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Synthesis of Alkyl Substituted Phenylated Poly(Ether Ether Ketone Ketone)s

Matthew Cerone
Wright State University

SYNTHESIS OF ALKYL SUBSTITUTED PHENYLATED POLY(ETHER ETHER KETONE KETONE)S

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

By

MATTHEW CERONE
B.S., The Ohio State University 2012

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Matthew Cerone ENTITLED Synthesis of Alkyl Substituted Phenylated Poly(Ether Ether Ketone Ketone)s. 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

Cerone, Matthew. M.S., Department of Chemistry, Wright State University, 2017.
Synthesis of Alkyl Substituted Phenylated Poly(ether ether ketone ketone)s.

A phenylated bis(fluorobenzoyl) monomer, 5-hexyl-2,3-diphenyl-1,4-bis(fluorobenzoyl)benzene, was synthesized via a four-step process. The first three compounds synthesized were diethyl 5-hexyl-2,3-diphenyl-1,4-benzenedicarboxylate, 5-hexyl-1,4-bis(hydroxymethyl)-2,3-diphenylbenzene and 5-hexyl-2,3-diphenyl-1,4-benzenedicarboxaldehyde. The final step involved the reaction of the Grignard formed from *p*-bromofluorobenzene with the dialdehyde to yield a diol intermediate which was oxidized to the bis(fluorobenzoyl) monomer by use of a Jones oxidation. The monomer was polymerized by nucleophilic aromatic substitution (NAS) with bisphenol-A, resorcinol, and hydroquinone in *N*-methyl-pyrrolidone (NMP) to yield novel, phenylated PEEKKs. The number-average molecular weights (M_n) for the polymers were found to be 35,700 g/mol, 34,800 g/mol and 28,000 g/mol, respectively and the weight-average molecular weights (M_n) for the polymers were found to be 63,000 g/mol, 85,100 g/mol and 55,600 g/mol, respectively with dispersities of 1.76, 2.44 and 1.98, respectively. Thermal analysis provided both the glass transition temperatures (T_g) of 164°, 148°, 162°, respectively and the 5% thermal decomposition temperatures ($T_{d5\%}$) of 460°, 448°, 458°, respectively. All of the polymers were highly soluble in chlorinated solvents and formed robust, free-standing, thin films.

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I would like to thank Kelly from the chemistry office for her help with all the paperwork and finally Dr. Eric Fossum, and Dr. Ken Turnbull for helping me defend this thesis and their enlightening classroom lectures.

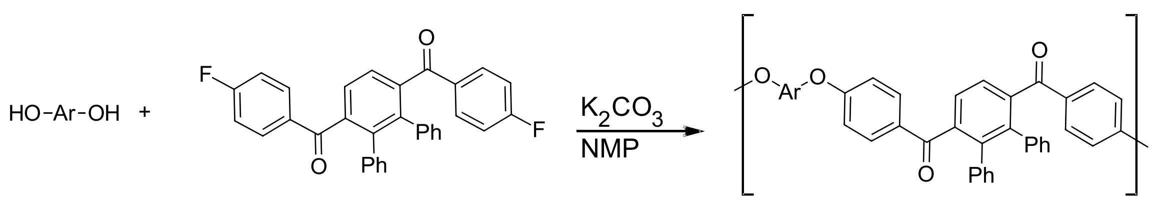
DEDICATION

I would like to dedicate this work to my wife Angelina. She gave me the courage to return to school and pursue my Masters' degree. She gave me soft words of sympathy in hard times, and the direction when I was lost. I love you dear.

INTRODUCTION

Poly(ether ether ketone)s (PEEK) are a useful class of engineering thermoplastics. They exhibit exceptional thermal stability, chemical resistance, and machinability. This is responsible for their use in the automotive and aerospace industries.[1-2]

Previous work[3] has shown that adding two phenyl rings to the backbone of poly(ether ether ketone)s results in the polymers having enhanced solubility in common organic solvents while many of the other desirable properties of PEEK such as thermooxidative stability were retained. The increased solubility of the phenyl substituted polymer backbone was due to an increase in the flexibility of the polymer and better solvent penetration.[3] These polymers are prepared via a nucleophilic aromatic substitution reaction in which aryl diols **1** react with the monomer 2,3 diphenyl-1,4-bis(fluorobenzoyl)benzene **2** in NMP using potassium carbonate as the base.



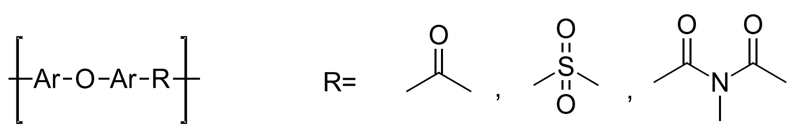
1 **2** **3**

The objectives of this research were to 1) synthesize and characterize an alkyl substituted phenylated bis(fluorobenzoyl) monomer, 2) polymerize the new monomer with bisphenols of varying rigidity, 3) characterize the resulting novel poly(ether ether ketone ketone)s (PEEKKs) and 4) compare the physical properties of the unsubstituted, the phenylated, and the phenylated and alkyl substituted PEEKKs.

