, 3059, 2965, 1600; ^{1}H NMR (CDCl$_3$) δ 7.30 (dd, 4H, $^4J_{HF}$ = 5.8 Hz , $^3J_{HH}$ = 8.8 Hz), 7.21 (dd, 2H, $^3J_{HH}$ = 8.3 Hz,), 6.98 (dd, 6H, $^3J_{HF}$ = 8.7 Hz, $^3J_{HH}$ = 8.7 Hz), 6.89 (dd, 2H, $^3J_{HH}$ = 8.0 Hz), 6.78 (dd, 2H, $^3J_{HH}$ = 8.5 Hz), 5.76 (s, 2H, CH), 4.14 (t, 4H, CH$_2$), 2.24 (q, 2H, CH$_2$); ^{13}C NMR (CDCl$_3$) ppm 162.13 (Ar. CF, d $^1J_{CF}$ = 245.5 Hz), 159.09 (Ar, C), 145.31 (Ar, C) 139.38 (Ar, C, d, $^4J_{CF}$ = 3.1 Hz),129.63 (Ar, CH), 128.25 (Ar, CH, d, $^2J_{CF}$ = 8.1 Hz), 118.90 (Ar, CH) 115.53 (Ar, CH, d $^2J_{CF}$ = 21.8 Hz), 113.61 (Ar, CH), 112.67 (Ar, CH),, 75.34 (CHOH), 64.34 (CH_2), 29.31 (CH_2).

1,4-Bis(3-[(4-fluorophenyl)hydroxymethyl]phenoxy)butane 101



A light tan solid was obtained in a yield of 82%; IR (KBr) cm^{-1} 3376, 3068, 2964, 1600; ^{1}H NMR ($CDCl_3$) δ 7.46 (dd, 4H, $^4J_{HF}$ = 5.5 Hz , $^3J_{HH}$ = 8.4 Hz), 7.21 (dd, 2H, $^3J_{HH}$ = 7.9 Hz,), 6.98 (dd, 6H, $^3J_{HF}$ = 7 Hz, $^3J_{HH}$ = 7 Hz), 6.79 (dd, 2H, $^3J_{HH}$ = 9.0 Hz), 6.78 (dd, 2H, $^3J_{HH}$ = 8.5 Hz), 5.74 (s, 2H, CH), 4.14 (t, 4H, CH_2), 1.97 (q, 4H, CH_2); ^{13}C NMR ($CDCl_3$) ppm 162.15 (Ar. CF, d $^1J_{CF}$ = 245.5 Hz), 159.03 (Ar, C), 145.40 (Ar, C) 142.55 (Ar, C),139.56 (Ar, C, d, $^4J_{CF}$ = 3.1 Hz), 129.57 (Ar, CH) 128.25 (Ar, CH, d, $^2J_{CF}$ = 8.1 Hz), 118.90 (Ar, CH) 115.53 (Ar, CH, d $^2J_{CF}$ = 21.8 Hz), 113.61 (Ar, CH), 112.67 (Ar, CH), 75.34 (CHOH), 64.34 (CH_2), 29.31 (CH_2).

1,5-Bis(3-[(4-fluorophenyl)hydroxymethyl]phenoxy)pentane 102



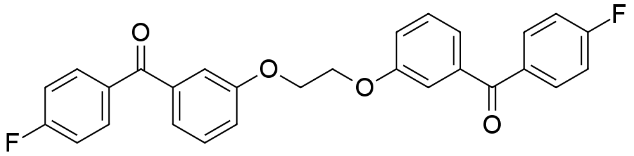
A light brown oil was obtained in 89% yield; IR (KBr) cm^{-1} 3384, 3064, 2871, 1581; ^{1}H NMR ($CDCl_3$) 7.21 (dd, 4H, $^4J_{HF}$ = 5.5 Hz , $^3J_{HH}$ = 8.6 Hz), 7.12 (dd, 2H, $^3J_{HH}$ = 7.9 Hz,), 6.88 (dd, 6H, $^3J_{HF}$ =8.7 Hz, $^3J_{HH}$ = 7 Hz), 6.78 (dd, 2H, $^3J_{HH}$ = 7.3 Hz), 6.69 (dd, 2H, $^3J_{HH}$ = 7.5 Hz), 5.61 (s, 2H, CH), 3.84 (t, 4H, CH_2), 1.73 (q, 4H, CH_2), 1.52 (q, 2H, CH_2); ^{13}C NMR ($CDCl_3$) ppm 162.15 (Ar. CF, d $^1J_{CF}$ = 245.5 Hz), 159.30 (Ar, C), 145.34 (Ar, C), 139.56 (Ar, C, d, $^4J_{CF}$ = 3.1 Hz), 129.57 (Ar, CH) 128.25 (Ar, CH, d, $^2J_{CF}$

= 8.1 Hz), 118.90 (Ar, CH) 115.53 (Ar, CH, d $^2J_{CF}$ = 21.8 Hz), 113.61 (Ar, CH), 112.67 (Ar, CH), 75.34 (CHOH), 64.34 (CH_2), 29.31 (CH_2), 21.03 (CH_2).

Monomer Synthesis

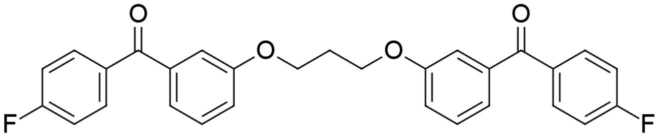
In a one-necked, 250 mL, round-bottomed flask, the appropriate diol (0.015 mol) was dissolved in 35 mL acetone. Jones reagent was prepared in 5% excess by dissolving sodium dichromate (0.010 mol) in water and then adding concentrated sulfuric acid (0.042 mol). The Jones reagent was added dropwise to the acetone solution. The reaction mixture was refluxed for 12 h. The reaction was allowed to cool to 30º and then 10 mL of isopropyl alcohol was added and the stirring was continued for 30 min. The product was extracted with $CHCl_3$ (40 mL). The $CHCl_3$ solution was washed twice with brine and twice with water. The organic layer was then dried over magnesium sulfate, filtered, and the solvent removed under vacuum.

1,2-Bis(3-(4-fluorobenzoyl)phenoxy)ethane 103



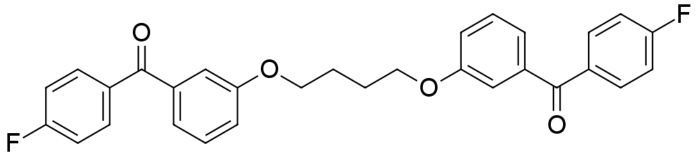
A white solid was obtained in 42% yield. The crude product was recrystallized from chloroform: m.p: 154-156º; IR (KBr) cm^{-1} 3064, 2937, 1656, 1596;^{1}H NMR ($CDCl_3$) δ 7.87 (dd, 4H, $^4J_{HF}$ = 5.5 Hz, $^3J_{HH}$ = 8.8 Hz), 7.40 (dd, 6H $^3J_{HH}$ = 8.8 Hz), 7.17 (dd, 6H, $^3J_{HF}$ = 8.8 Hz, $^3J_{HH}$ = 8.8 Hz) 4.46 (s, 4H, CH_2); ^{13}C NMR ($CDCl_3$) ppm 194.99 (C= O), 164.56 (Ar, CF, d $^1J_{CF}$ = 254.1 Hz), 158.87 (Ar, C), 138.88 (Ar, C), 133.74 (Ar, C, d, $^4J_{CF}$ = 3.0 Hz), 132.57 (Ar, CH, d, $^4J_{CF}$ = 9.1 Hz), 129.32 (Ar, CH), 122.70 (Ar, CH), 119.25 (Ar, CH), 115.30 (Ar, CH, d, $^2J_{CF}$ = 22.4 Hz), 67.51 (CH_2). Anal. Calcd. for $C_{28}H_{20}F_2O_4$: C, 73.36%; H, 4.40%. Found C, 73.21%; H, 4.56%.

1,3-Bis(3-(4-fluorobenzoyl)phenoxy)propane 104



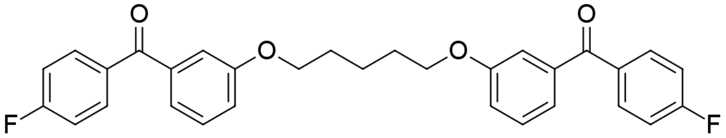
An off-white solid was formed in 64% yield. The crude product was recrystallized from acetone: m.p: 94-96º; IR (KBr) cm^{-1} 3064, 2937, 1658, 1592;^{1}H NMR ($CDCl_3$) δ ^{1}H NMR ($CDCl_3$) δ 7.85 (dd, 4H, $^{4}J_{HF}$ = 5.4 Hz, $^{3}J_{HH}$ = 8.8 Hz), 7.35 (dd, 6H $^{3}J_{HH}$ = 7.7 Hz), 7.17 (dd, 6H, $^{3}J_{HF}$ = 8.9 Hz, $^{3}J_{HH}$ = 8.9 Hz) 4.24 (t, 4H, CH_2), 2.32 (q, 2H, CH_2)^{13}C NMR ($CDCl_3$) ppm 194.99 (C= O), 164.56 (Ar, CF, d $^{1}J_{CF}$ = 254.1 Hz), 158.87 (Ar, C), 138.88 (Ar, C), 133.84 (Ar, C, d, $^{4}J_{CF}$ = 3.2 Hz), 132.57 (Ar, CH, d, $^{4}J_{CF}$ = 9.1 Hz), 129.32 (Ar, CH), 122.70 (Ar, CH), 119.25 (Ar, CH), 115.30 (Ar, CH, d, $^{2}J_{CF}$ = 22.9 Hz), 64.51 (CH_2), 29.16 (CH_2). Anal. Calcd for $C_{29}H_{22}F_2O_4$: C, 73.72%; H, 4.69%. Found C, 73.35%; H, 4.85%.

1,4-Bis(3-(4-fluorobenzoyl)phenoxy)butane 105



A white solid was obtained in a yield of 50%. Crude product was recrystallized from ethanol; m.p : 151º-152º; IR (KBr) cm-^{1} 3075, 2957, 1659, 1586; ^{1}H NMR ($CDCl_3$) δ 7.87 (dd, 4H, $^{4}J_{HF}$ = 5.5 Hz, $^{3}J_{HH}$ = 8.8 Hz), 7.32 (m, 6H $^{3}J_{HH}$ = 7.8 Hz), 7.17 (dd, 6H, $^{3}J_{HF}$ = 8.8 Hz, $^{3}J_{HH}$ = 8.8 Hz) 4.24 (t, 4H, CH_2), 2.32 (q, 2H, CH_2)^{13}C NMR ($CDCl_3$) ppm 195.07 (C= O), 165.15 (Ar, CF, d $^{1}J_{CF}$ = 254.1 Hz), 159.08 (Ar, C), 138.81 (Ar, C), 133.83 (Ar, C, d, $^{4}J_{CF}$ = 3.0 Hz), 132.57 (Ar, CH, d, $^{4}J_{CF}$ = 9.1 Hz), 129.32 (Ar, CH), 122.52 (Ar, CH), 119.28 (Ar, CH), 115.30 (Ar, CH, d, $^{2}J_{CF}$ = 22.9 Hz), 67.98 (CH_2), 28.94 (CH_2). Anal. Calcd. for $C_{30}H_{24}F_2O_4$: C, 74.01%; H, 4.94%. Found: C, 73.52%; H, 5.09%.

1,5-Bis(3-(4-fluorobenzoyl)phenoxy)pentane 106

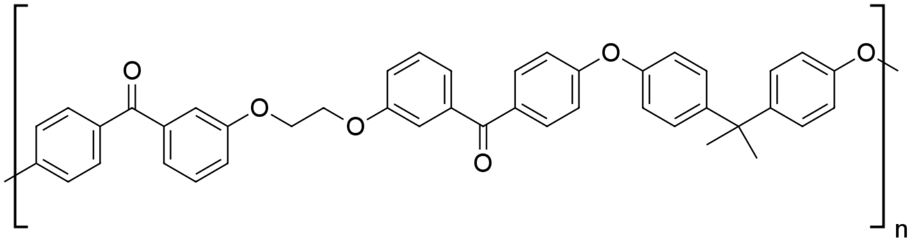


An off-white solid was obtained in 51 % yield. Crude product was recrystallized from ethanol; IR (KBr) cm-^{1} 3070, 2942, 1656, 1596; ^{1}H NMR ($CDCl_3$) δ 7.86 (dd, 4H, $^4J_{HF}$ = 5.4 Hz, $^3J_{HH}$ = 8.9 Hz), 7.39 (dd, 6H $^3J_{HH}$ = 8.8 Hz), 7.17 (dd, 6H, $^3J_{HF}$ = 8.8 Hz, $^3J_{HH}$ = 8.9 Hz), 4.06 (t, 4H, CH_2), 1.91 (q, 4H, CH_2), 1.67 (q, 2H, CH_2); ^{13}C NMR ($CDCl_3$) ppm 194.99 (C= O), 165.15 (Ar, CF, d $^1J_{CF}$ = 254.1 Hz), 159.10 (Ar, C), 138.78 (Ar, C), 133.84 (Ar, C, d, $^4J_{CF}$ = 3.0 Hz), 132.65 (Ar, CH, d, $^4J_{CF}$ = 9.0 Hz), 129.32 (Ar, CH), 122.52 (Ar, CH), 119.25 (Ar, CH), 115.29 (Ar, CH, d, $^2J_{CF}$ = 21.9 Hz), 67.98 (CH_2), 28.94 (CH_2), 22.74 (CH_2). Anal. Calcd. for $C_{31}H_{26}F_2O4$: C, 74.39%; H, 5.20%. Found: C, 74.46%; H, 5.31%

General Polymerization Procedure

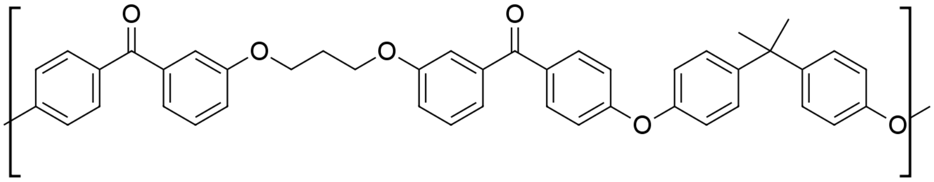
The polymerizations were carried out in a Q-tube™ equipped with a stir bar. Calculated molar quantities of the diketone compound and bisphenol-A were dissolved in N-methyl-2-pyrrolidone, NMP (7.5 mL). Finely crushed potassium carbonate was also added. The reaction was run at 170º for 12 h. After cooling to 68º, the reaction mixture was precipitated into a methanol-water solution (80/20 v/v) acidified with glacial acetic acid and stirred for 1 h. The polymer was collected by filtration. The polymer was dissolved in chloroform and precipitated into methanol twice. After filtration, the polymer was dried under vacuum.

Poly(oxy-1,4-phenylene-carbonyl-1,3-phenylene-oxy-ethylene-oxy-1,3-phenylene-carbonyl-1,4-phenylene-oxy-1,4-phenylene-1-methylethylidene-1,4-phenylene) 107



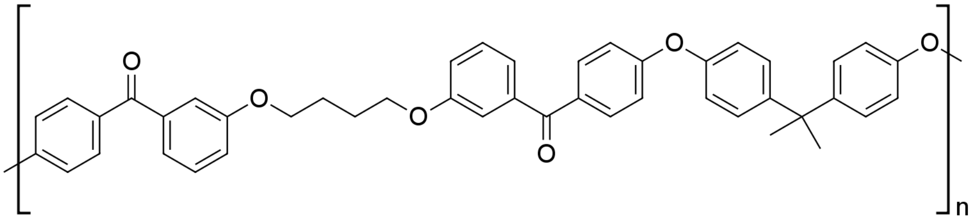
A tan powder was obtained in a yield of 80%; IR (KBr) cm^{-1} 3059, 2932, 1646, 1585; ^{1}H NMR ($CDCl_3$) δ 7.00-7.84 (m, 24H, Ar), 4.41 (s, 4H, CH_2), 1.73 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$) ppm 195.19 (C= O), 161.71 (Ar, C), 158.80 (Ar, C), 153.35 (Ar, C), 146.80 (Ar, C), 139.29 (Ar, C), 132.45 (Ar, CH), 131.80 (Ar, CH), 129.20 (Ar, CH), 128.35 (Ar, CH), 122.62 (Ar, CH), 119.65 (Ar, CH), 118.90 (Ar, CH), 117.06 (Ar, CH), 114.90 (Ar, CH), 66.70 (CH_2), 42.38 (C), 31.02 (CH_3). Anal. Calcd. for $C_{43}H_{34}O_6$: C, 77.6%, H, 5.25%. Found: C, 78.02%; H, 5.33%.

Poly(oxy-1,4-phenylene-carbonyl-1,3-phenylene-oxy-trimethylene-oxy-1,3-phenylene-carbonyl-1,4-phenylene-oxy-1,4-phenylene-1-methylethylidene-1,4-phenylene) 108



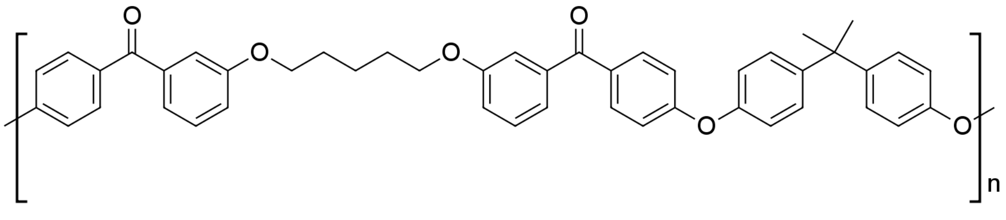
An off-white powder was obtained in a yield of 85%; IR (KBr) cm^{-1} 3064 , 2937, 1654, 1591; ^{1}H NMR ($CDCl_3$) δ 7.00-7.83 (m, 24H, Ar), 4.23 (t, 4H, CH_2), 2.32 (q, 2H, CH_2), 1.73 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$) ppm 195.19 (C= O), 161.71 (Ar, C), 158.80 (Ar, C), 153.35 (Ar, C), 146.80 (Ar, C), 139.29 (Ar, C), 132.45 (Ar, CH), 131.80 (Ar, CH), 129.20 (Ar, CH), 128.35 (Ar, CH), 122.62 (Ar, CH), 119.65 (Ar, CH), 118.90 (Ar, CH), 117.06 (Ar, CH), 114.90 (Ar, CH), 64.53 (CH_2), 42.38 (C), 31.02 (CH_3), 29.19 (CH_2). Anal. Calcd. for $C_{44}H_{36}O_6$: C, 77.65%; H, 5.44%. Found: C, 77.91%; H, 5.50%.

Poly(oxy-1,4-phenylene-carbonyl-1,3-phenylene-oxy-tetramethylene-oxy-1,3-phenylene-carbonyl- 1,4-phenylene-oxy-1,4-phenylene-1-methylethylidene-1,4-phenylene) 109



A tan powder was obtained in a yield of 64%; IR (KBr) cm^{-1} 3058, 2902, 1659, 1587; ^1H NMR ($CDCl_3$) δ 7.00-7.83 (m, 24H, Ar), 4.10 (t, 4H, CH_2), 2.02 (q, 4H, CH_2), 1.73 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$) ppm 195.19 (C= O), 161.71 (Ar, C), 158.80 (Ar, C), 153.35 (Ar, C), 146.80 (Ar, C), 139.29 (Ar, C), 132.45 (Ar, CH), 131.80 (Ar, CH), 129.20 (Ar, CH), 128.35 (Ar, CH), 122.62 (Ar, CH), 119.65 (Ar, CH), 118.90 (Ar, CH), 117.06 (Ar, CH), 114.90 (Ar, CH), 67.67 (CH_2), 42.38 (C), 31.02 (CH_3), 25.95 (CH_2). Anal. Calcd. for $C_{45}H_{38}O_6$: C, 77.81%; H, 5.62%. Found: C, 78.63%, H, 5.87%.