HISTORICAL

History of Poly(aryl ether)s

Poly(aryl ethers)s (PAE) **4a-c** are a class of high-performance engineering thermoplastics. PAEs are known for exhibiting excellent chemical resistance, possessing high thermal stability, demonstrating strong mechanical properties, and having decent processability. Also, compared to other high performance thermoplastics, PAEs are relatively inexpensive.[4] They generally consist of phenylene units activated by electron-withdrawing groups connected by ether linkages.

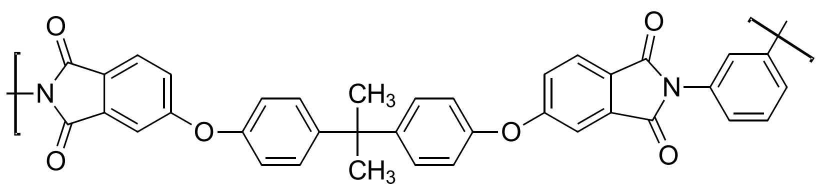


4 **a** **b** **c**

The most commonly used method for synthesizing PAEs is by the formation of ether links via nucleophilic aromatic substitution (NAS). To accomplish this, the polymerization usually occurs between an activated dihalo compound and a bisphenolate. In order to activate the dihalo compound, a withdrawing group is needed, and one of the more common activating groups is a ketone as shown in **4a**.[4]

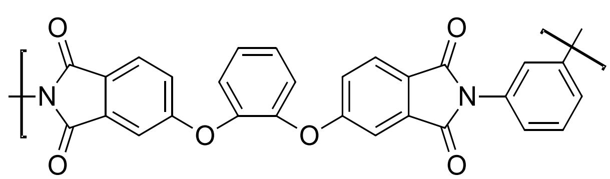
PAEs are further classified based on which activating group is employed. The three most common activating groups are imides, sulfones, and ketones resulting in poly(ether imide)s, poly(aryl ether sulfone)s and poly(ether ether ketone)s, respectively. With such a variety in the structure of PAEs, these polymers are used in many different applications.

Poly(ether imide)s differ from common polyimides in that they contain ether linkages. These linkages provide flexibility in the polymer backbone, which in turn lowers the glass transition temperature of the polymer and make it easier to process.[5] Without the ether linkages, aromatic polyimides are generally difficult to process due to the rigidity of the polymer and frequently must be processed as the poly(amic acid) precursor and then cycloimidized to the polyimide.[5] As for the use of poly(ether imide)s in industry, they are most prevalent in the aerospace and electronics industry in the form of films and moldings. One of the most well-known commercial poly(ether imide)s is Ultem 1000® **5**. One of the reasons that polyimide **5** is useful is that it has reasonable processing parameters. This is due to the small aliphatic region of the polymer that increases flexibility making the polymer more soluble.[6]



5

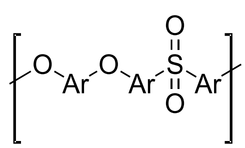
In 1997, Hsiao[7] reported a series of poly(ether imide)s that were soluble and processable like **5** but had better thermal stability. These polymers utilized an ortho substituted ring between the ether linkages.



6

The ortho substitution of polymer **6** gave similar flexibility as the aliphatic region of **5** gives**,** but without the thermal vulnerability of the aliphatic unit. It was shown that polymer **6** had only a slightly elevated T_g of 224° versus 212° for **5,** and an even greater thermal stability with a 5% decomposition temperature of 533° versus 505° for **5**. The number-average molecular weights (M_n) achieved for **6** was 11,700 g/mol and the weight average-molecular weight (M_w) achieved was 44,000 g/mol. Polymer **6** also showed excellent solubility in several common organic solvents such as NMP and DMSO, as well as chlorinated solvents like dichloromethane and chloroform.[7]

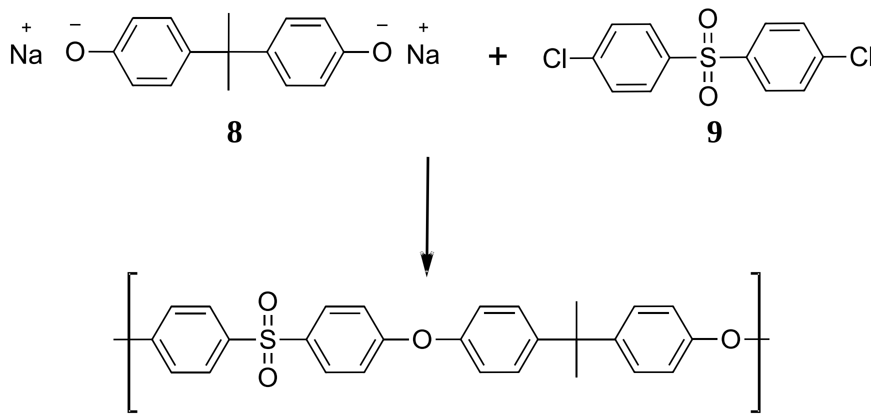
Poly(arylene ether sulfone)s PAES, are a subset of poly(arylene ethers) that are completely amorphous. PAES consist of the subunit aryl-sulfone-aryl connected by ether linkages as shown in polymer **7**.[8]



7

Most recently they have been employed as membranes in fuel cells. The use of PAES as anion exchange membranes is due to their excellent physical properties and chemical resistance as well as their high thermal stability. Alkaline anion exchange membrane fuel cells (AAEMFCs) operate using electrolytes like KOH, a strong base, at temperatures up to 90°. PAES are some of the few membranes that can survive these conditions.[9]

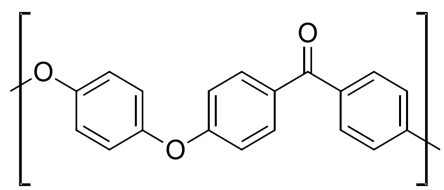
The first commercial poly(arylene ether sulfone) was Udel® **10**, developed by Union Carbide in 1965.[10] This was synthesized by an NAS polycondensation method using the bis-sodium salt of bisphenol-A **8** and 4,4-dichlorodiphenyl sulfone **9**. The reaction was performed in a high-boiling polar aprotic solvent such as NMP.



8 **9** **10**

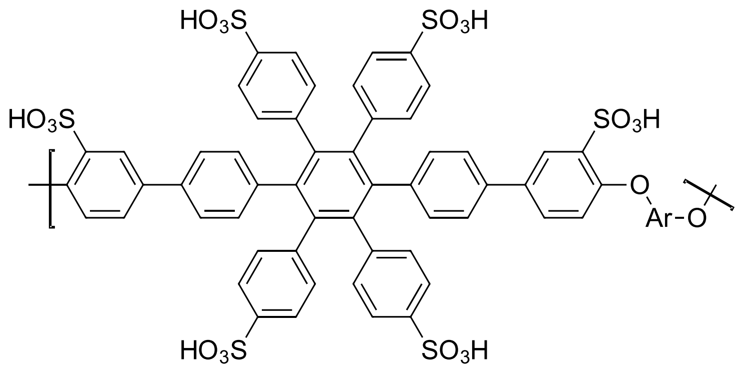
NAS is typically the preferred method to synthesize these polymers because the reagents used are inexpensive and this method yields the highest molecular weight polymers.[10]

Poly(ether ether ketone)s, PEEK are very similar to poly(arylene ether sulfone)s in chemical resistance and thermal stability. PEEK polymers like **11** are defined as having a ketone between two aryl groups. Each subunit is connected by ether linkages.[11]

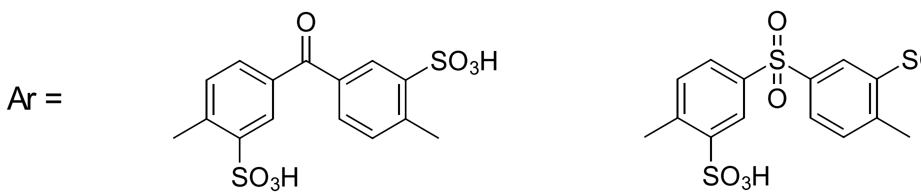


11

One example of how similar the properties of PAES and PEEK can be seen in the synthesis of anion exchange membranes. In 2016, Lee[12] showed that for a series of sterically encumbered, sulfonated, alternating poly(arylene ether) copolymers, **12a** and **12b**, there was virtually no difference between the corresponding PEEK and PAES in terms of proton exchange membrane performance.