Poly(oxy-1,4-phenylene-carbonyl-1,3-phenylene-oxy-pentamethylene-oxy-1,3-phenylene-carbonyl-1,4 phenylene-oxy-1,4-phenylene-1-methylethylidene-1,4-phenylene) 110



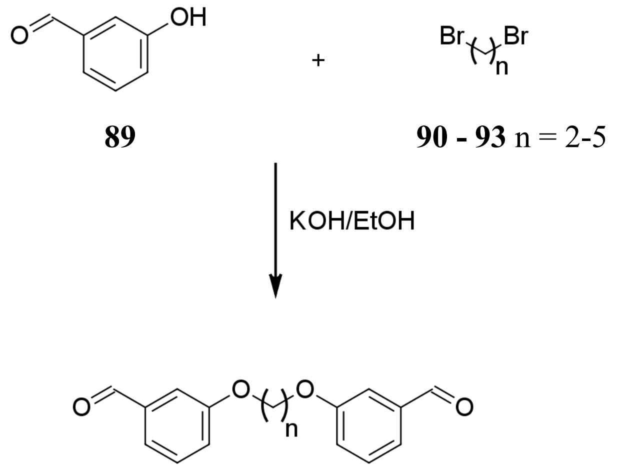
A tan powder was obtained in a yield of 53%; IR (KBr) cm^{-1} 3072, 2928, 1653, 1577; ^1H NMR ($CDCl_3$) δ 7.00-7.83 (m, 24H, Ar), 4.10 (t, 4H, CH_2), 2.02 (q, 4H, CH_2), 1.73 (s, 6H, CH_3), 1.70 (s, 2H, CH_2); ^{13}C NMR ($CDCl_3$) ppm 195.19 (C= O), 161.71 (Ar, C), 158.80 (Ar, C), 153.35 (Ar, C), 146.80 (Ar, C), 139.29 (Ar, C), 132.45 (Ar, CH), 131.80 (Ar, CH), 129.20 (Ar, CH), 128.35 (Ar, CH), 122.62 (Ar, CH), 119.65 (Ar, CH), 118.90 (Ar, CH), 117.06 (Ar, CH), 114.90 (Ar, CH), 67.96 (CH_2), 42.38 (C), 31.02 (CH_3), 28.96 (CH_2), 22.74 (CH_2). Anal. Calcd. for $C_{46}H_{40}O_6$: C, 78.10%, H, 5.79%. Found: C, 79.39%, H, 5.97%.

RESULTS AND DISCUSSION

The objectives of this research were to 1) generate a series of poly(ether ether ketones containing alkylenedioxy subunits AND meta linkages and 2) characterize all new monomers and polymers and 3) compare the thermal properties of the new polymers to existing alkylenedioxy all para linked poly(ether ether ketones).

Dialdehyde Synthesis

The reaction of 3-hydroxybenzaldehyde **89** with 1,2-dibromoethane **90,** 1,3-dibromopropane **91,** 1,4-dibromobutane **92** and 1,5-dibromopentane **93** in ethanol/KOH yielded 1,2-bis(3-formylphenoxy)ethane **94**, 1,3-bis(3-formylphenoxy)propane **95**, 1,4-bis(3-formylphenoxy)butane **96** and 1,5-bis(3-formylphenoxy)pentane **97**, respectively.[22,23] A methanol/water mixture was used for recrystallization. The yields were 40%, 88%, 88% and 77%, respectively.



89 **90 - 93** n = 2-5

94 – 97 n = 2-5

Table 4. Melting Points and Yields of Compounds **94-97**.

n	**Yield (%)**	**m.p (°C)**	**m.p (lit[22, 23])**
2	40	85-87	79-81
3	88	52-53	48-50
4	88	55-57	49-50
5	77	51-53	55-57

Compounds **94-97** were characterized by IR, ^{1}H NMR and ^{13}C NMR. The Infrared (IR) spectra (**Figures 15, 18, 21, 24**) were similar in that they all exhibited an aldehyde carbonyl absorption at about 1680 cm^{-1}.

The ^{1}H NMR **(Figure 3** stacked**, Figures 13, 16, 19, 22)** spectra indicate the presence of an aldehyde by an absorption at about 10 δ. The aromatic region showed two multiplets with absorptions at about 7.28 δ and 7.51 δ. The aliphatic region showed

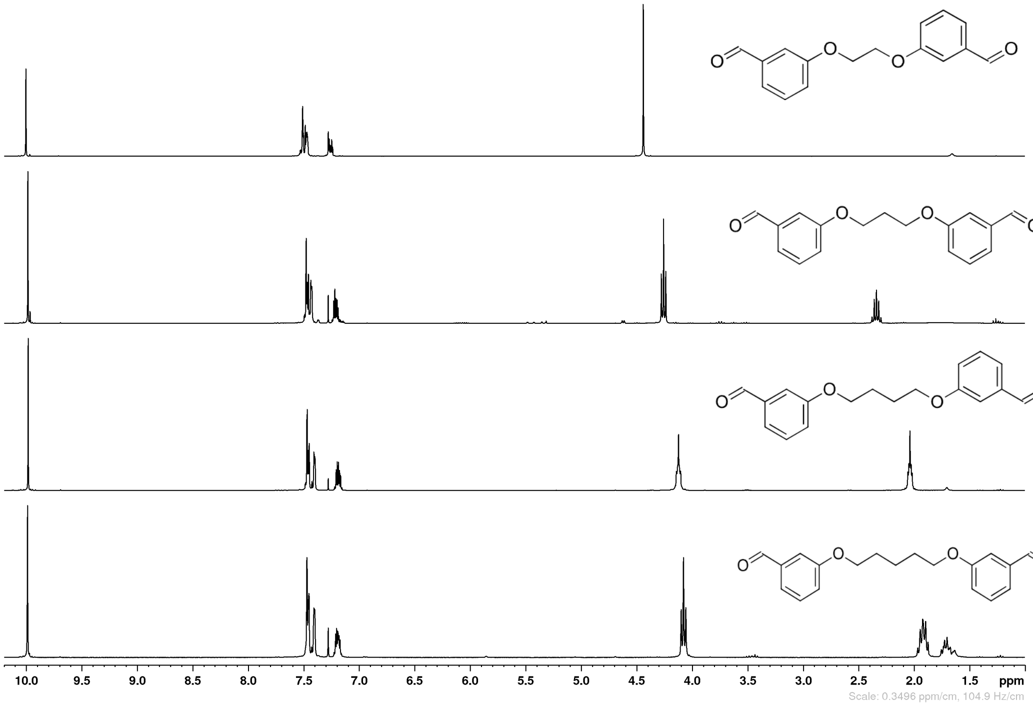


Figure 3. Stacked ^{1}H NMR plots of compounds **94-97**

absorptions corresponding to the chain length of each compound. Compound **94** had only a singlet absorption at 4.5 δ, **95** had a triplet at 4.3 δ and a quintet at 2.3 δ, **96** showed a triplet at 4.1 δ and a triplet at 2.0 δ and **97** showed a triplet at 4.1 δ and two quintets at 1.9 δ and 1.6 δ, respectively.

The ^{13}C NMR **(Figure 4** stacked**, Figures 14, 17, 20, 23)** spectra for all the compounds showed absorptions at about 192 ppm indicative of an aldehyde. In addition, there were six aromatic carbon absorptions in the 115-160 ppm range with two quaternary carbons and four CH absorptions. The aliphatic region, as observed in the ^{1}H NMR, showed absorptions corresponding to the length of the alkylenedioxy link. Compound **94** exhibited just one absorption, **95** and **96** exhibited two absorptions and **97** exhibited three absorptions.

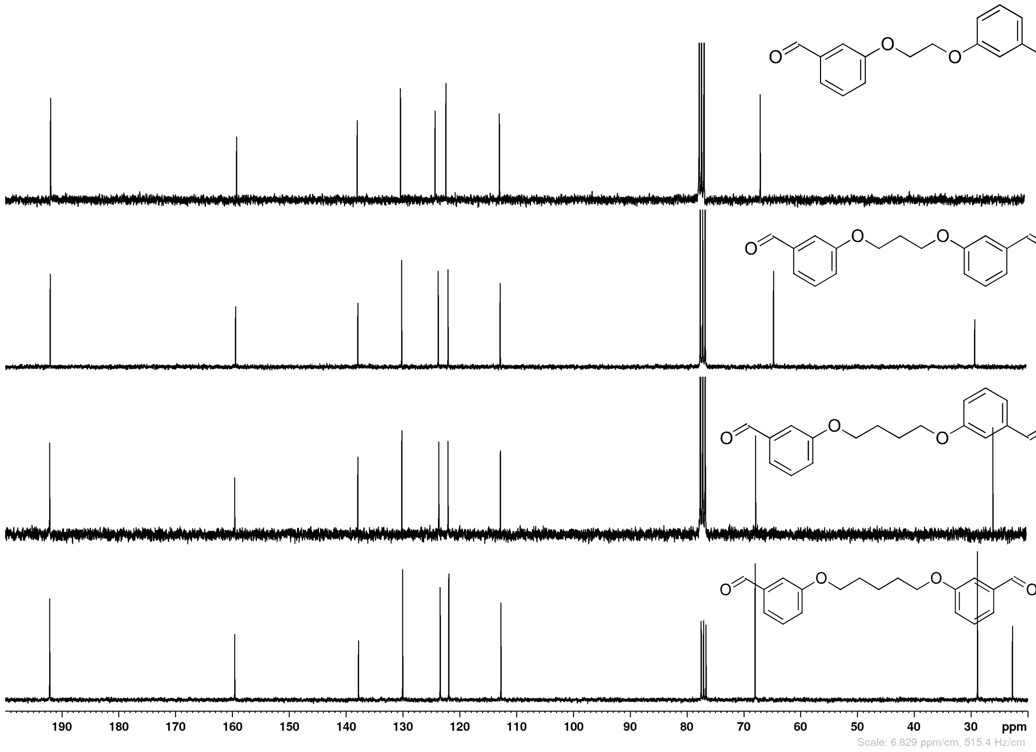
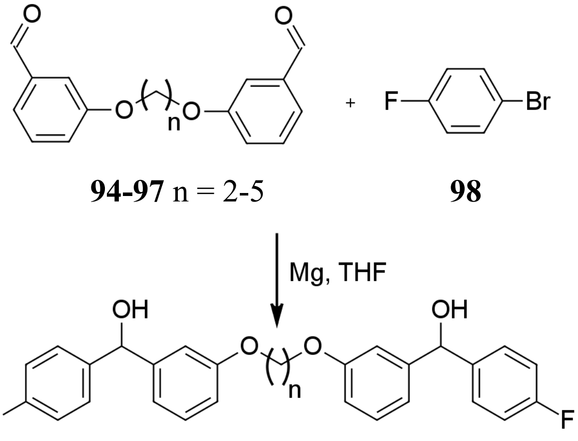


Figure 4. Stacked ^{13}C NMR plots of **94-97.**

Grignard Reactions

The next phase involved the synthesis of a diol by the reaction of compounds **94-97** with a Grignard reagent. Thus, the reaction of 1-bromo-4-fluorobenzene **98** with magnesium in tetrahydrofuran (THF) was used to form the corresponding Grignard which was then reacted with **94-97** to form 1,2-bis(3-[(4-fluorophenyl)hydroxymethyl]-phenoxy)ethane **99,** 1,3-bis(3-[(4-fluorophenyl)hydroxymethyl]phenoxy)propane **100,** 1,4-bis(3-[(4-fluorophenyl)hydroxymethyl]phenoxy)butane **101** and 1,5-bis(3-[(4-fluorophenyl)hydroxymethyl]phenoxy)pentane **102**, respectively. The yields were 84%, 87%, 84% and 89%, respectively.



99-102 n = 2-5

The products from this step were used without purification but could be partially characterized using IR, ^{1}H NMR and ^{13}C NMR. As expected, the IR spectra (**Figures 27, 30, 33, 36**) showed the disappearance of the C=O peak at 1685 cm^{-1} and the appearance of an OH peak around 3400 cm^{-1}.

The ^{1}H NMR spectra (**Figure 5** stacked**, Figures 25, 28, 31, 34**) were typically determined in $CDCl_3$ except the spectrum for **99** that was run in acetone-d_6. The ^{1}H NMR spectra of the diols **99-102** (**Figure 5)** typically show the disappearance of the aldehyde peak at 10 δ and the appearance of the secondary alcohol C**H**-OH at about 5.5 δ.[21] The incorporation of the para substituted fluorophenyl ring is characterized, in the case of **99**, by the appearance of a doublet of doublets absorption at 7.46 δ with coupling constants of $^3J_{\mathrm{HF}}$ = 5.5 Hz and $^3J_{\mathrm{HH}}$ = 8.4 Hz corresponding to protons meta to the fluorine and another doublet of doublets (looks like a triplet) absorption at 7.07 δ with coupling constants of $^3J_{\mathrm{HF}}$ = 8.9 Hz and $^3J_{\mathrm{HH}}$ = 8.9 Hz) corresponding to protons ortho to the fluorine. Other members of the series exhibited similar absorptions. Peak picking and integration allow the identification of other relevant peaks corresponding to the expected protons in these spectra.

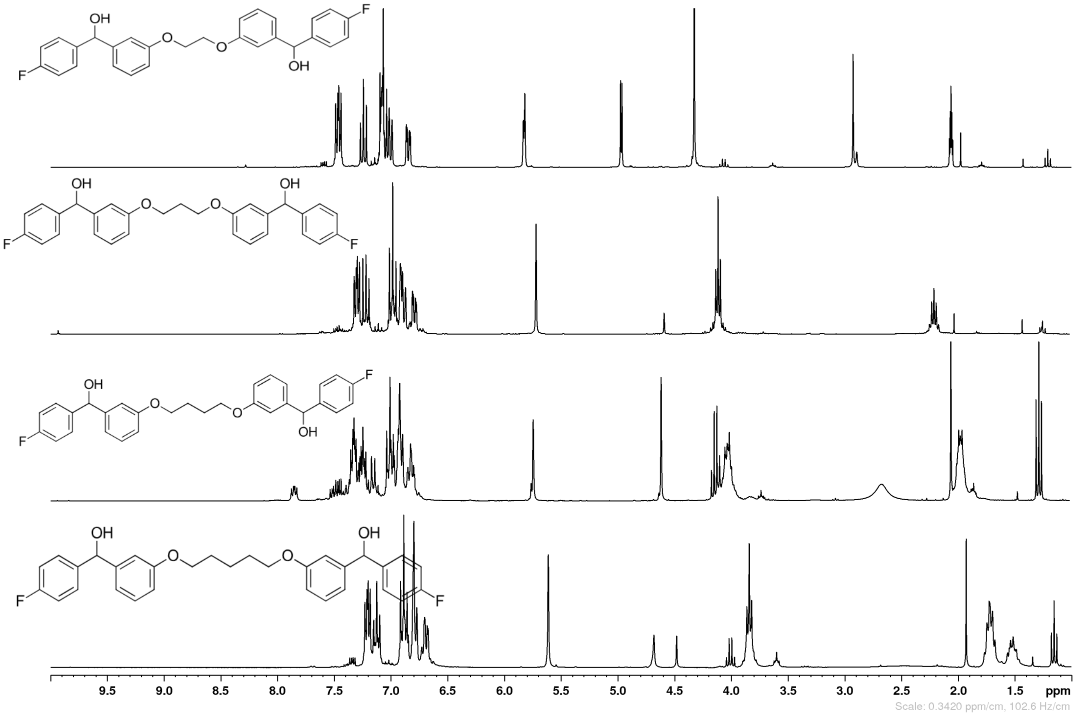


Figure 5. Stacked ^{1}H NMR plots of **99-102.**

The ^{13}C NMR spectra (**Figure 6** stacked**, Figures 26, 29, 32, 35)** of **99-102** all clearly show the disappearance of an absorption at 190 ppm and the appearance of an absorption at about 75 ppm indicative of the carbon of the **C**HOH group.[21] In addition, a doublet absorption at 162.67 ppm (ipso, ${}^{1}J_{\mathrm{CF}}$ = 245 Hz) appears indicating the incorporation of the fluorophenyl group.

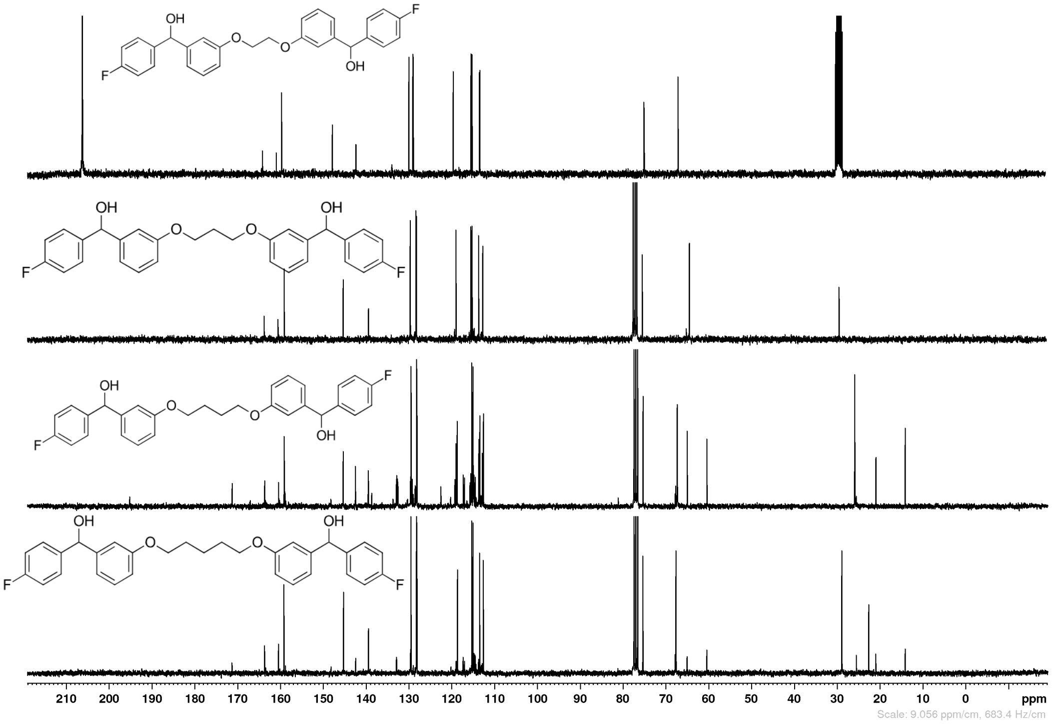
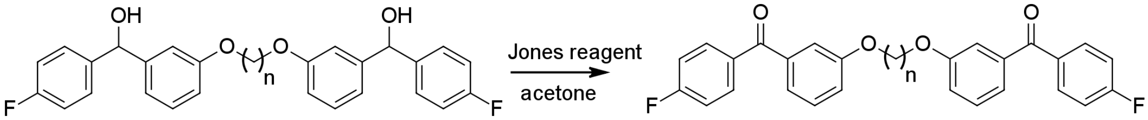


Figure 6. Stacked ^{13}C NMR plots of **99-102.**

Monomer Synthesis

After isolation of **99-102,** a Jones oxidation was used to obtain the bis(fluorobenzophenone) monomers **103-106**. The Jones reagent, composed of a sulfuric acid/sodium dichromate mixture, was added dropwise to the diol dissolved in acetone to produce 1,2-bis(3-(4-fluorobenzoyl)phenoxy)ethane **103,** 1,3-bis(3-(4-fluorobenzoyl)-phenoxy)propane **104,** 1,4-bis(3-(4-fluorobenzoyl)phenoxy)butane **105,** 1,5-bis(3-(4-fluorobenzoyl)phenoxy)pentane **106.** The yields of the reaction were 42%, 64%, 50% and

51%, respectively. The products could be recrystallized from ethanol. The melting points showed an alternating behavior associated previously with the alkylenedioxy links.



99-102 n = 2-5 **103-106** n = 2-5

The IR spectra (**Figures 39, 42, 45, 48**) of compounds **103-106** all exhibited absorptions at around 1656 cm^{-1} characteristic of conjugated ketones. The disappearance of the OH peak around 3300 cm^{-1} also indicated successful conversion of the diol derivatives to the corresponding diketones.