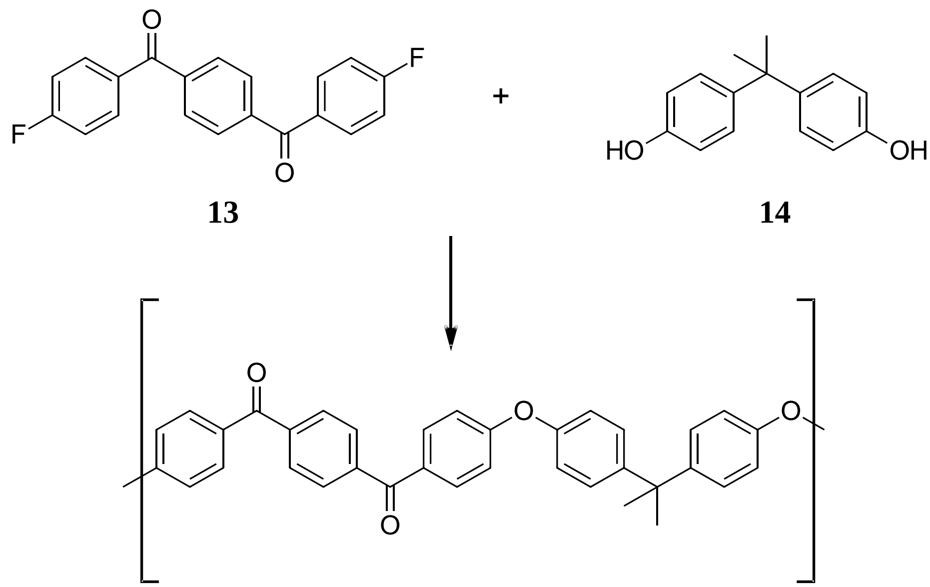


12



a **b**

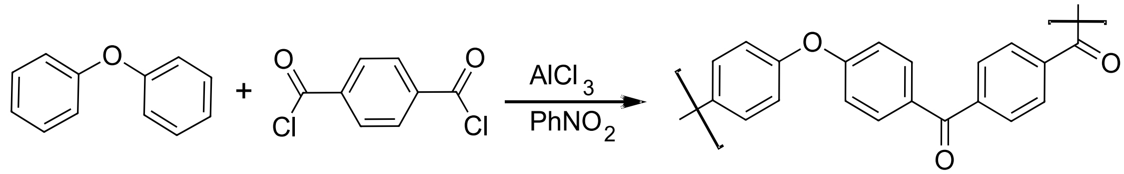
PEEK and PAES differ structurally and therefore stereochemically. The ketone and ether functionalities in PEEK can adopt a planar geometry. Also, the bond angle and bond distances of the ketone and ether linkages in PEEK are the same giving the polymer a strong affinity towards crystallinity.[13] PAES on the other hand have the built-in tetrahedral structure of the sulfonyl unit and thus cannot adopt a planar geometry. This means that most PEEK polymers have at least a small degree of crystallinity whereas PAES are completely amorphous.[14] This crystallinity causes many PEEK polymers to be insoluble in many common organic solvents, and soluble only in concentrated sulfuric acid or other similarly strongly acidic solvents. Amorphous PEEK polymers are typically soluble in chlorinated solvents and are easier to process due to their lower glass transition temperatures (T_g). The reason for this amorphous nature and increased solubility is usually due to the presence of bulky side groups on the polymer backbone, or, in the case of bis(fluorobenzoyl) monomer **13,** the use of nonlinear bisphenols **14,** leading to flexibility in the polymer backbone because of the tetrahedral geometry of the bisphenol-A as seen in **15**.[13]



13 **14**

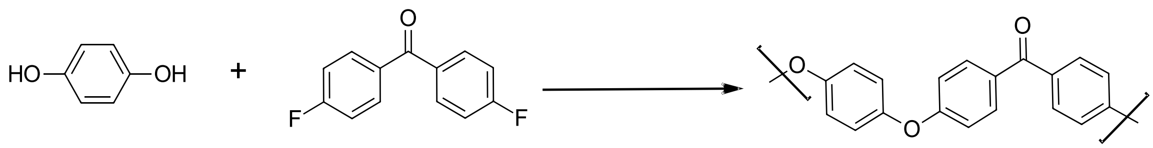
15

There are two main ways to synthesize poly(ether ketone) polymers. The earliest method used by Bonner of DuPont in 1962 employed Friedel-Crafts acylation.[15] Unfortunately, this method only produced low molecular weight polymeric material. The poly(ether ketone ketone) **18** was synthesized by the reaction of diphenyl ether **16** and terephthaloyl chloride **17** using nitrobenzene as a solvent and aluminum chloride as a catalyst.[15]



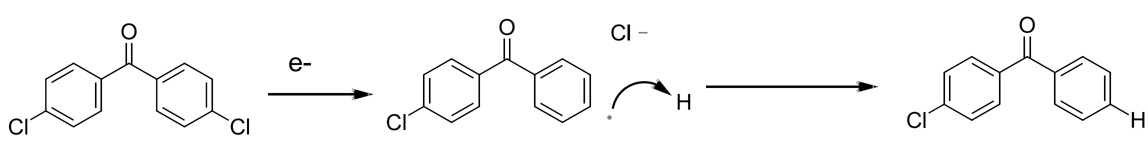
16 **17** **18**

A later, and more effective, method to synthesize PEEK polymers employed NAS polycondensation systems. The original reaction was carried out in DMSO using hydroquinone **19** and bis(fluorobenzophenone) **20**. This led to low molecular weight because of the crystallinity and the resulting insolubility of the polymer in DMSO.[16] In order to increase the molecular weight, Atwood[17] carried out the polymerization using diphenyl sulfone as the solvent and kept the temperature of the reaction near the melting point of the polymer to promote solubility and increase the molecular weight.



19 **20** **11**

With appropriate optimization, high-molecular-weight polymer was achieved. For the nucleophilic route, fluoro-monomers work the best but are also expensive. The less reactive monomers, the dichlororo monomers, do not easily produce high molecular weight polymers. One reason for this is the tendency for side reactions such as single electron transfer in which 4,4’-dichlorobenzophenone **21** could be reduced by one electron to the radical anion that quickly decomposes to the halide anion and the aryl radical **22**. The aryl radical then abstracts a hydrogen atom from the solvent to yield chain terminating 4-chlorobenzophenone **23**.[18]

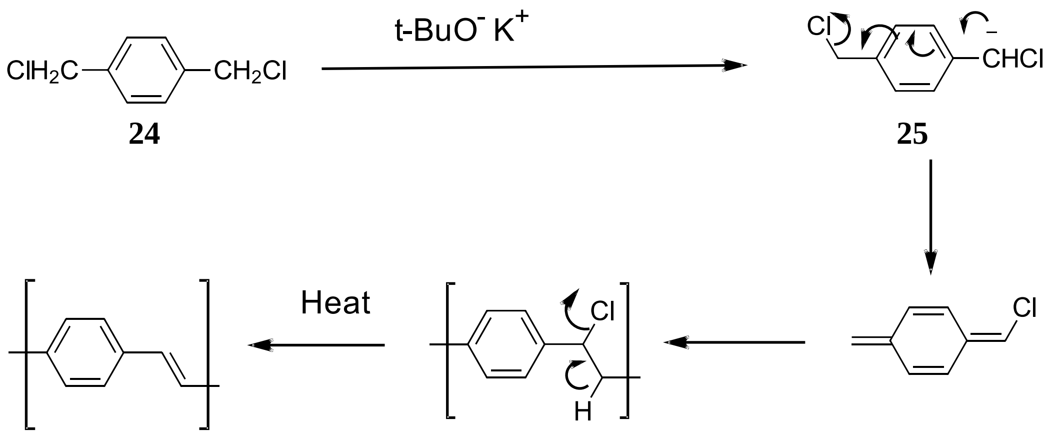


21 **22** **23**

Poly(phenylene vinylene)s (PPV)

Phenylene vinylenes **28** were first reported by Gilch and Wheelwright in 1965. While originally named poly(xylylidene)s, the more common name currently is poly(phenylene vinylene)s.[20] The original study was focused on the reaction of α, α‘-

dihalo-p-xylenes **24** with base. The reaction produced **28** via a proposed 1,6-dehydrohalogenation.[19]



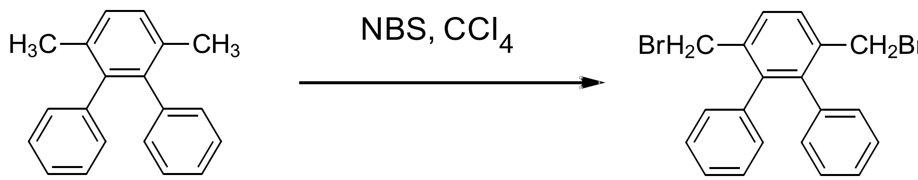
24 **25** **28** **27** **26**

The mechanism for this reaction involves initial removal of an alpha proton in **24**. The resulting anion **25** then eliminates a chlorine to give the quinoid structure **26**. This molecule polymerizes by an addition process to form **27**, which undergoes thermal dehydrohalogenation to yield polymer **28**.[20]

These polymers were insoluble in almost all common organic solvents but had excellent thermal stability. While the thermal properties were desirable, the polymer's usefulness was greatly diminished because the polymer was so difficult to process. Since the backbone of the PPV polymer consists of a completely conjugated system, no modification that significantly disrupts this conjugation can be proposed as a solubility enhancement. This means that to increase the solubility or processability, substituent groups must be added onto the aromatic ring.

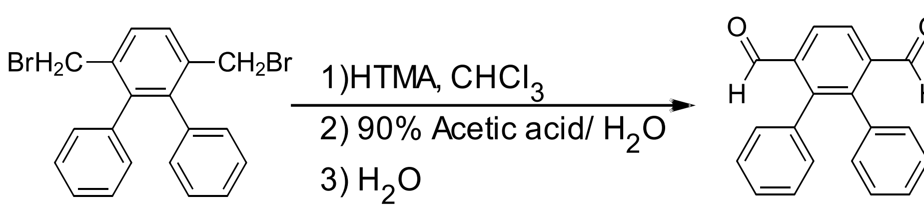
Highly Substituted Aromatic Dialdehydes for PPV Synthesis

The first attempt to make a phenylated PPV occurred in 1982.[21] The phenylated dialdehyde monomer, 2,3-diphenylterephthaldehyde **31,** was synthesized by a two-step process starting with 3',6'-dimethyl-o-terphenyl **29.** The dimethyl compound **29** was reacted with N-bromosuccinimide in carbon tetrachloride to yield 3',6'-bis(bromomethyl)-o-terphenyl **30** in a 86% yield.[21]