The ^{1}H NMR spectra (**Figure 7** stacked**, Figures 37, 40, 43, 46**) of **103-106** all lacked the C**H**-OH peak around 5.5 δ. The incorporation of the para substituted

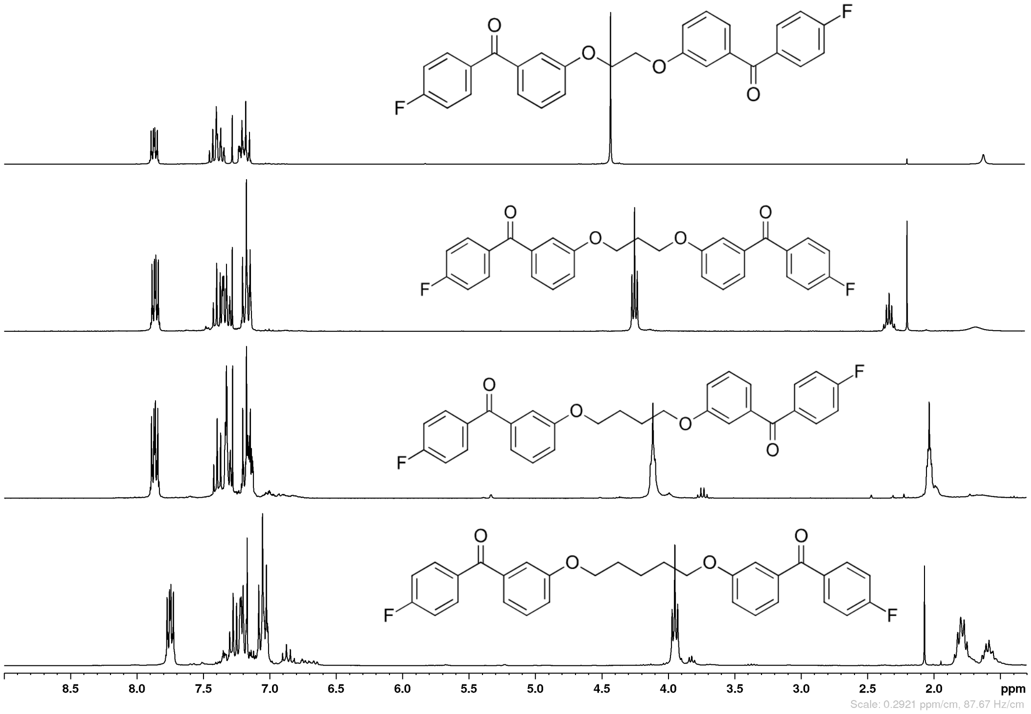


Figure 7. Stacked ^{1}H NMR plots of **103-106**.

fluorophenyl ring is characterized, in the case of **103**, by the appearance of a doublet of doublets absorption at 7.87 δ with coupling constants of $^4J_{HF}$ = 5.4 Hz and $^3J_{HH}$ = 8.8 Hz corresponding to protons meta to the fluorine and another doublet of doublets (looks like a triplet) absorption at 7.17 δ with coupling constants of $^3J_{HF}$ = 8.5 Hz and $^3J_{HH}$ = 8.7 Hz) corresponding to protons ortho to the fluorine. Other members of the series exhibited similar absorptions. The ^{13}C NMR spectra (**Figure 8** stacked**, Figures 38, 41, 44, 47)** of compounds **103-106,** showed the disappearance of the absorption at around 75 ppm that corresponded to the carbon of the **C**HOH and the appearance of a carbonyl absorption at about 195 ppm. In addition, the para fluoro substituted aromatic ring was characterized,

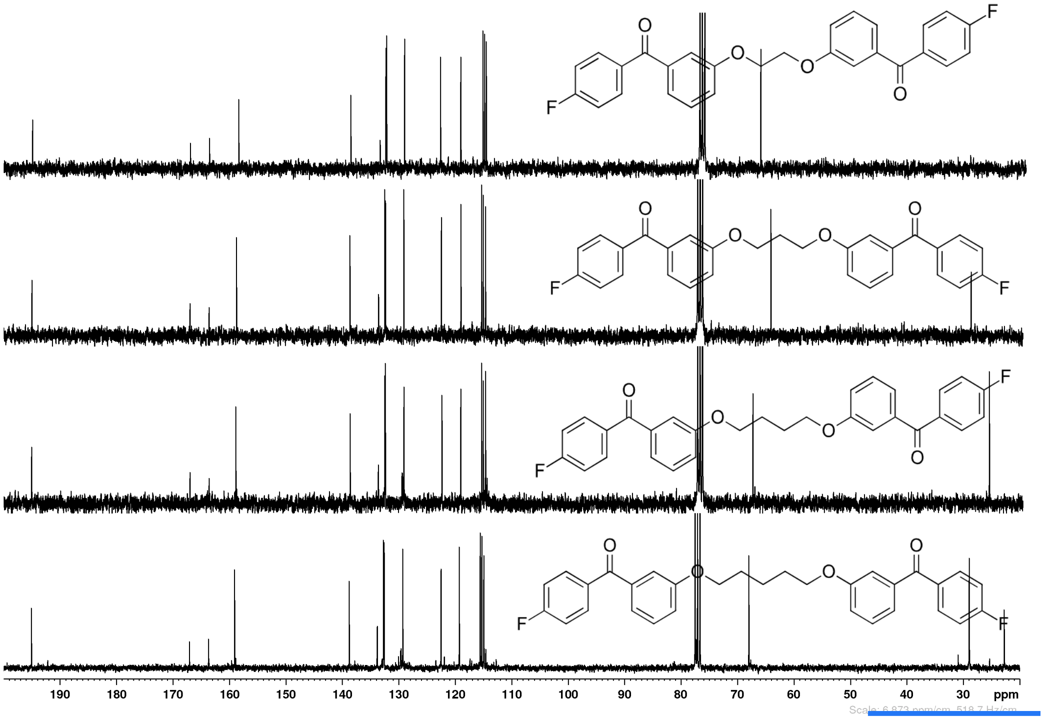


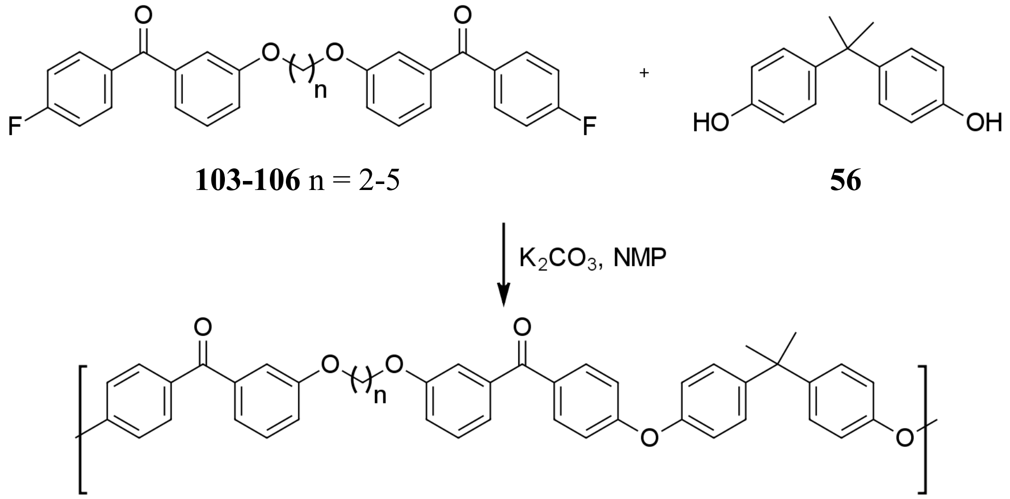
Figure 8. Stacked ^{13}C NMR plots of **103-106**

in the case of **103**, by doublet absorptions corresponding to fluorine coupling at 165.42 ppm (ipso, $^1J_{CF}$ = 254 Hz), 133.74 ppm (para, $^4J_{CF}$ = 3.0 Hz), 132.60 ppm (meta, $^3J_{CF}$ =

9.1 Hz) and 115.49 ppm (ortho, ${}^2J_{CF}$ = 21.9 Hz). Other members of the series exhibited similar absorptions.

Polymerization of Bis(fluorobenzophenones)

The bis(fluorobenzophenone) monomers **103-106** were polymerized with bisphenol-A **56** using potassium carbonate as base in NMP to yield the corresponding poly(ether ether ketone)s **107-110.**



103-106 n = 2-5

56

107-110 n = 2-5

Characterization of compounds **107-110** was done by ^{1}H NMR, ^{13}C NMR, Thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC) and Gel Permeation Chromatography (GPC). The polymers were soluble in various organic solvents including NMP, THF and chloroform and formed transparent films.

The ^{1}H NMR (**Figure 9** stacked**, Figures 49, 52, 55, 58)** spectra showed the appearance of the methyl groups of the bisphenol-A at around 1.72 δ. This indicated the successful polymerization of the monomers with the bisphenol-A. The methylene groups next to the oxygen absorbed as triplets, farthest downfield, at 4 δ for all the polymers. The sandwiched methylene group in **108** absorbed at 2.3 δ, in **109** the middle methylene protons absorbed as a triplet at 2.1 δ while the sandwiched methylene group in **110** was hidden under the end-group absorption. The presence of the small peak beside the bisphenol-A methyl peak may be due to the end groups, which resulted from the low molecular weight polymers that were synthesized.

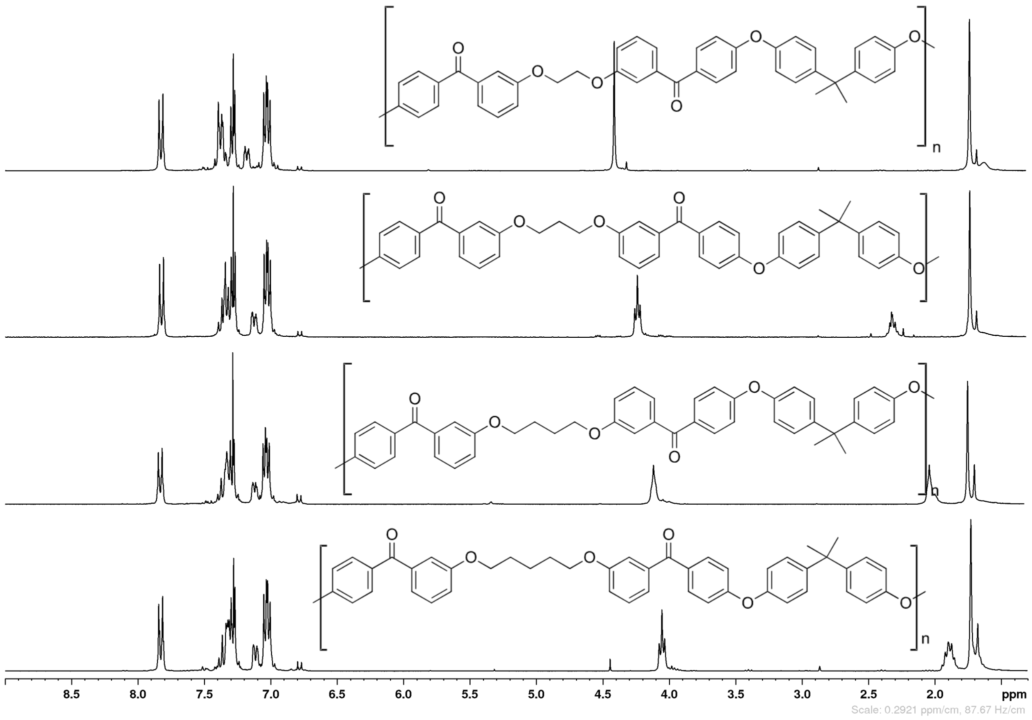


Figure 9. Stacked ^{1}H NMR plots of polymers **107-110**.

The ^{13}C NMR (**Figure 10** stacked**, Figures 50, 53, 56, 59)** spectra exhibited the appearance of the quaternary carbon of the bisphenol-A absorbing at 42 ppm along with the methyl groups that absorbed at 32 ppm. The methylene carbons closest to the oxygen absorbed highest at 70 ppm. The sandwiched methylene carbons in **108 and 109** absorbed at 25 ppm while the middle methylene carbon in **110** absorbed higher up the field at 22 ppm. There were six quaternary carbons in the aromatic region that absorbed between 140-160 ppm.

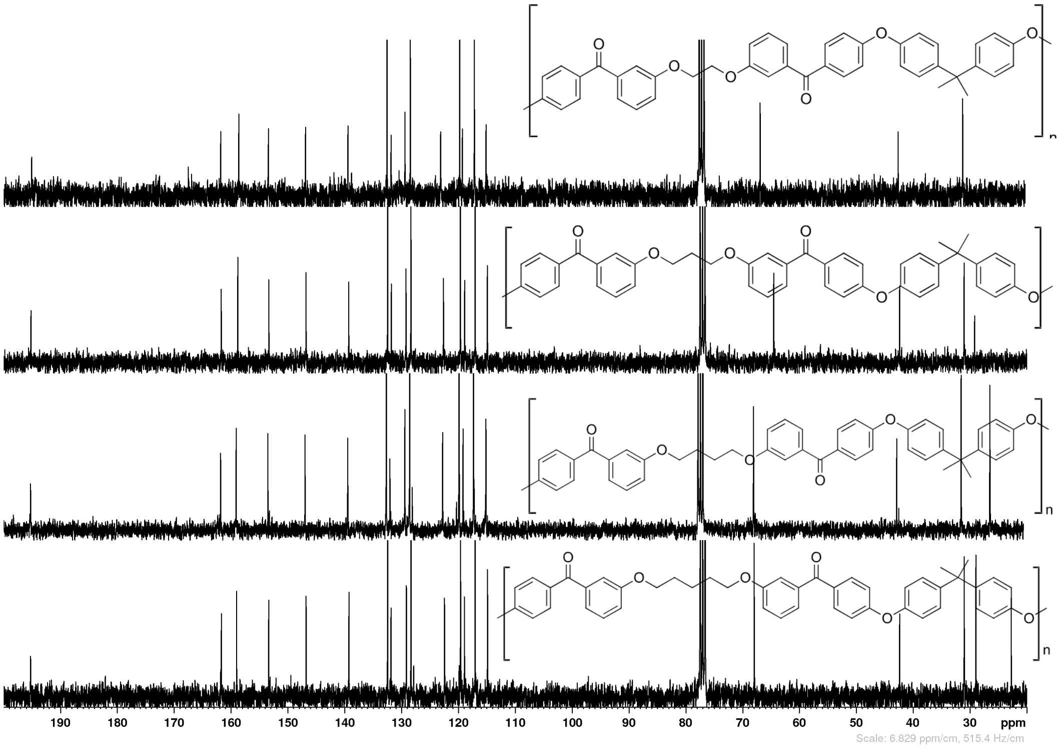


Figure 10. Stacked ^{13}C NMR plots of polymers **107-110.**

The DSC's **(Figure 11)** of the polymers **107-110** were run in a nitrogen atmosphere. The residual solvent and thermal history might affect the first heating run of

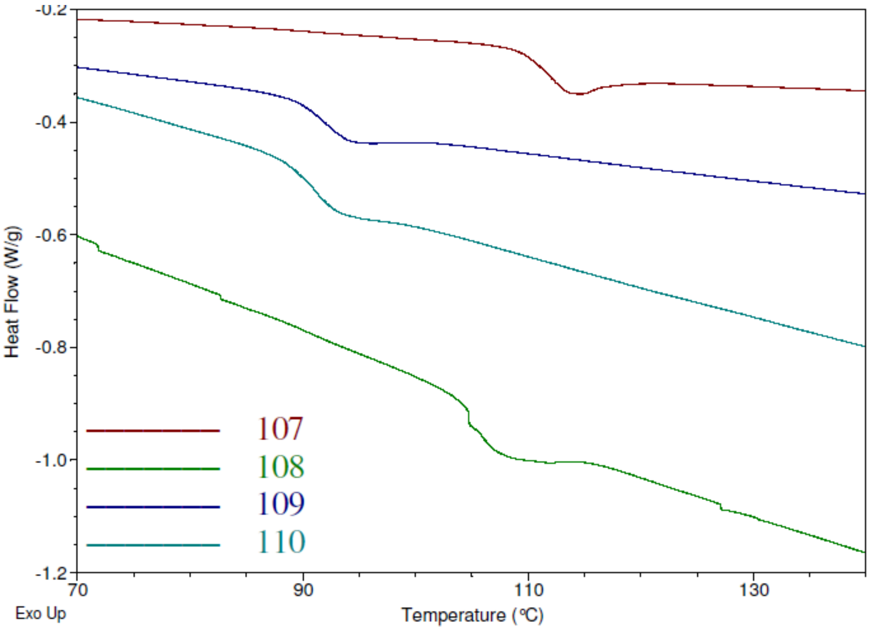


Figure 11. DSC scans in nitrogen for polymers **107- 110.**

DSC,[19] samples were heated to 350º and held at this temperature for 10 min, then cooled to 40º at a cooling rate of 20º min^{-1} and the DSC data were determined according to the second heating run. The data showed that the polymers were amorphous and the T_g decreased with increasing length of the alkylenedioxy unit **(Table 4)**.

The thermal stabilities of the polymers were evaluated using TGA **(Figure 12)** under nitrogen atmosphere. They all decomposed in one step and their 5% weight loss temperatures are all above 380º as depicted in **Table 5**.

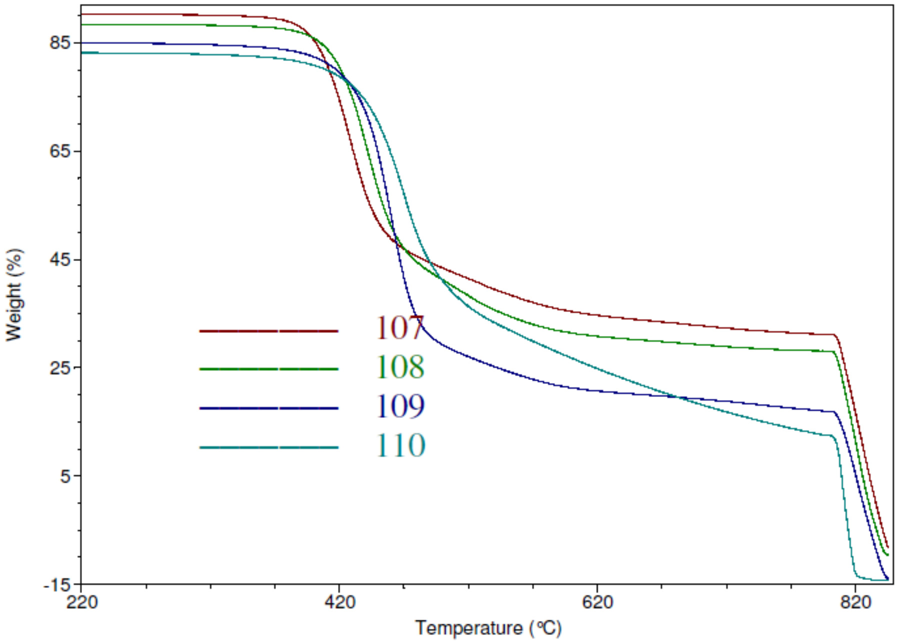


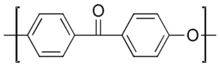
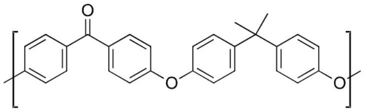
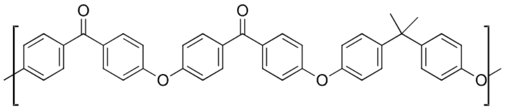
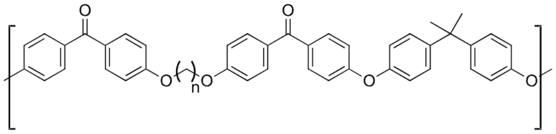
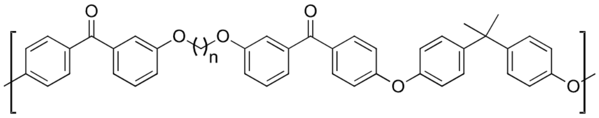
Figure 12. TGA scans in nitrogen for polymers **107-110.**

Table 5. Physical Properties of Polymers **107-110.**

n	% yield	M_w	M_n	PDI	T_g (ºC)	$T_{d5\%}$ (N_2)
2	72	21841	8721	2.50	112	389
3	85	21195	7569	2.8	106	410
4	64	9107	2819	3.23	92	411
5	53	12990	4723	2.75	91	414

The rigidity of the polymer backbone is reduced by the presence of the alkylenedioxy unit. **Table 6** compares the glass transition temperature of meta alkylenedioxy linked PEEK with the para-linked counterpart, synthesized by Patel,[10] and other PEEK with more rigid backbones.[3,4] The meta-linked PEEK appear to be the most flexible derivatives in the series.

Table 6. Glass Transition Temperatures for Selected PEEK Modifications.

Author	Compound	Tg (ºC)
Attwood		145
Hergenrother		155
		162
Patel		n = 2, 3, 4, 5 136, 125, 114, 108
Ohaeri		n = 2, 3, 4, 5 112, 106, 92, 91

CONCLUSIONS

- The monomers **103-106** can be synthesized by a dialdehyde/Grignard/oxidation route. The yields are good and the monomers can be easily purified by recrystallization.
- Polymerization of the monomers with bisphenol-A proceeds smoothly and yields a series of polymers **107-110** that are amorphous and exhibit excellent thermal stability.
- The glass-transition temperatures (T_g) of the meta-linked polymers **107-110** fit nicely into a series of related poly(ether ether ketone)s that have structures that are related to the length and orientation (meta/para) of the linkage between the two fluorophenylcarbonyl units.
- The molecular weights of polymers **107-110** are low but the polymers form films.