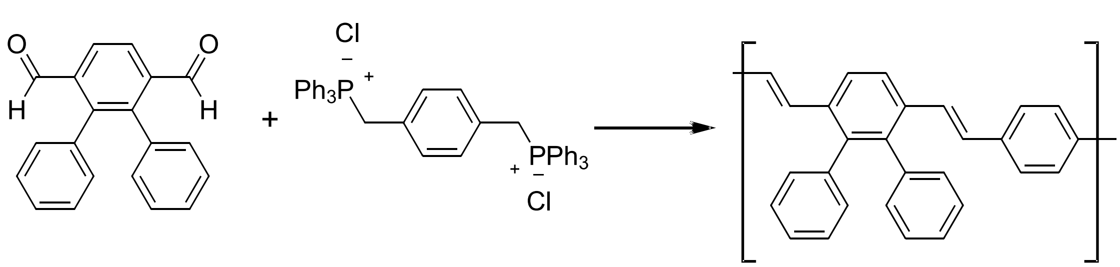
29 **30**

The Sommelet reaction was used to convert the 3',6'-bis(bromomethyl)-o-terphenyl **30** to the corresponding dialdehyde, 2,3-diphenyltetephthaldehyde **31**. This reaction is a process in which aldehydes are made from alkyl halides using hexamethylene tetramine (HTMA). In this particular instance, the solvent that produced the best yields was 90/10 acetic acid/water. The 2,3-diphenylterephthaldehyde **31** was recovered in 65% yield.[21]



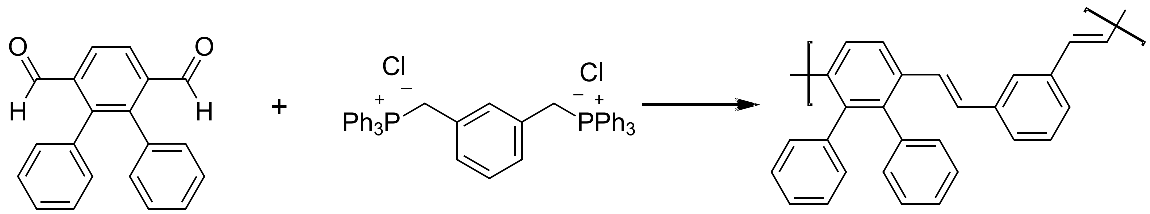
30 **31**

Dialdehyde **31** was then reacted with p-xylenebis(triphenylphosphonium chloride) **32** to yield polymer **33** in 83% yield via a phase transfer catalyzed Wittig reaction.[21]



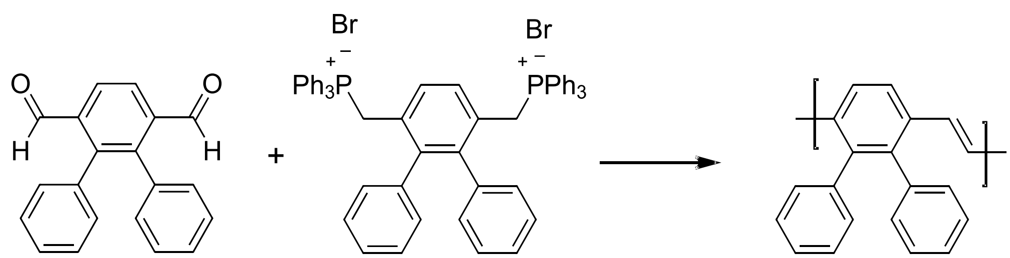
31 **32** **33**

A similar reaction was then carried out using m-xylenebis(triphenylphosphonium chloride) **34** to produce polymer **35**.



31 **34** **35**

A third polymer, **37** was synthesized using the phenylated dialdehyde **31** combined with 2,3-diphenyl-p-xylenebis(triphenylphosphonium bromide) **36**.

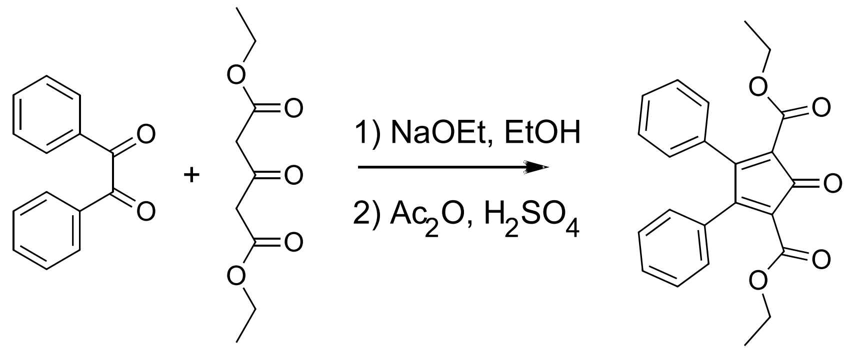


31 **36** **37**

The incorporation of phenyl substituents appeared to be responsible for the solubility of polymers **33, 35** and **37** in chlorinated solvents and partial solubility in aliphatic ketones.[22] Polymers **33, 35** and **37** were found to have number-average molecular weights (M_n) of 2157 g/mol, 1963 g/mol, and 1470 g/mol, respectively.[21] These are extremely low molecular weights and the materials are better considered oligomeric than polymeric. They were, however, highly fluorescent.

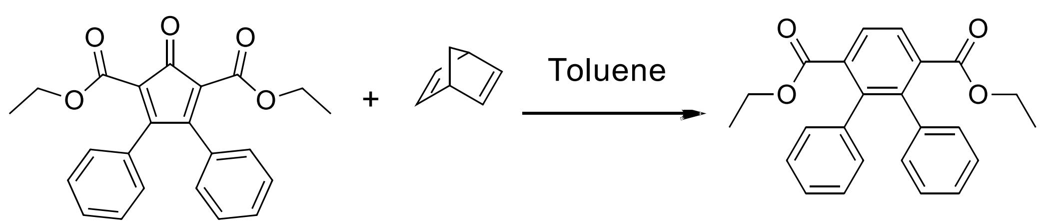
The yield of the Sommelet reaction was inconsistent. However, the success of producing a soluble PPV led to a search for a better synthetic pathway for dialdehyde **31**, and thus a better overall method for producing soluble phenylated PPV and other phenylated polymeric material.

The sequence that resulted as a response to the previous study begins with the synthesis of 2,5-bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone **40**. This is formed from the reaction of benzil **38** and diethyl 1,3-acetonedicarboxylate **39** with sodium ethoxide in ethanol. A second step employs acetic anhydride and sulfuric acid.[23]



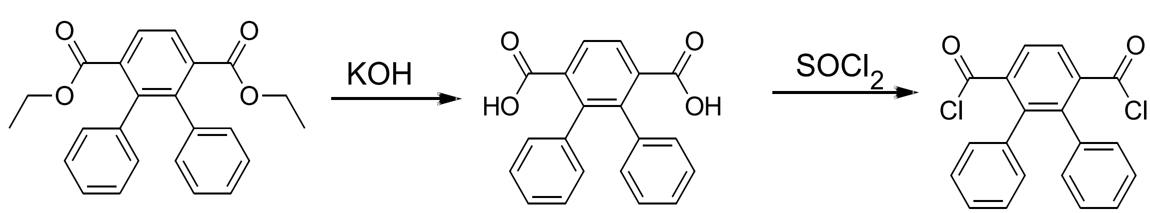
38 **39** **40**

The cyclopentadienone **40** was then reacted with norbornadiene **41**, that can be viewed a hidden acetylene, in toluene in a Diels-Alder reaction to form 2,3-diphenyl-1,4-benzenedicarboxylate **42** in 85% yield.[24]



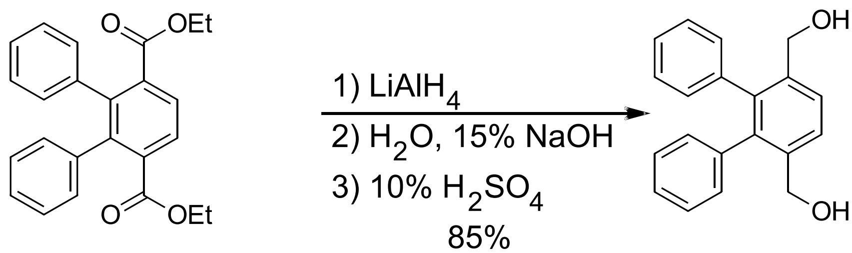
40 **41** **42**

As anticipated, the diester **42** could be hydrolyzed to the corresponding diacid **43** which could be smoothly converted to the diacid halide **44** by the use of thionyl chloride. Diacid halide **44** proved to be an important intermediate in future reactions.



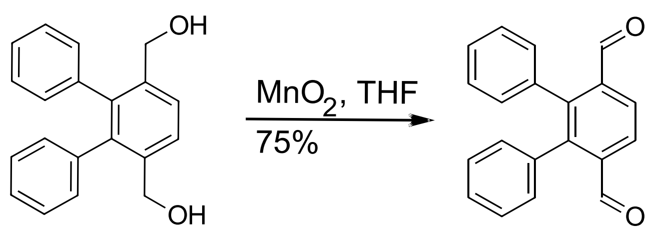
42 **43** **44**

The corresponding diol, 3,6-bis(hydroxymethyl)-1,2-diphenylbenzene **45,** can be synthesized by reducing **42** with lithium aluminum hydride. This resulted in fine white crystals recovered in a yield of 86%.[3]