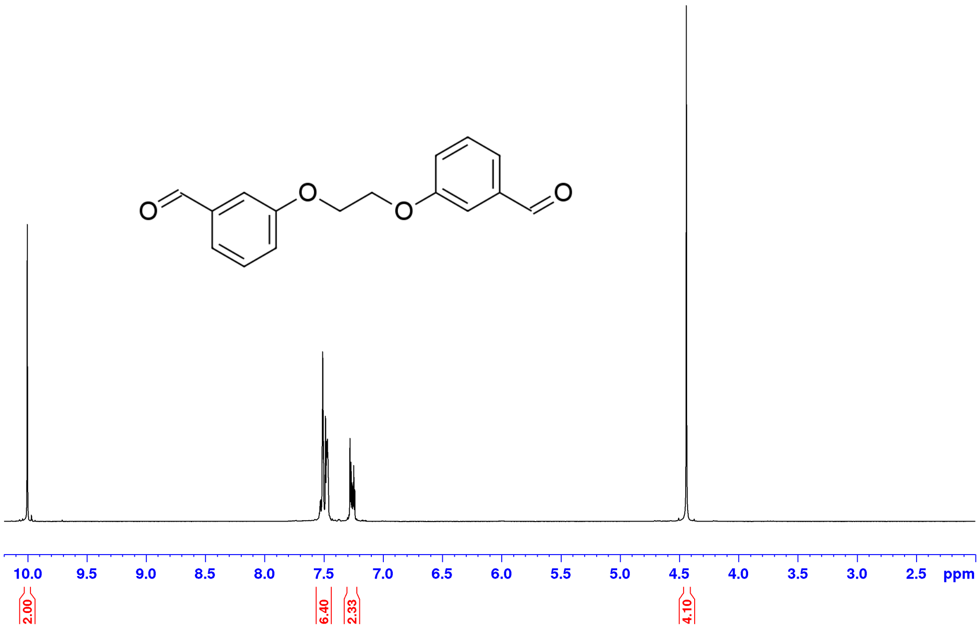


Figure 13. 300 MHz ^{1}H NMR Spectrum (CDCl$_3$) of **94**.

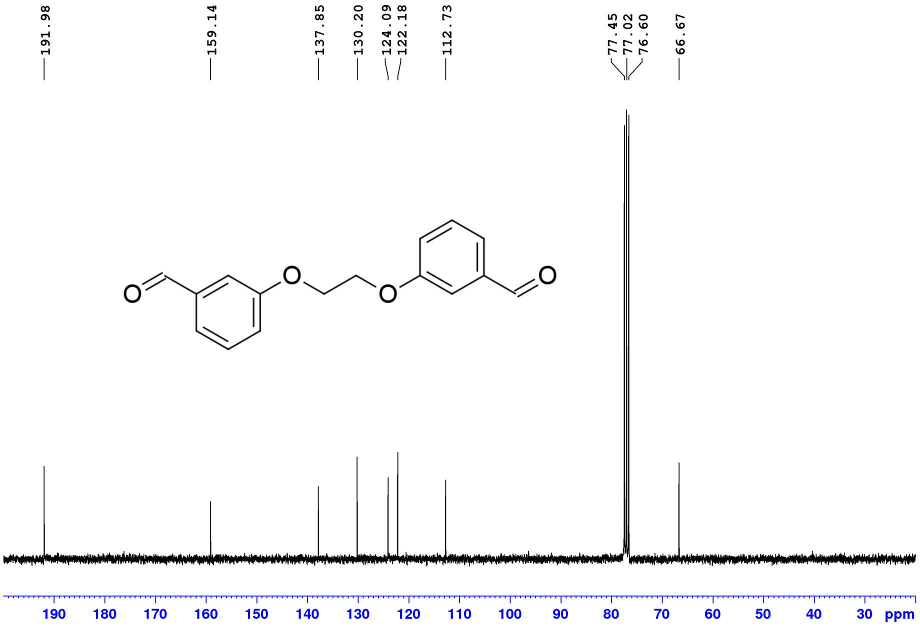


Figure 14. 75 MHz ^{13}C NMR Spectrum (CDCl$_3$) of **94**.

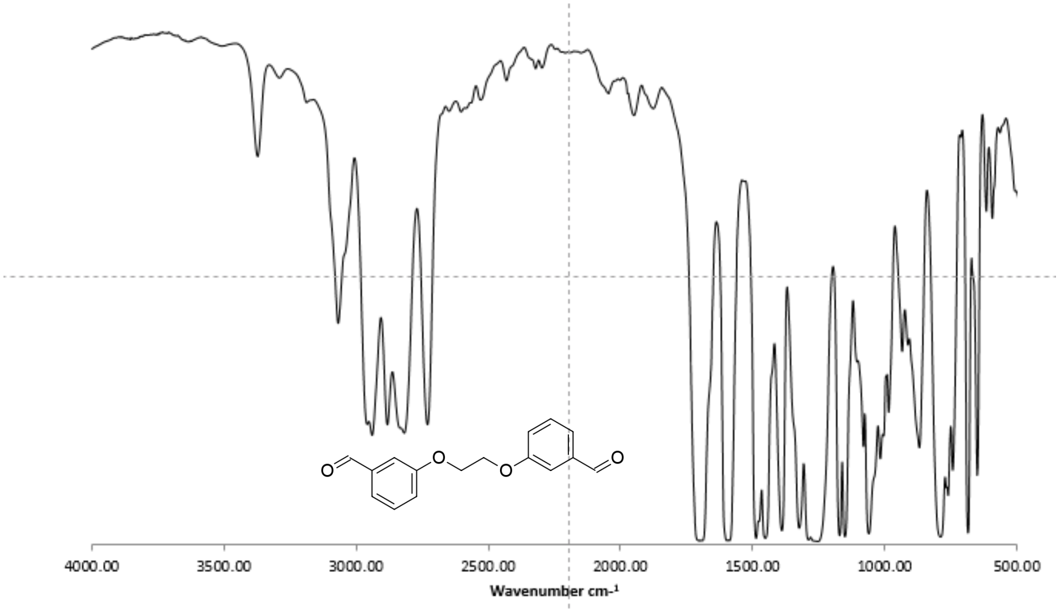


Figure 15. IR Spectrum (KBr) of **94**.

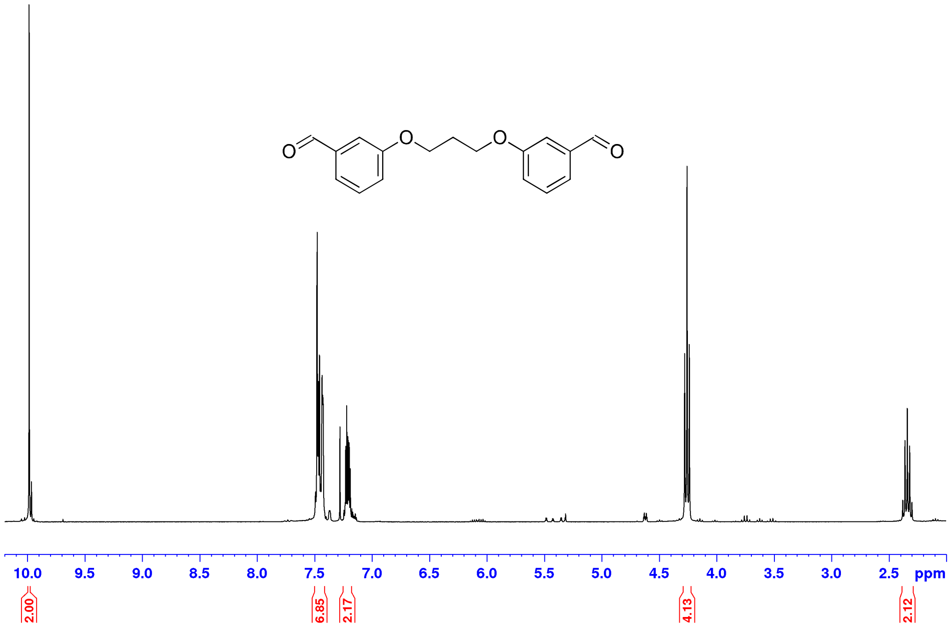


Figure 16. 300 MHz ^{1}H NMR Spectrum ($CDCl_3$) of **95**.

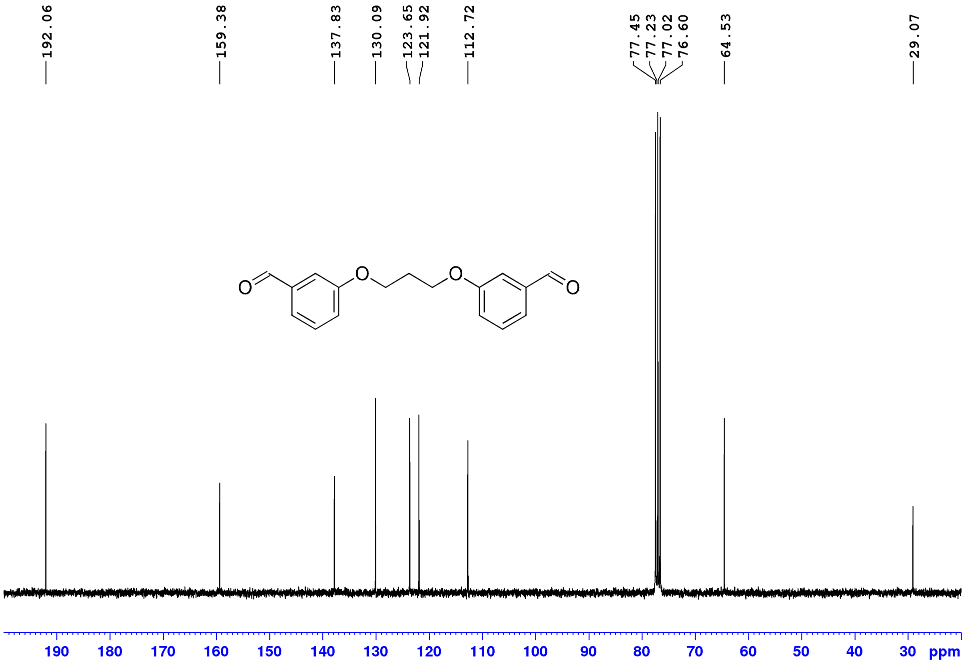


Figure 17. 75 MHz ^{13}C NMR Spectrum ($CDCl_3$) of **95**.

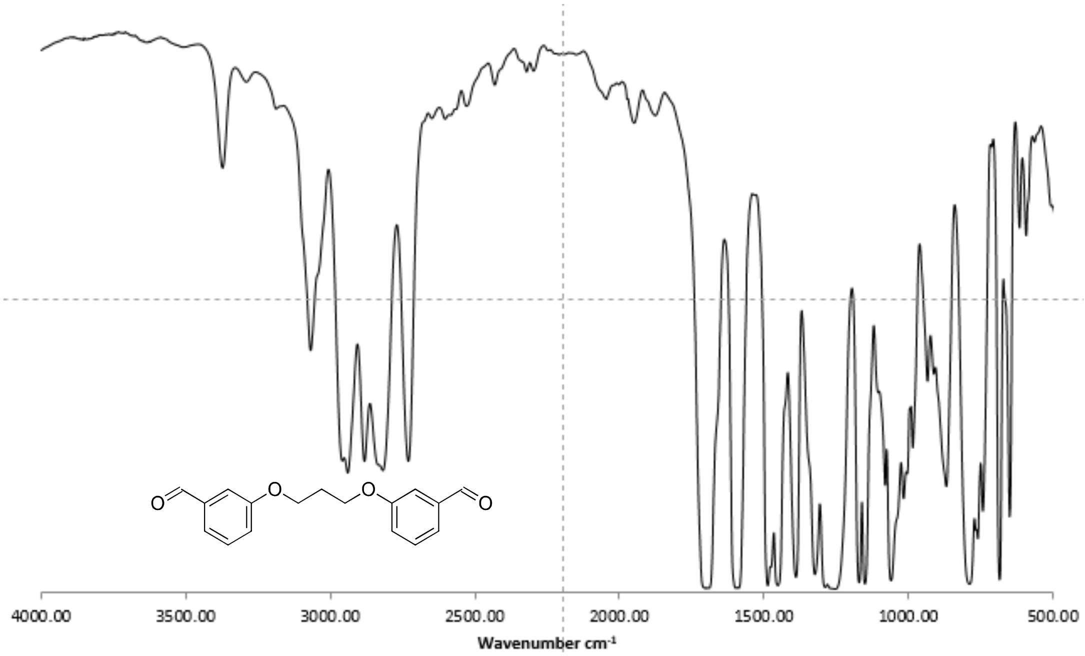


Figure 18. IR Spectrum (KBr) of **95**.

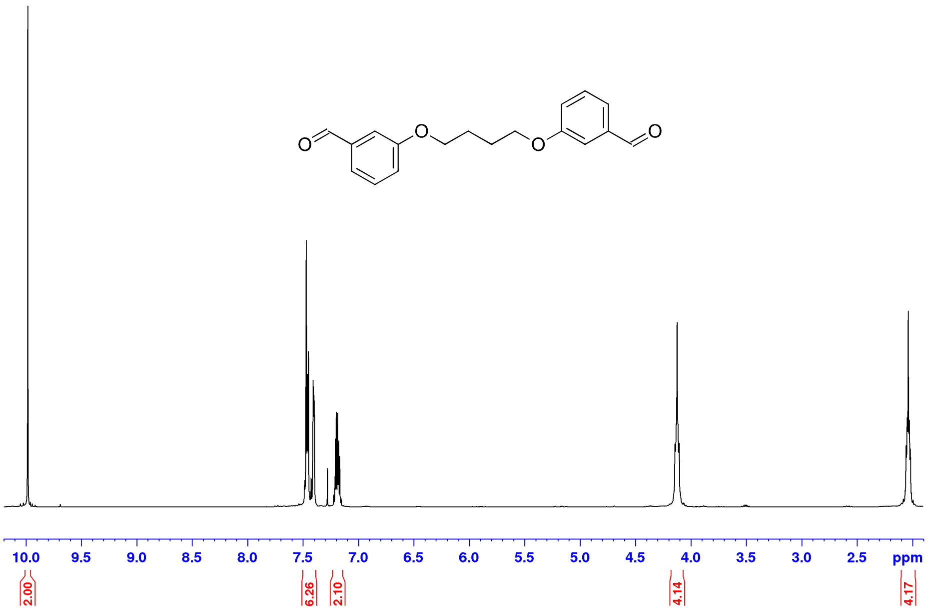


Figure 19. 300 MHz ^{1}H NMR Spectrum (CDCl$_3$) of **96**.

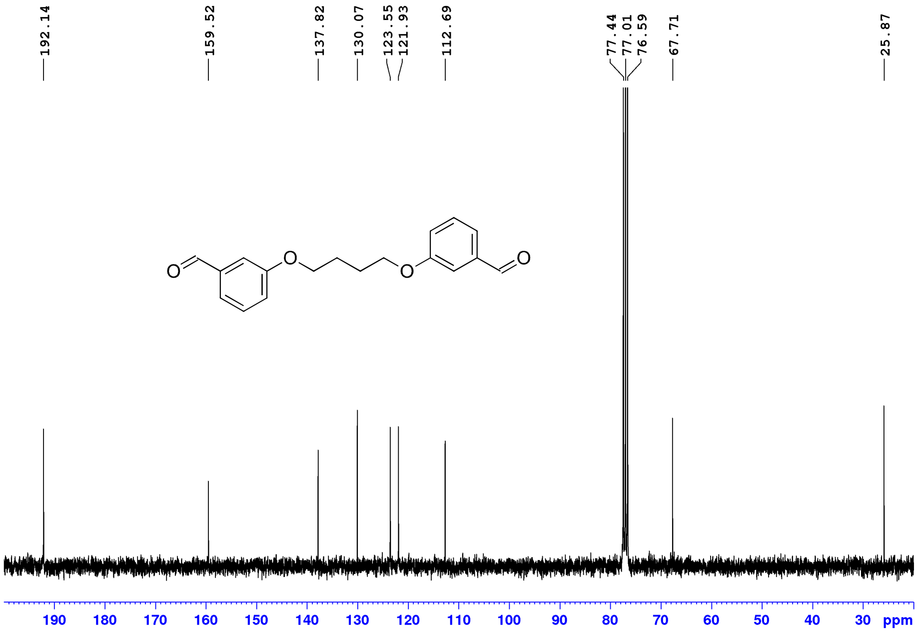


Figure 20. 75 MHz ^{13}C NMR Spectrum (CDCl$_3$) of **96**

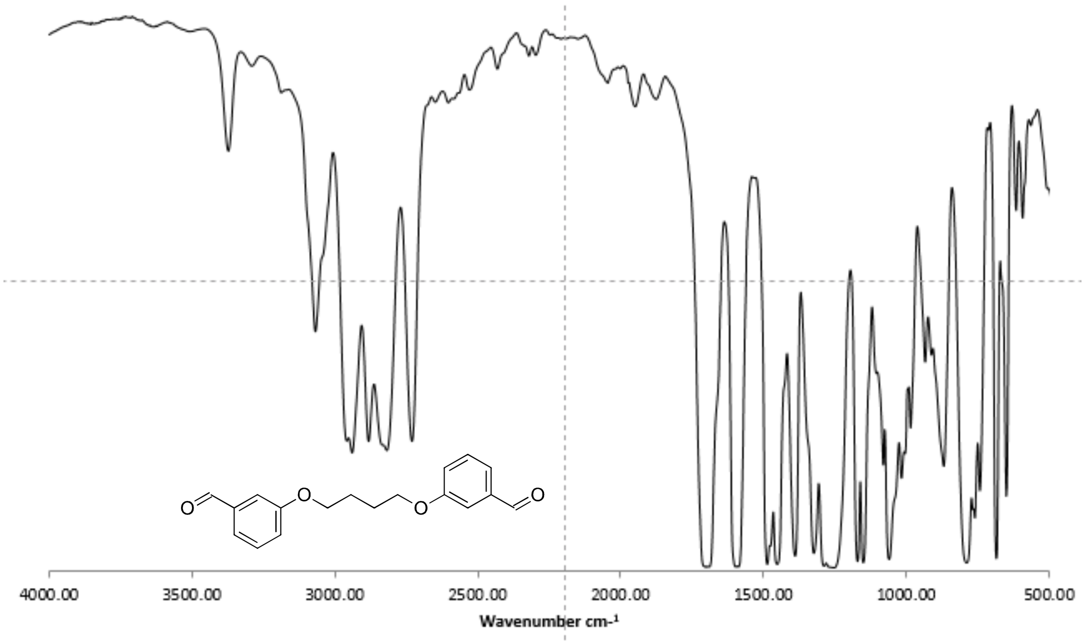


Figure 21. IR Spectrum (KBr) of **96**.

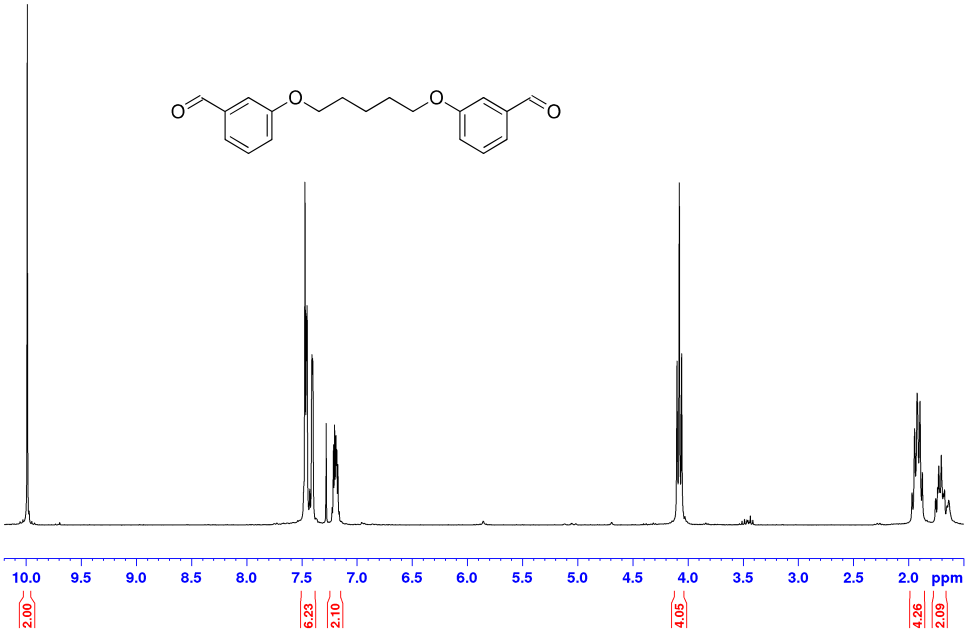


Figure 22. 300 MHz ^{1}H NMR Spectrum (CDCl$_3$) of **97.**

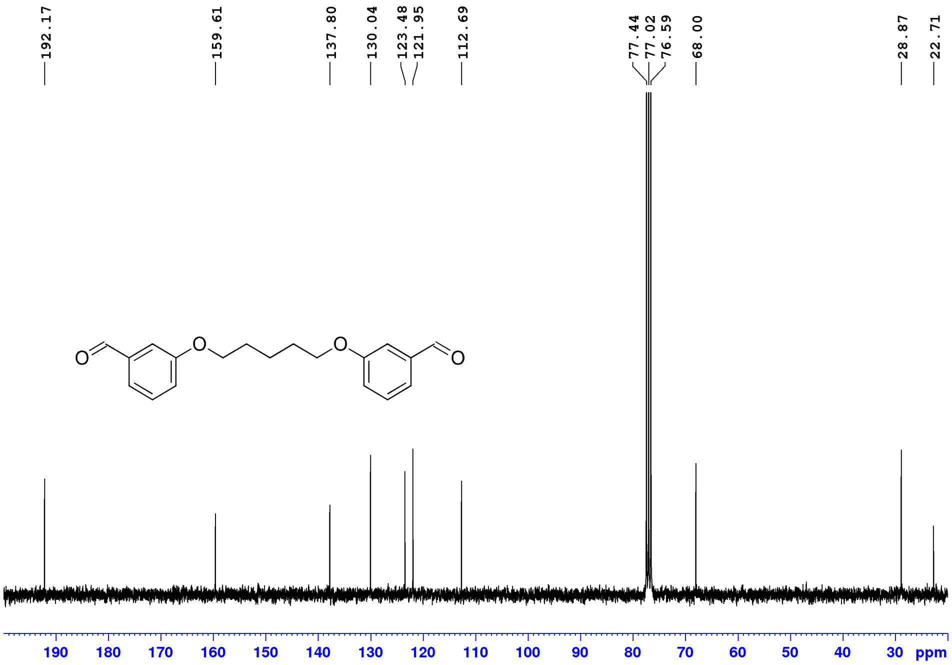


Figure 23. 75 MHz ^{13}C NMR Spectrum (CDCl$_3$) of **97.**

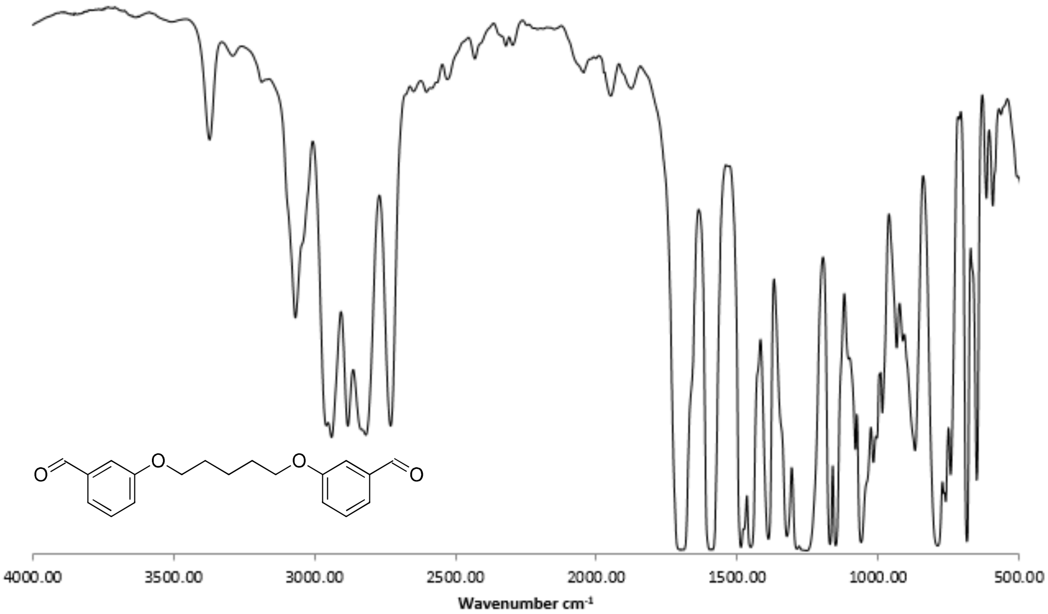


Figure 24. IR spectrum (KBr) of **97**.

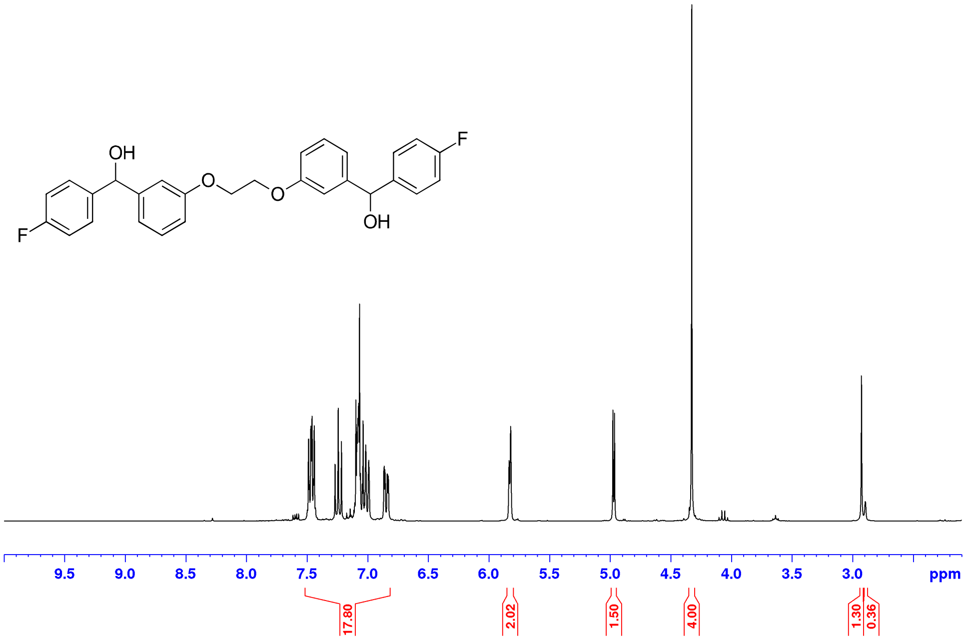


Figure 25. 300 MHz ^{1}H NMR Spectrum (Acetone-d_6) of **99**.

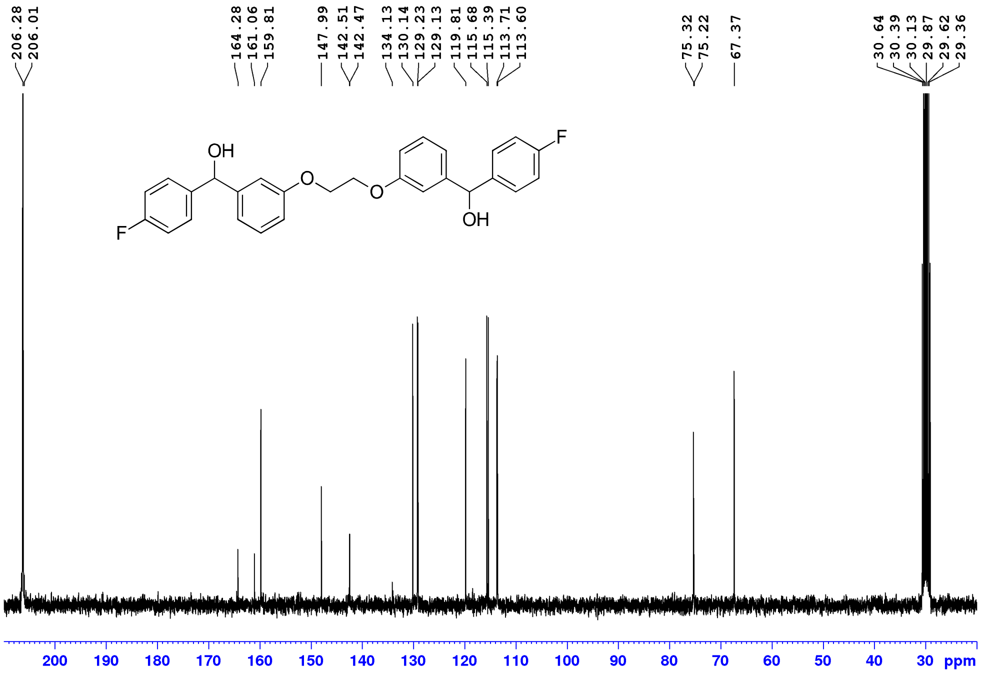


Figure 26. 75 MHz ^{13}C NMR Spectrum (Acetone-d_6) of **99**.

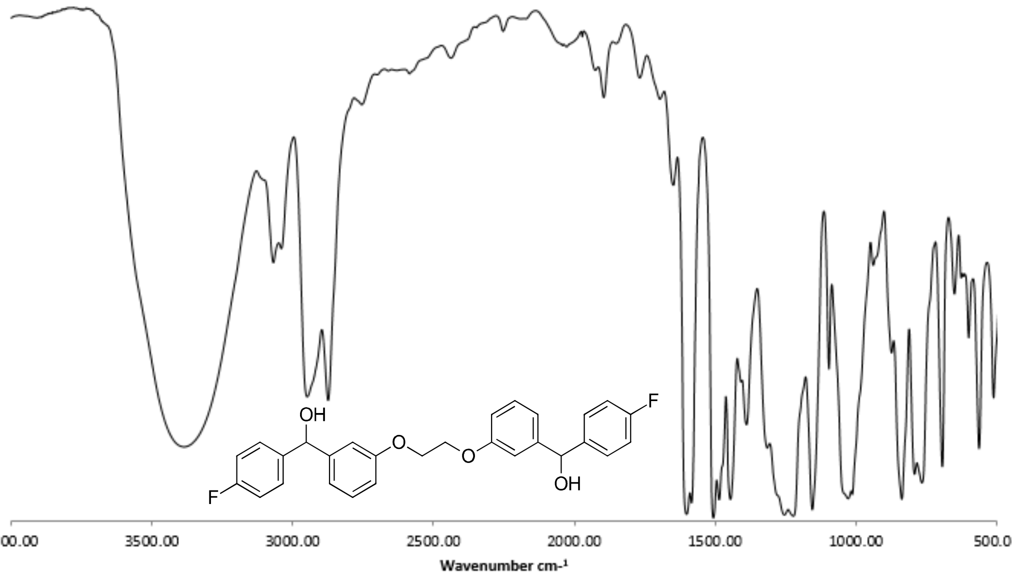


Figure 27. IR Spectrum (KBr) of **99**.

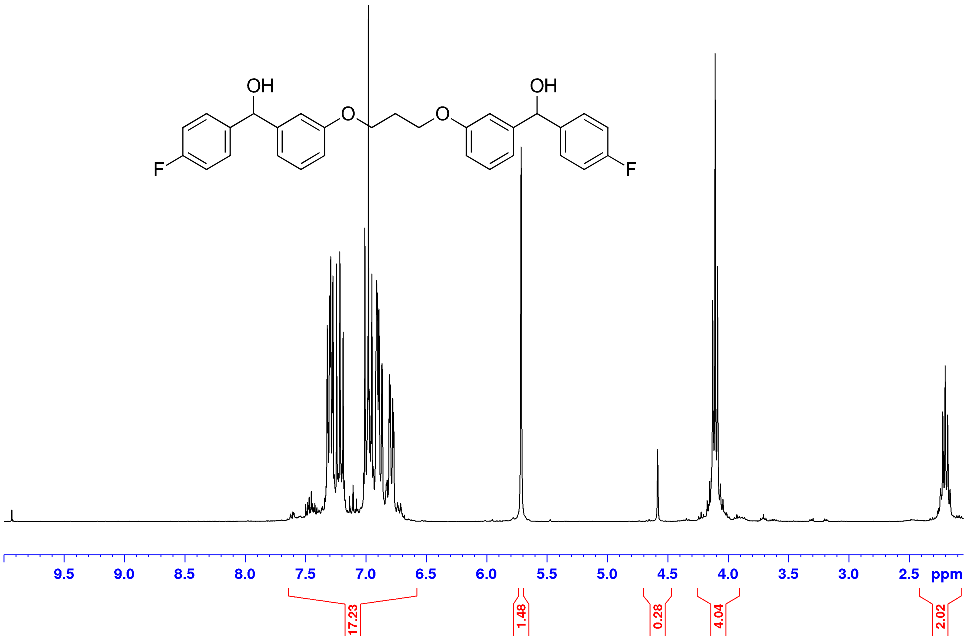


Figure 28. 300 MHz ^{1}H NMR Spectrum (CDCl$_3$) of **100**.

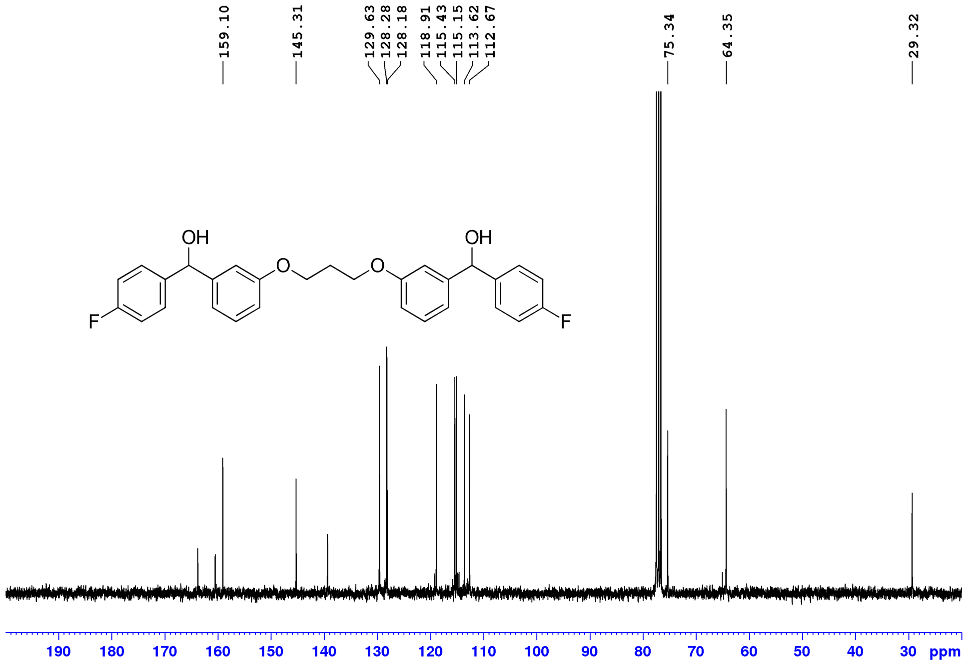


Figure 29. 75 MHz ^{13}C NMR Spectrum ($CDCl_3$) of **100**.

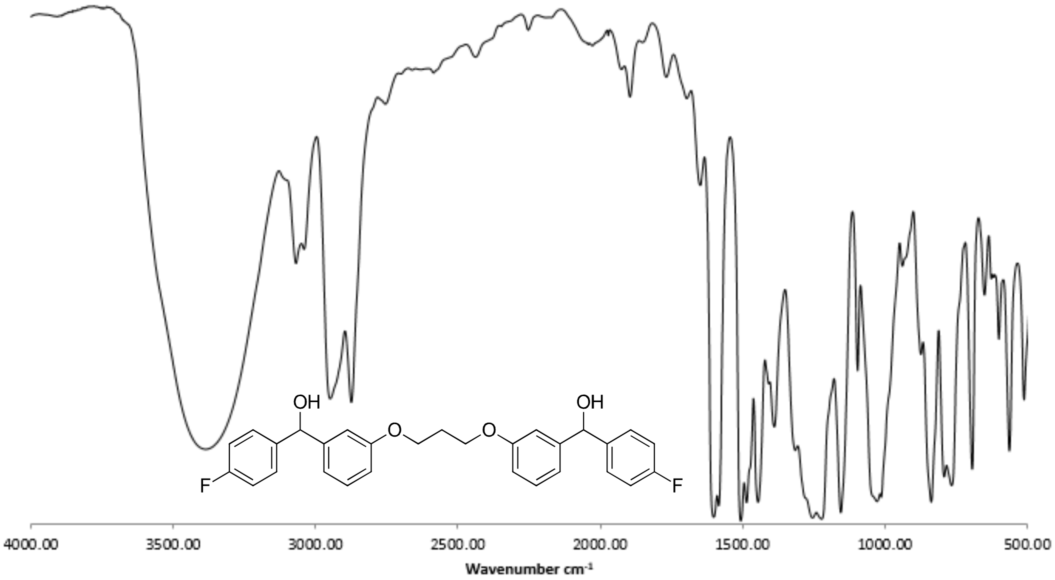


Figure 30. IR Spectrum (KBr) of **100**.

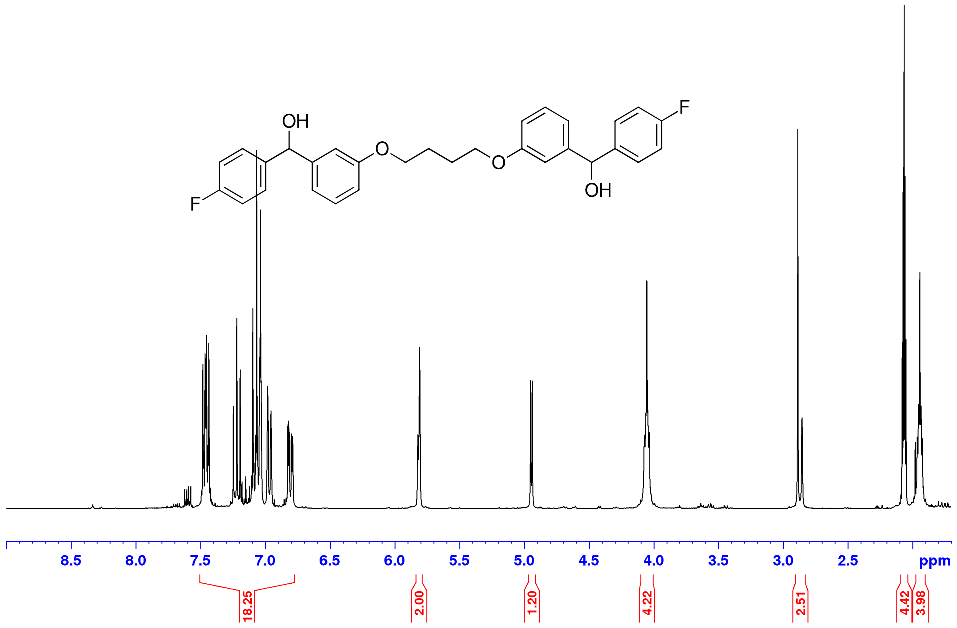


Figure 31. 300 MHz ^{1}H NMR Spectrum (CDCl$_3$) of **101**.

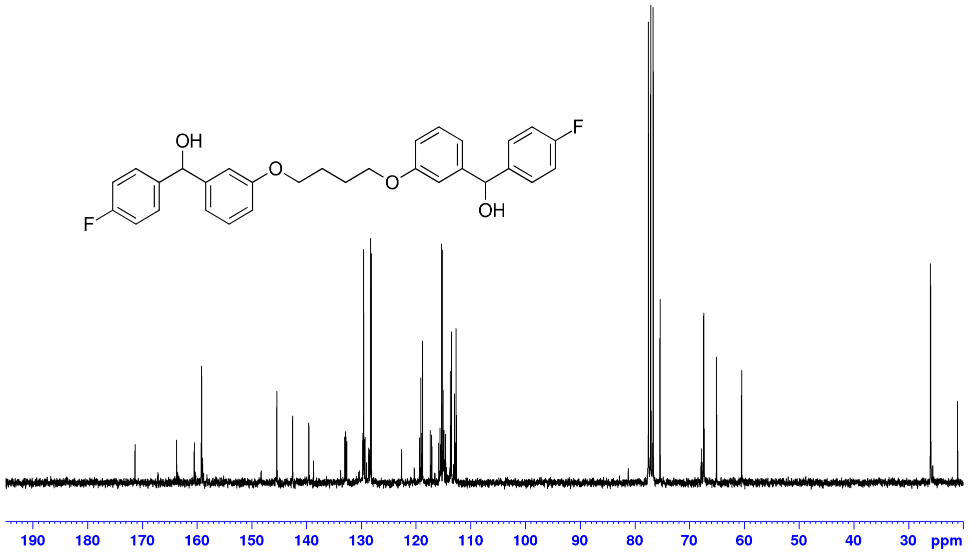


Figure 32. 75 MHz ^{13}C NMR Spectrum (CDCl$_3$) of **101**.

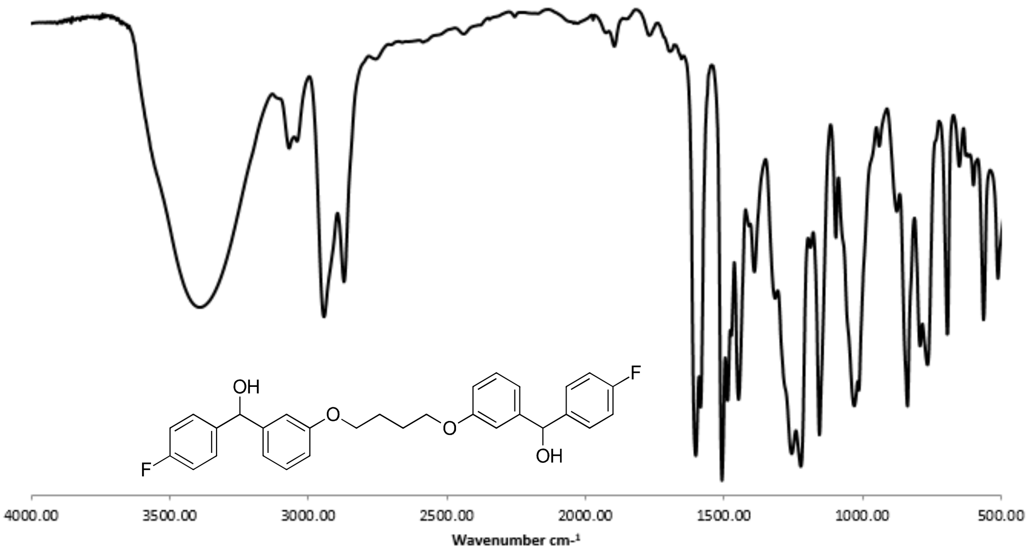


Figure 33. IR spectrum (KBr) of **101**.

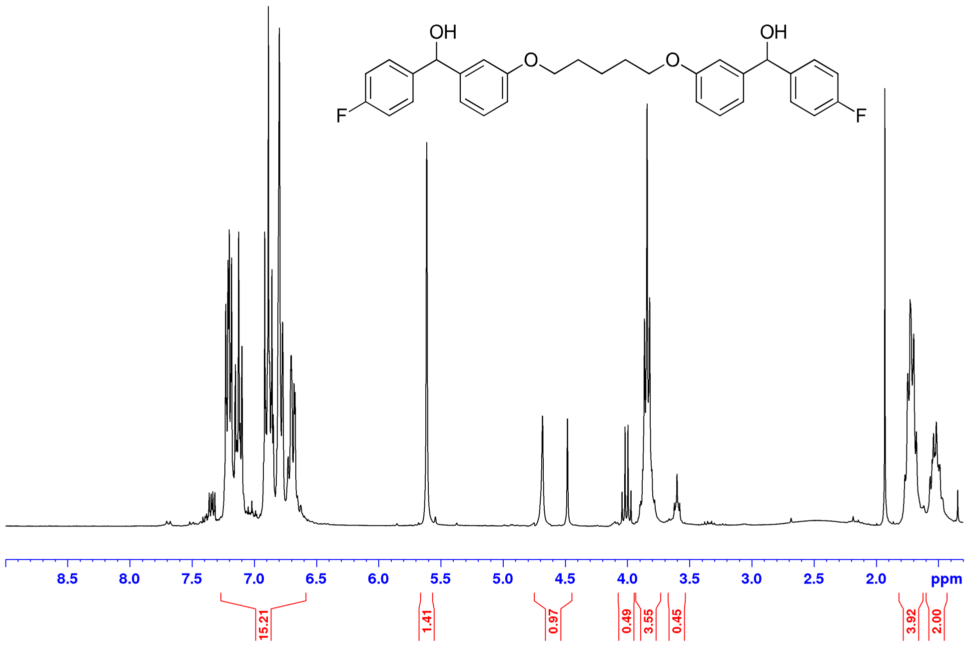


Figure 34. 300 MHz ^{1}H NMR Spectrum ($CDCl_3$) of **102**.

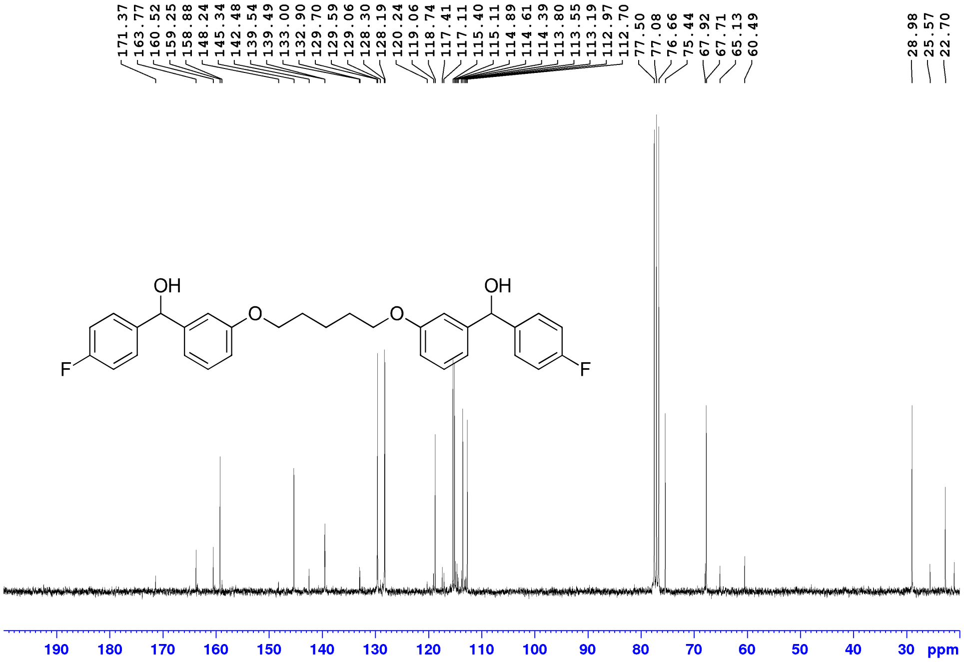


Figure 35. 75 MHz ^{13}C NMR Spectrum ($CDCl_3$) of **102**.

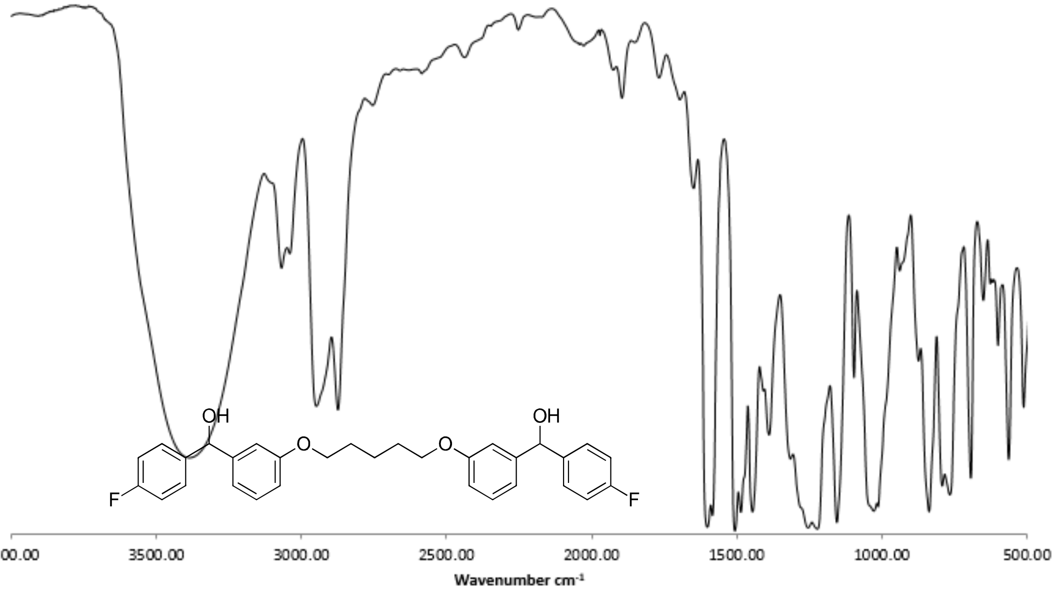


Figure 36. IR Spectrum (KBr) of **102**.

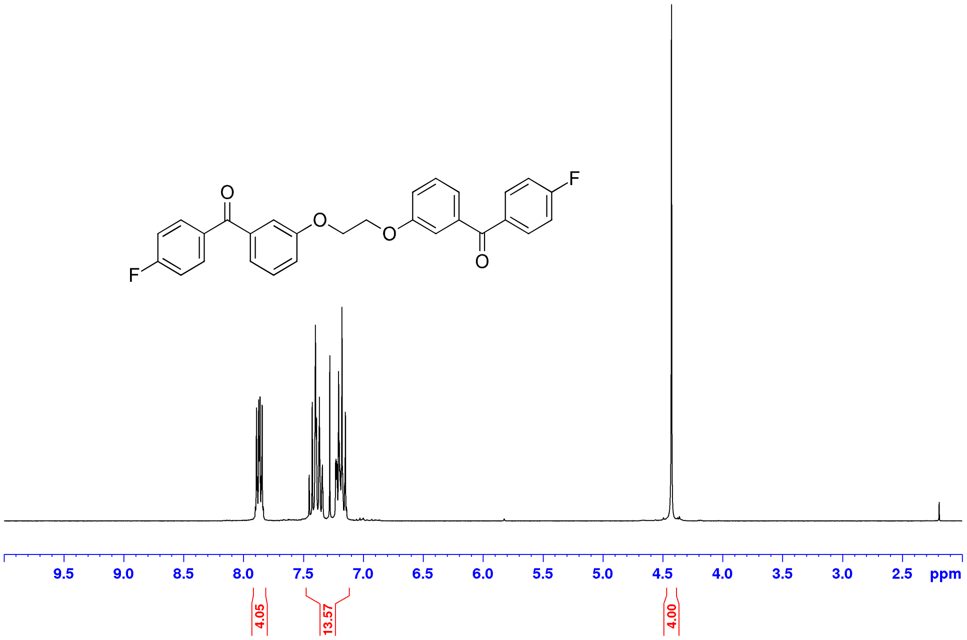


Figure 37. 300 MHz ^{1}H NMR Spectrum ($CDCl_3$) of **103**

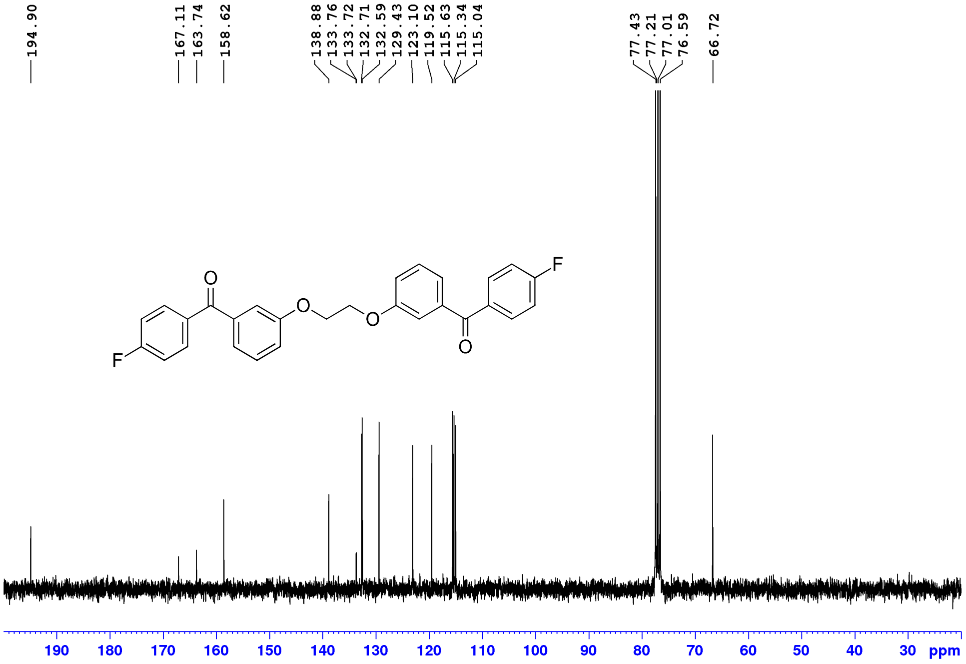


Figure 38. 75 MHz ^{13}C NMR Spectrum ($CDCl_3$) of **103**.

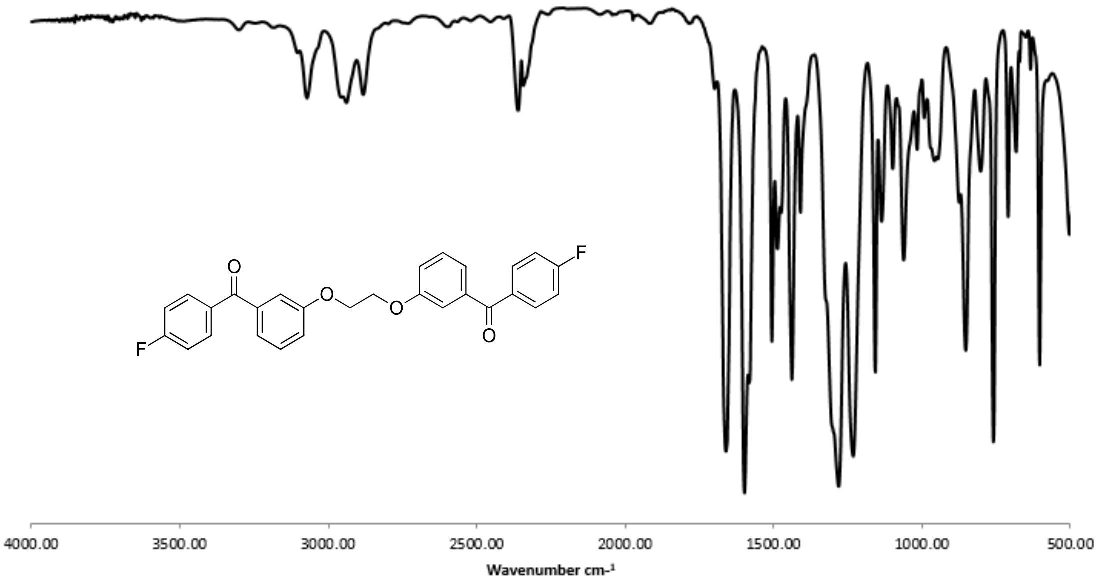


Figure 39. IR Spectrum (KBr) of **103**.

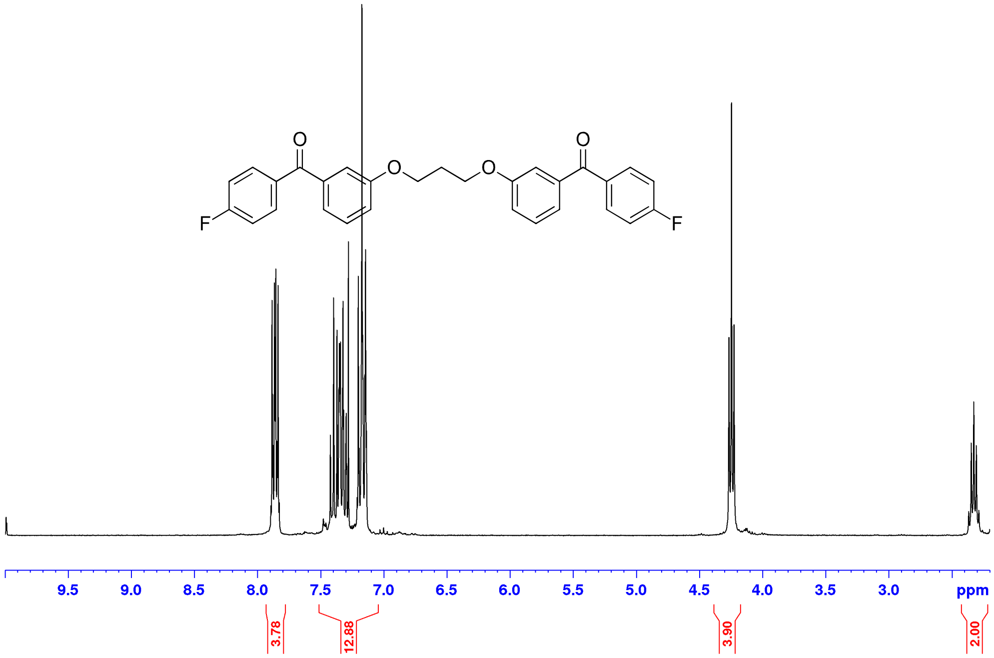


Figure 40. 300 MHz ^{1}H NMR Spectrum (CDCl$_3$) of **104**.

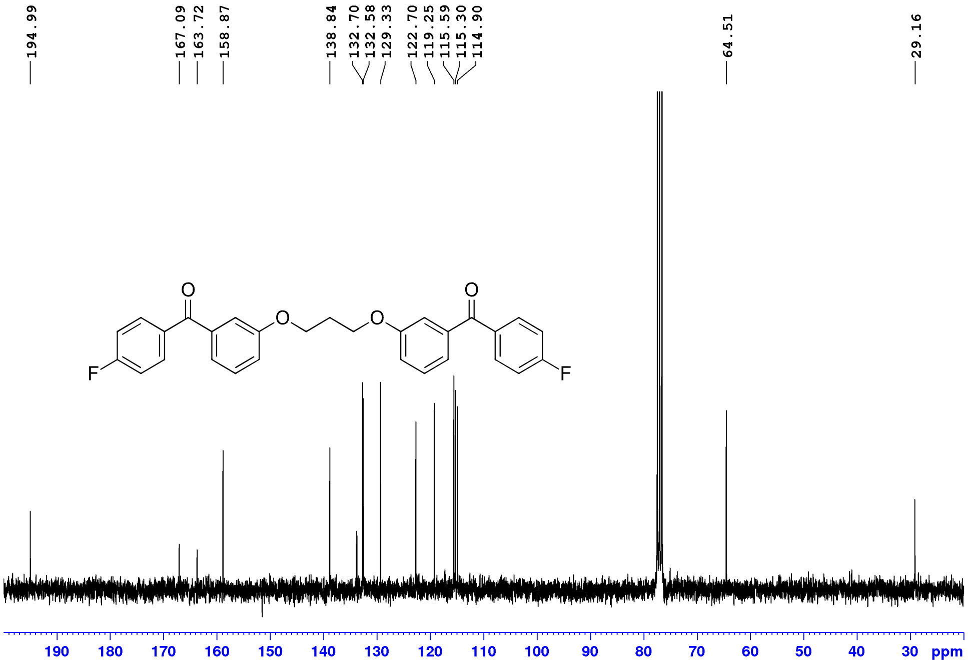


Figure 41. 75 MHz ^{13}C NMR Spectrum (CDCl$_3$) of **104**.

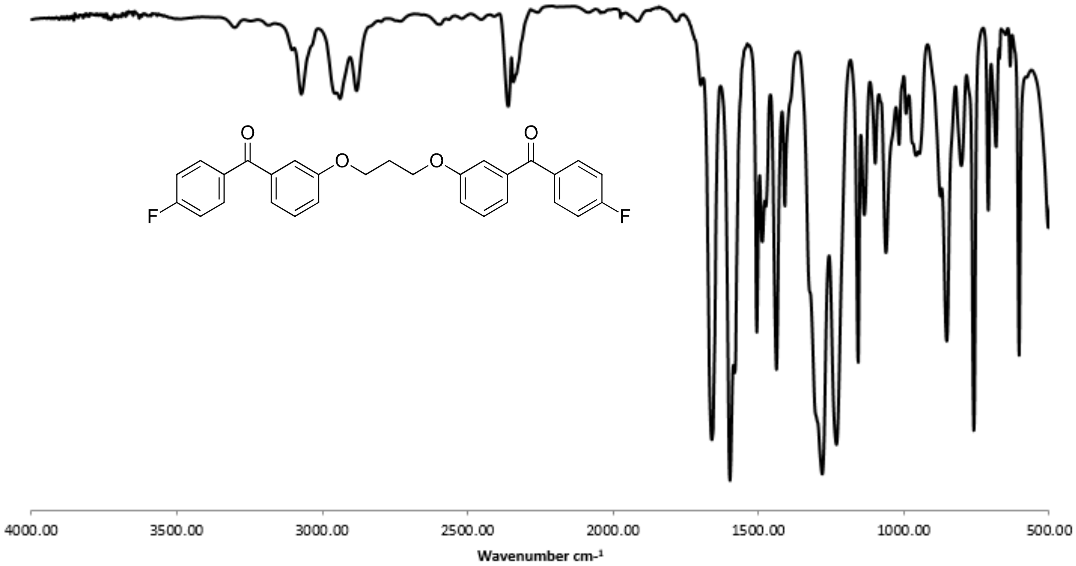


Figure 42. IR Spectrum (KBr) of **104**.

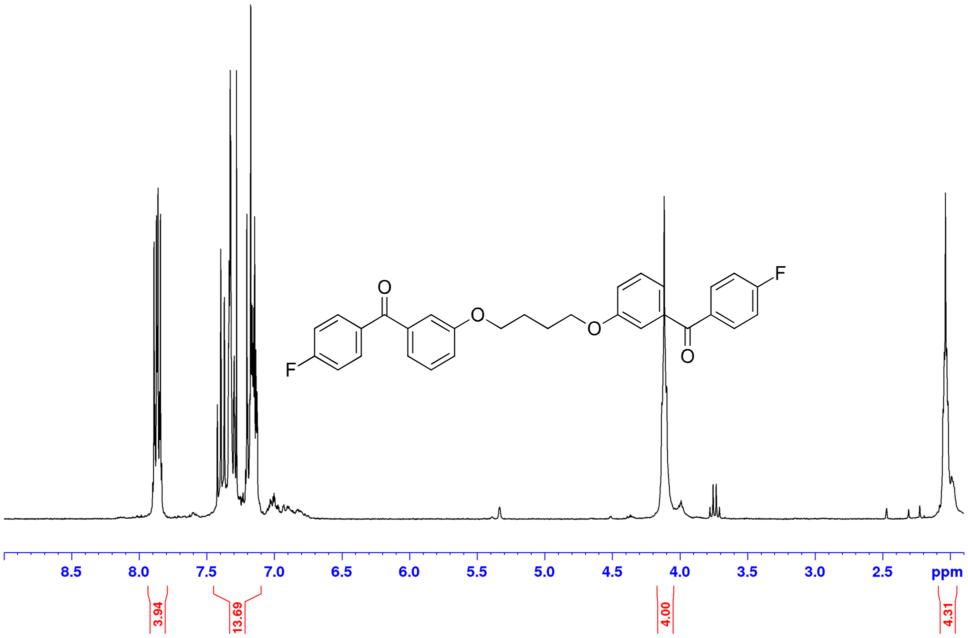


Figure 43. 300 MHz ^{1}H NMR Spectrum ($CDCl_3$) of **105**.

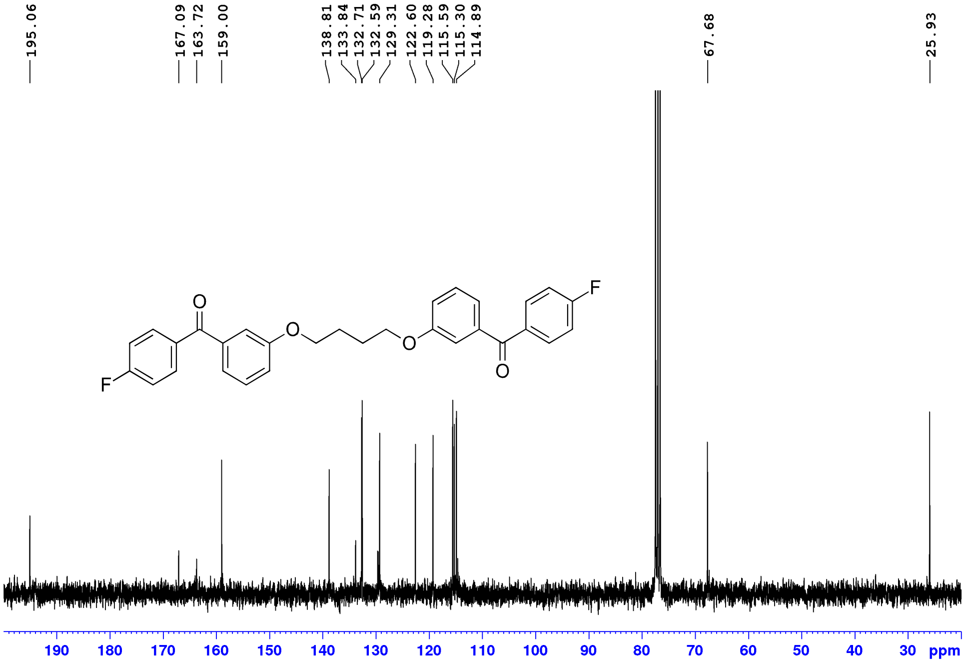


Figure 44. 75 MHz ^{13}C NMR Spectrum ($CDCl_3$) of **105**.

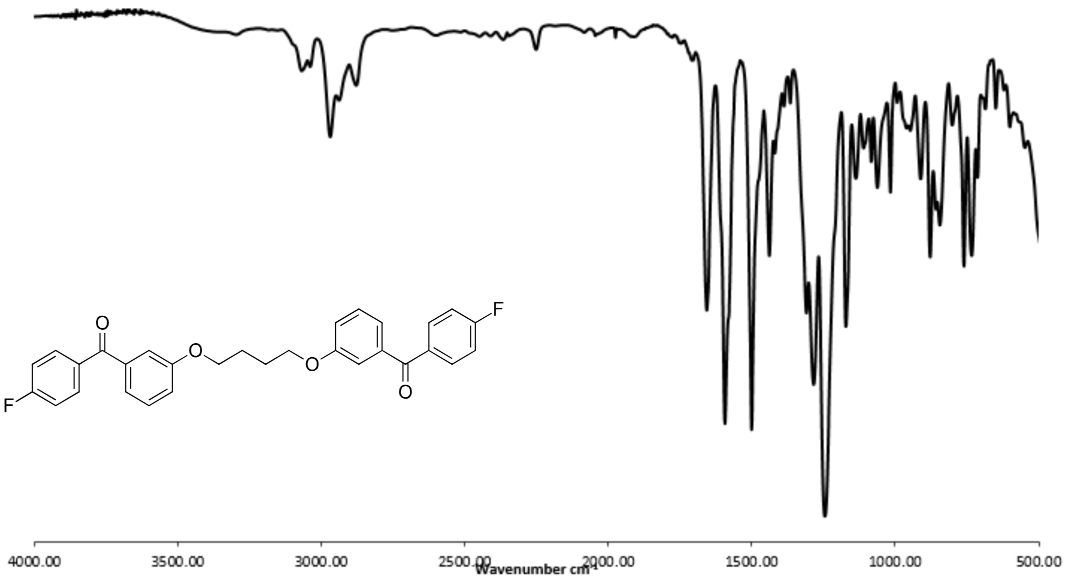


Figure 45. IR Spectrum (KBr) of **105**.

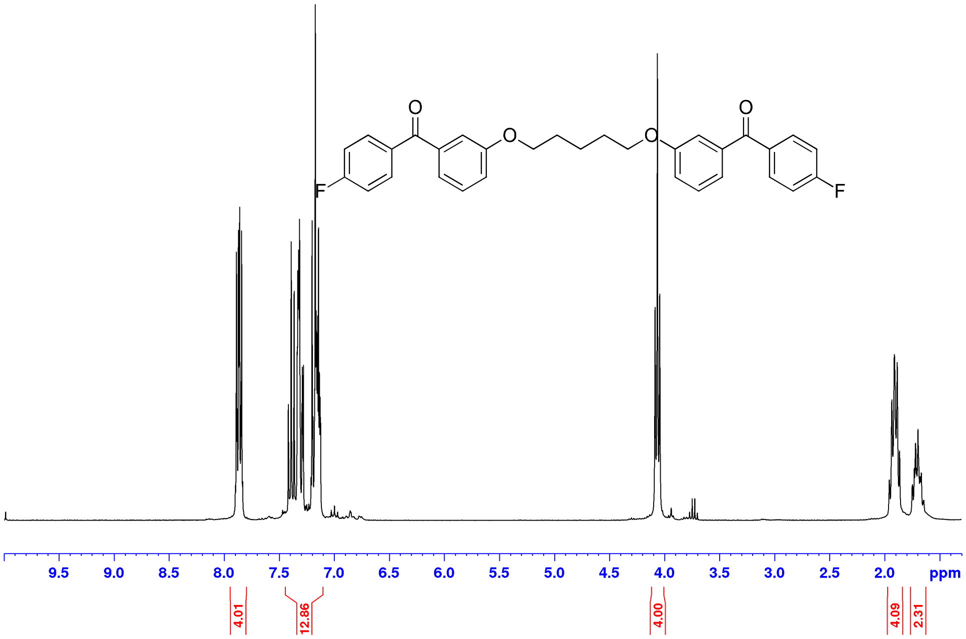


Figure 46. 300 MHz ^{1}H NMR Spectrum ($CDCl_3$) of **106**.

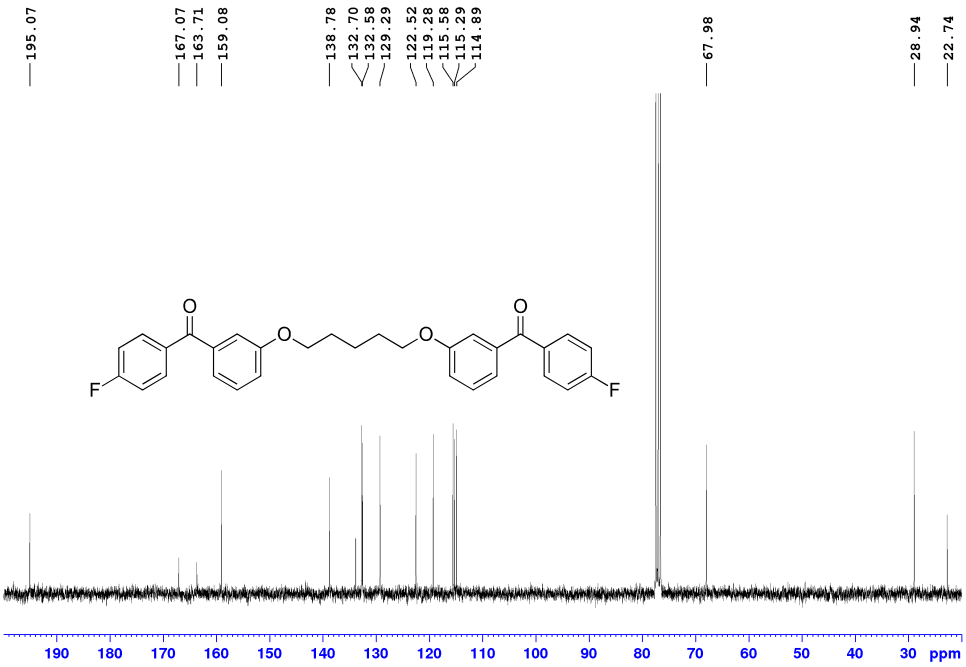


Figure 47. 75 MHz ^{13}C NMR Spectrum (CDCl$_3$) of **106**.

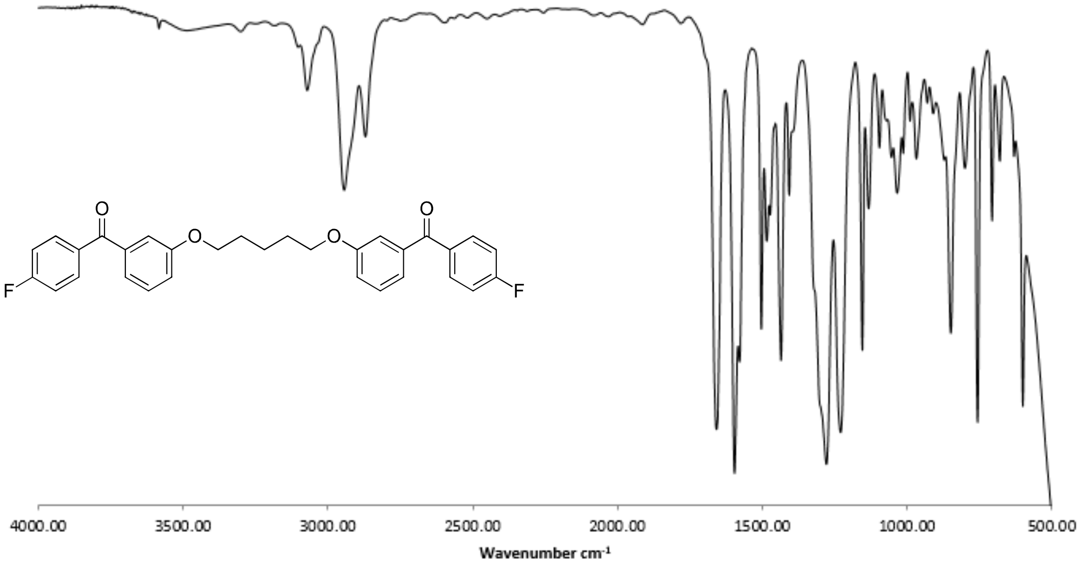


Figure 48. IR Spectrum (KBr) of **106**.

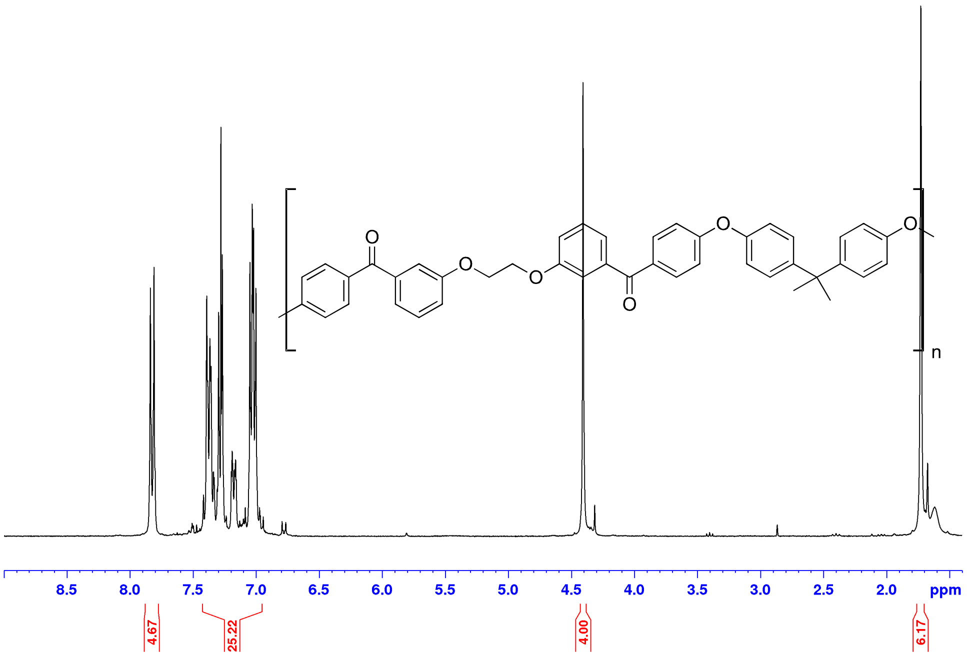


Figure 49. 300 MHz ^{1}H NMR Spectrum (CDCl$_3$) of **107**.

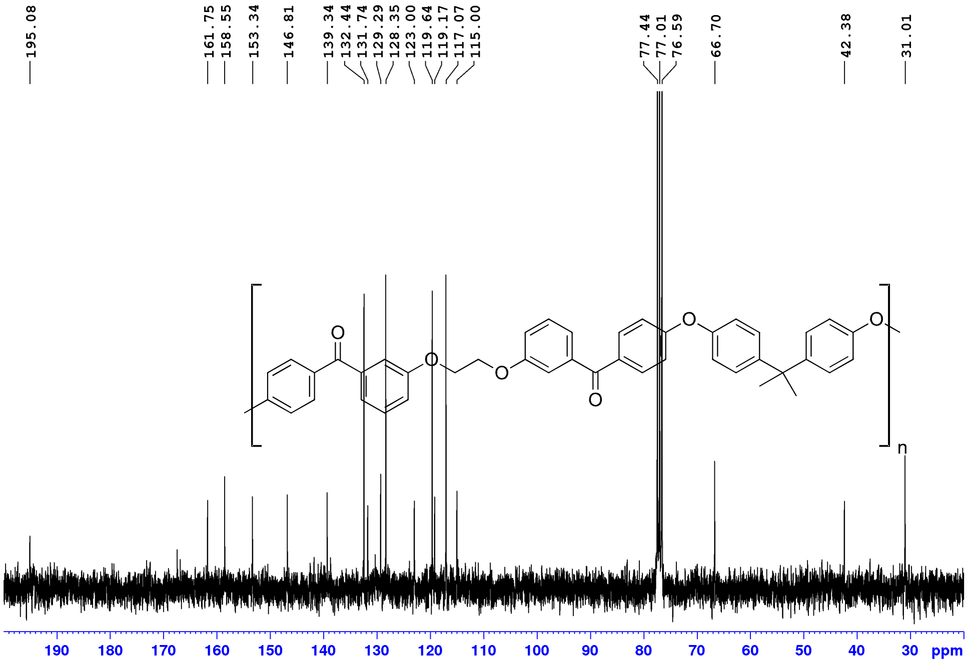


Figure 50. 75 MHz ^{13}C NMR Spectrum (CDCl$_3$) of **107** .

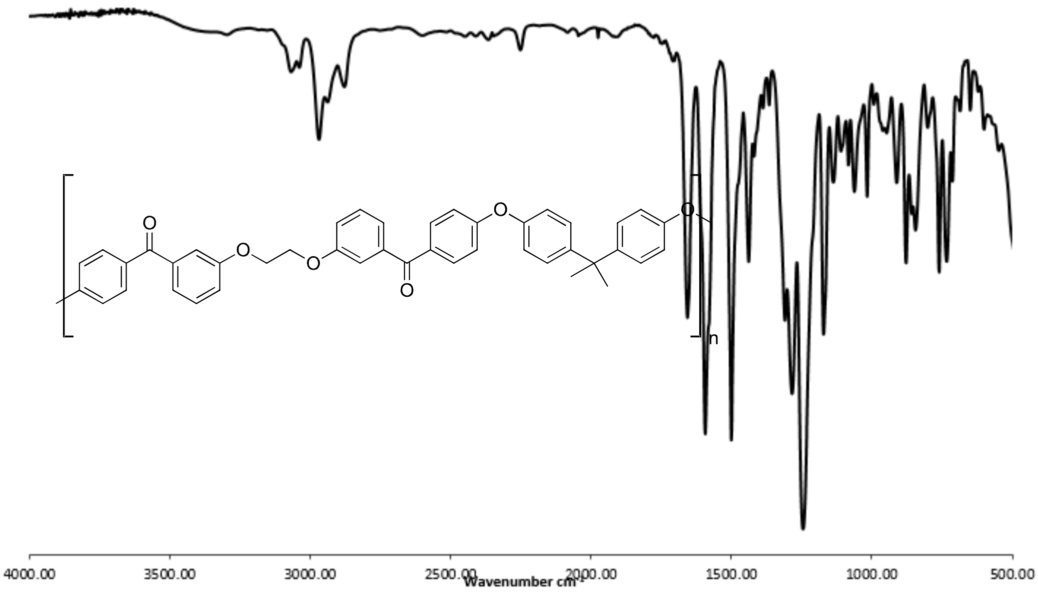


Figure 51. IR Spectrum (KBr) of **107.**

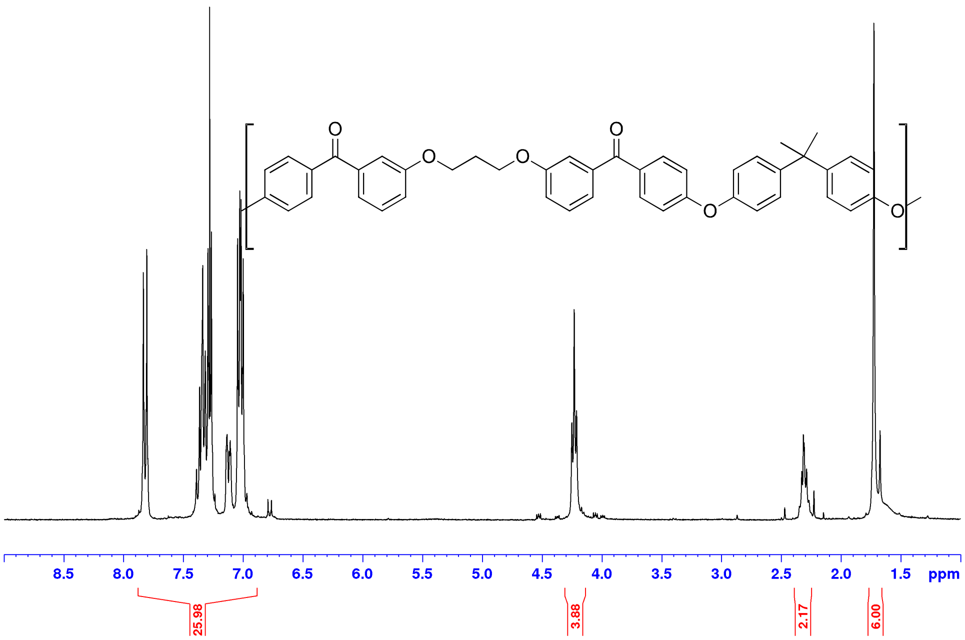


Figure 52. 300 MHz ^{1}H NMR Spectrum (CDCl$_3$) of **108.**

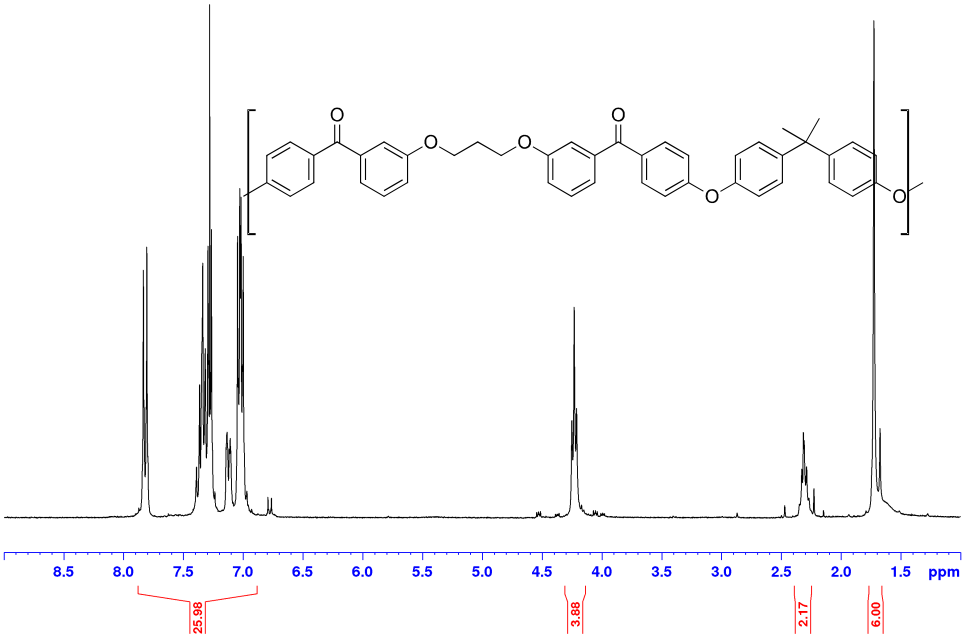


Figure 53. 75 MHz ^{13}C NMR Spectrum (CDCl$_3$) of **108.**

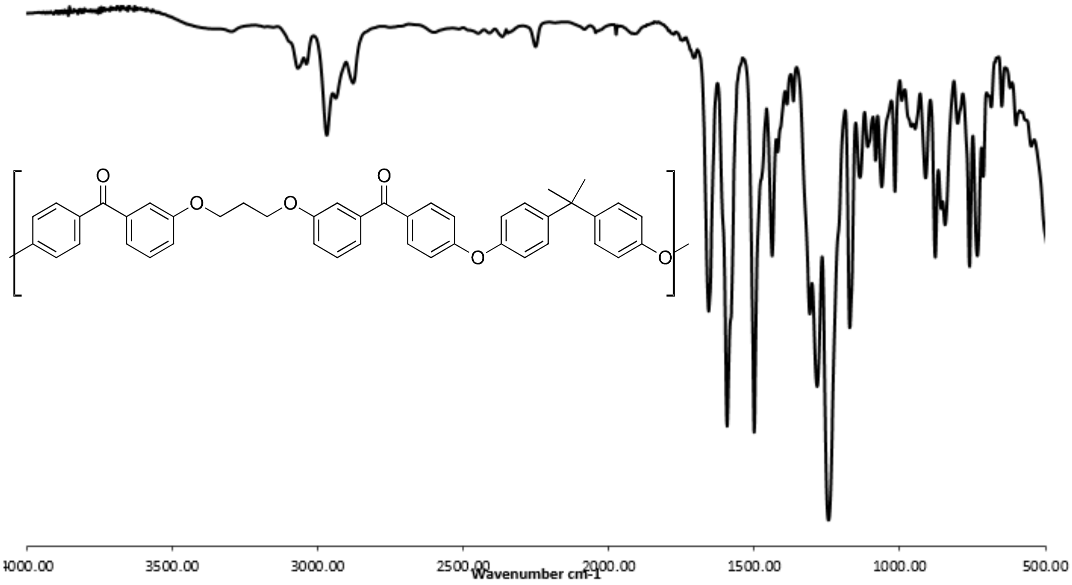


Figure 54. IR Spectrum (KBr) of **108.**

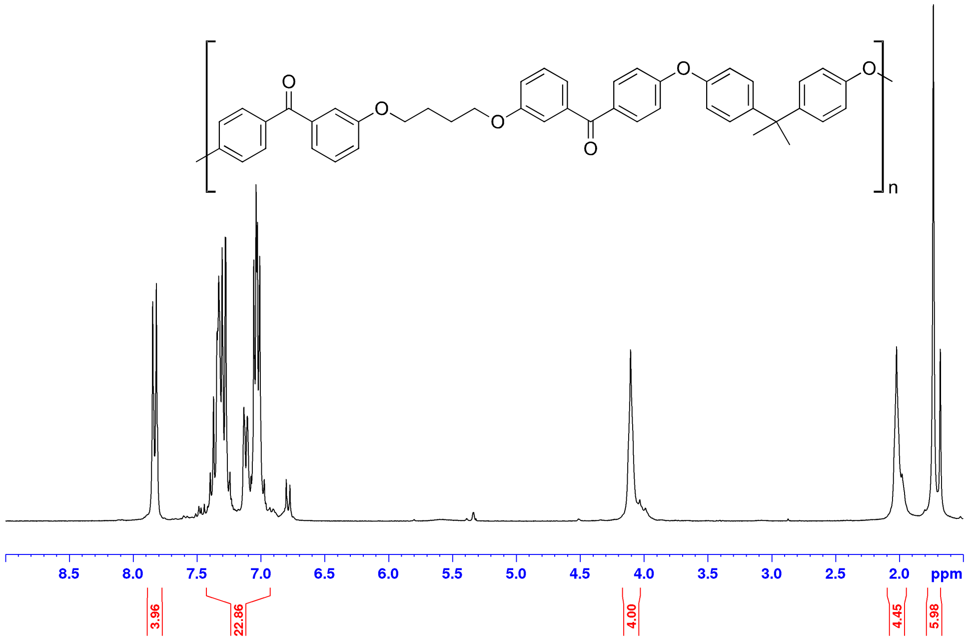


Figure 55. 300 MHz ^{1}H NMR Spectrum (CDCl$_3$) of **109.**

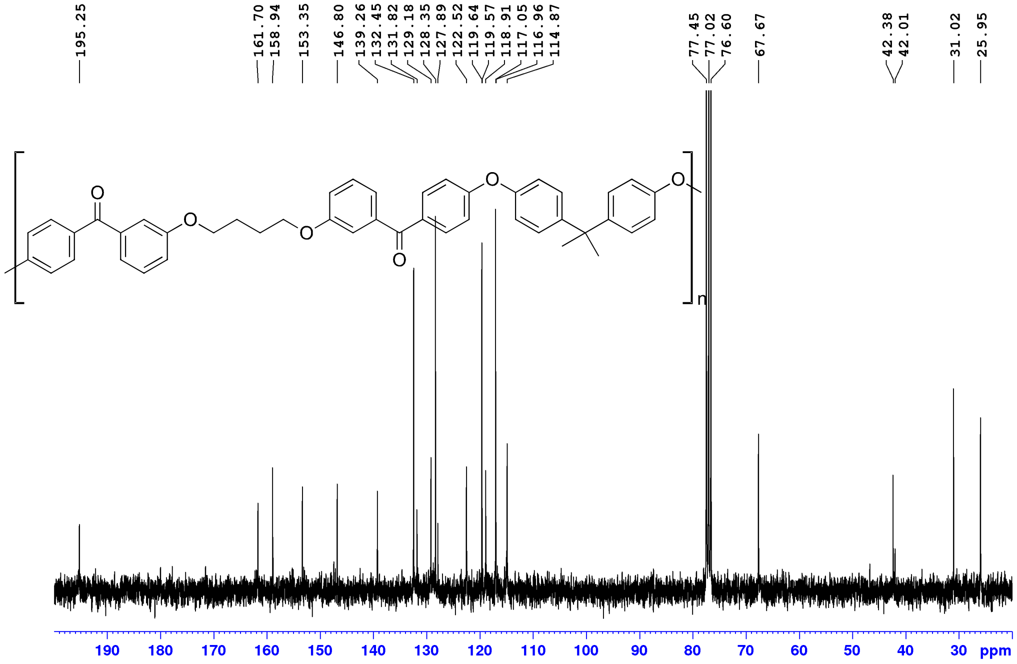


Figure 56. 75 MHz ^{13}C NMR Spectrum (CDCl$_3$) of **109.**

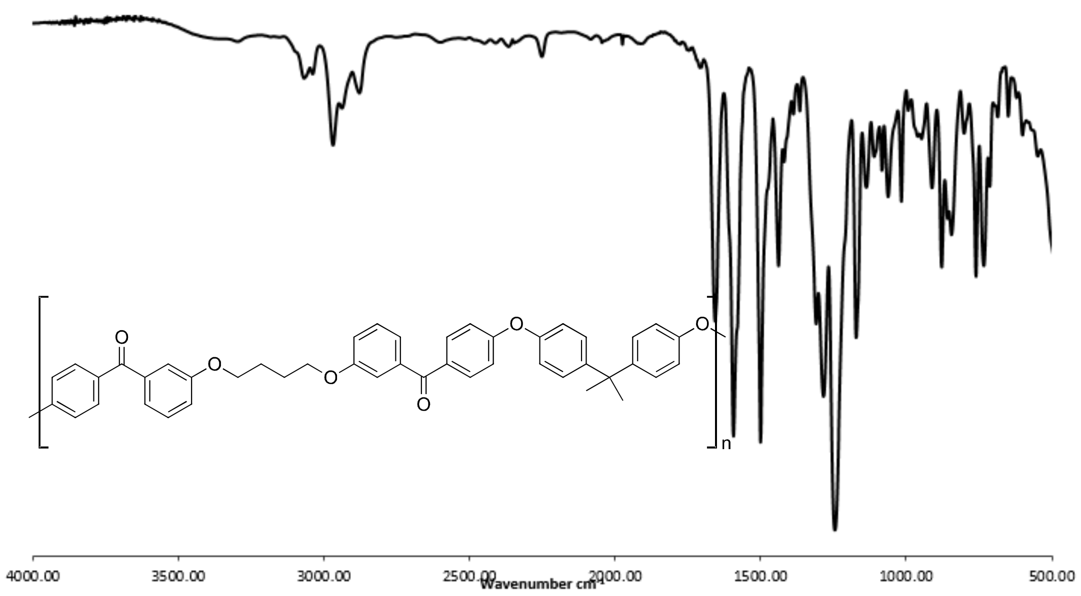


Figure 57. IR Spectrum (KBr) of **109.**

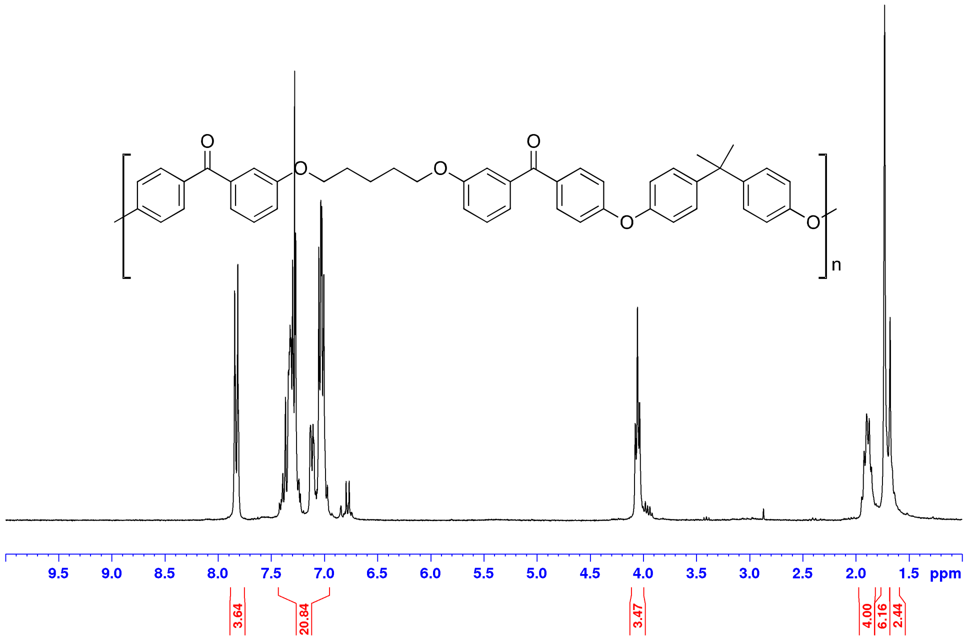


Figure 58. 300 MHz ^{1}H NMR Spectrum (CDCl$_3$) of **110.**

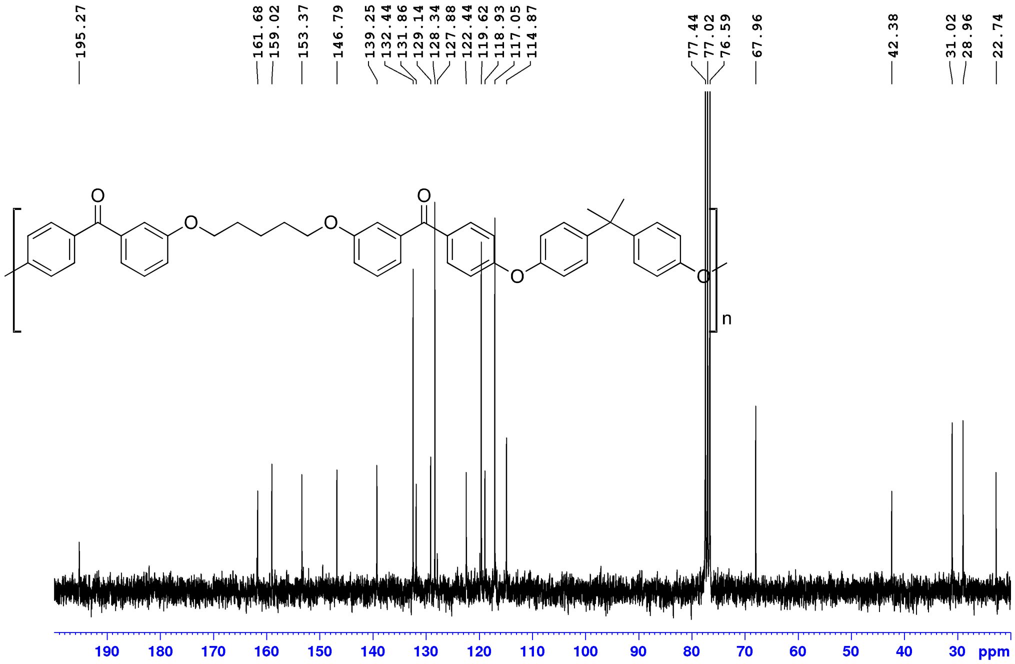


Figure 59. 75 MHz ^{13}C NMR Spectrum (CDCl$_3$) of **110**

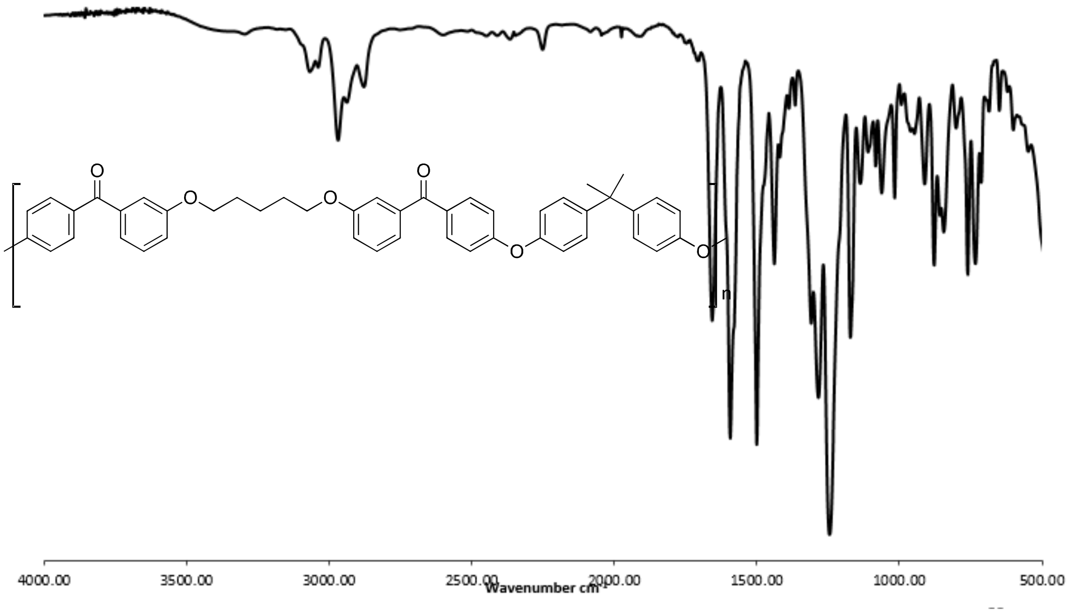


Figure 60. IR Spectrum (KBr) of **110.**

REFERENCES

1. C.E. Sroog, *Journal of Polymer Science: Macromolecular Reviews*, **1976**, 11(1), 161-208

2. Stephanie L. Kwolek, Paul W. Morgan, *Journal of Polymer Science: Part A- Polymer Chemistry,* **1964**, 2(16), 2693-2703.

3. P.M. Hergenrother, H.L. Levine, *Journal of Polymer Science: Part A- Polymer Chemistry,* **1967,** 5(6), 1453-1466.

4. T.E. Attwood, P.C. Dawson, J.L. Freeman, L.R.J. Hoy, J.B. Rose and P.A. Staniland, *Polymer,* **1981**, 22, 1096.

5. J.F. Wolfe, B.H. Loo, F.E.Arnold, *Macromolecules,* **1981**, 14, 915-920.

6. J.F. Wolfe, F.E. Arnold, *Macromolecules,* **1981,** 14, 909-915.

7. R.C. Evers, F.E. Arnold, T.E. Helminiak, *Macromolecules,* **1981**, 14, 925-930.

8. W.A. Feld, B. Ramalingam, F.W. Harris, *J. Poly. Sci: Polymer Chemistry Edition,* **1983**, 21**,** 326.

9. P.M. Hergenrother, F.W. Harris, S.J. Havens, *Journal of Applied Polymer Scinece,* **1986,** 32, 5957-5964.

10. A.J. Sanders, Bo Li, Christopher Bieniarz, F.W. Harris.

11. Bharat P. Patel, "The Synthesis of poly(ether ether ketone)s from bis(fluorobenzophenone) monomers containing oxyethylene linkages"*,*M.S. Thesis, W.S.U. (1992).

12. Meena V. Patel, "The synthesis of poly(ether ether ketone)s containing oxyethylene linkages", M.S. Thesis, W.S.U. (1992).

13. P.M. Hergenrother, H.H. Levine, *Journal of Polymer Science: Part A-1,***1967,** 5, 1453-66.

14. F.N. Cogswell, *Thermoplastic Aromatic Polymer Composites*, Butterworth-Heinemann, Oxford, UK, **1992**.

15. Qui, Zhaobin; Mo, Zhishen; Zhang, Hongfang; Sheng, Shouri; Song, Caisheng, *Journal of Macromolecular Science, Physics* **2000,** B39(3), 373-385.

16. Rajendra K.K., Douglass S.K., *Polymer Engineering and Science,* **1996,** 36 (6), 786-796.

17. J.F. Bunnett and R.E. Zahler, *Chem. Rev.*,**1951**, 49, 273.

18. P.M. Hergenrother, B.J. Jensen and S.J. Havens, *Polymer,* 1988, **29**, 358.

19. Wu, T.; Liu, P.; Shi, M; Lu, J.; Ye, G.; Xu, J. "Novel copoly(ether ether ketone)s with pendant phenyl groups: Synthesis and Characterization," *Polym. Int.,* **2011,** 60(9), 1318-1323.

20. Tina Dancevic, "Synthesis of phenylated poly(arylene ether)s: phenylated poly(ether ether ketone ketone)s" M.S. Thesis, W.S.U. (2005).

21. Krishnamurthy, M; Gurley, S; Moore,B.M., *Bioorg Med Chem.,* **2008,** 16(13), 6489-6500

22. Mondal, R., Mandal, T.K., Mallik, A.K., *ARKIVOC*, **2012**, 2012(9), 95-110.

23. Kamal, Ahmed, *European Journal of Medicinal Chemistry*, **2011**, 46(8).

VITAE

James Uchenna Ohaeri was born on May 8, 1989. He graduated from University of Cincinnati where he earned her Bachelor of Science in Chemistry in 2010. He expects to receive her Master of Science Degree in Chemistry in May 2016.