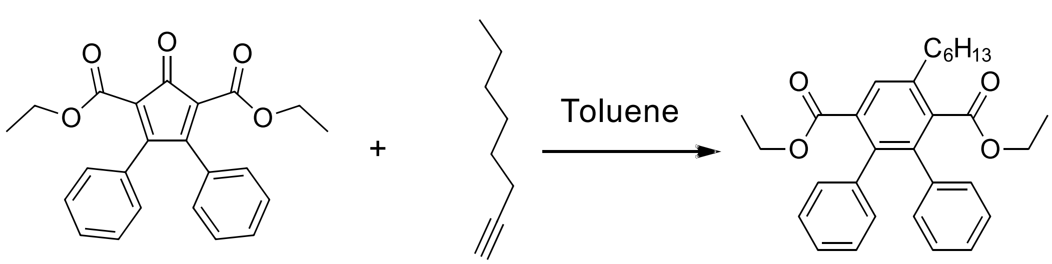
42 **45**

Diol **45** was then oxidized to the corresponding dialdehyde, 2,3-diphenylterephthaldehyde **46,** by reaction with manganese dioxide in THF. The crude product was recrystallized from absolute methanol to yield white flaky crystals in a 75% yield.[3]



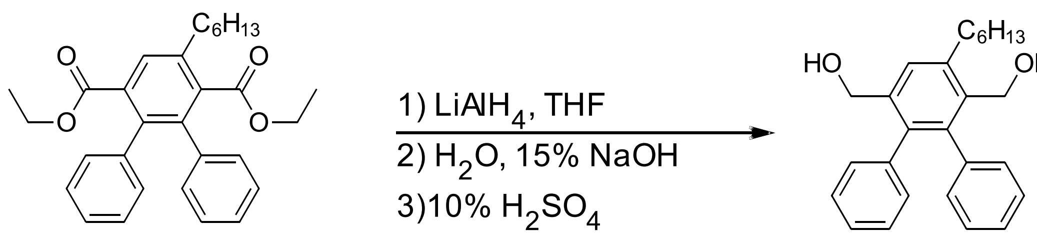
45 **46**

The Diels-Alder reaction of **40** can also be used in several different ways to functionalize **46**. In 1998, Cheek synthesized diethyl 5-hexyl-2,3-diphenyl-1,4-benzenedicarboxylate **48** by reacting cyclopentadienone **40** with 1-octyne **47**.[25]



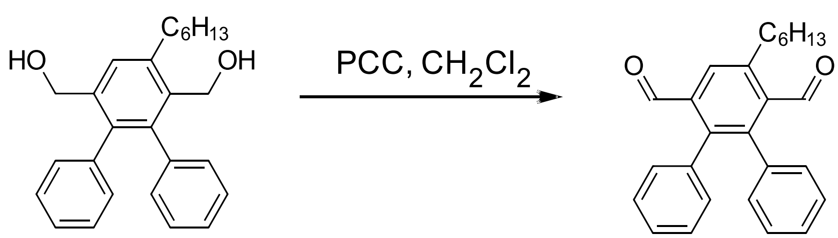
40 **47** **48**

Following the Diels-Alder reaction, diester **48** was reduced with lithium aluminum hydride to yield 5-hexyl-1,4-bis(hydroxymethyl)-2,3-diphenylbenzene **49** in 64% yield. The diol was purified by aqueous ethanol recrystallization.



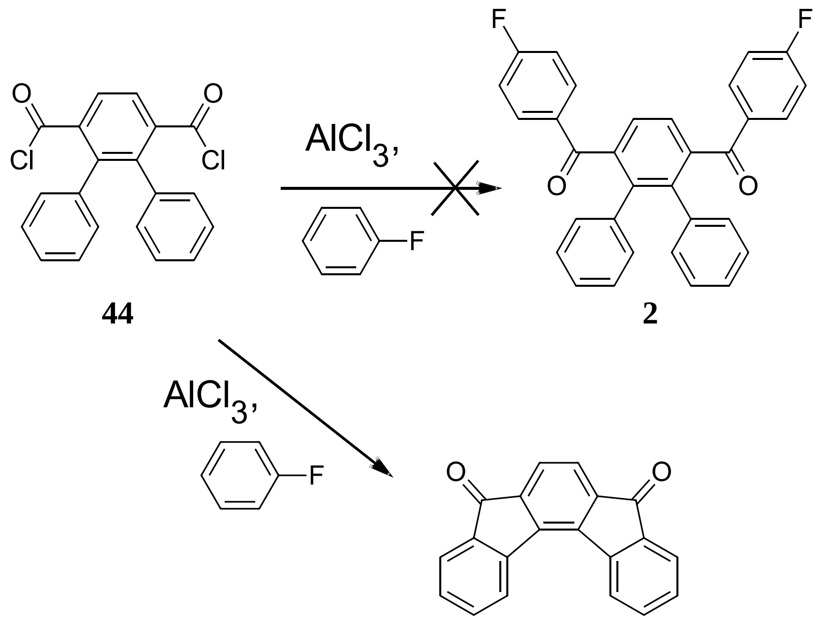
48 **49**

Diol **49** was oxidized to the corresponding alkyl substituted dialdehyde 5-hexyl-2,3-diphenyl-1,4-benzenedicarboxaldehyde **50** using pyridinium chlorochromate (PCC) in dichloromethane.[25] The use of MnO_2 resulted in only one of the primary benzylic alcohols, the least hindered one, being oxidized. Dialdehyde **50** was not employed to prepare any PPV polymeric material but would prove to be a useful intermediate later.



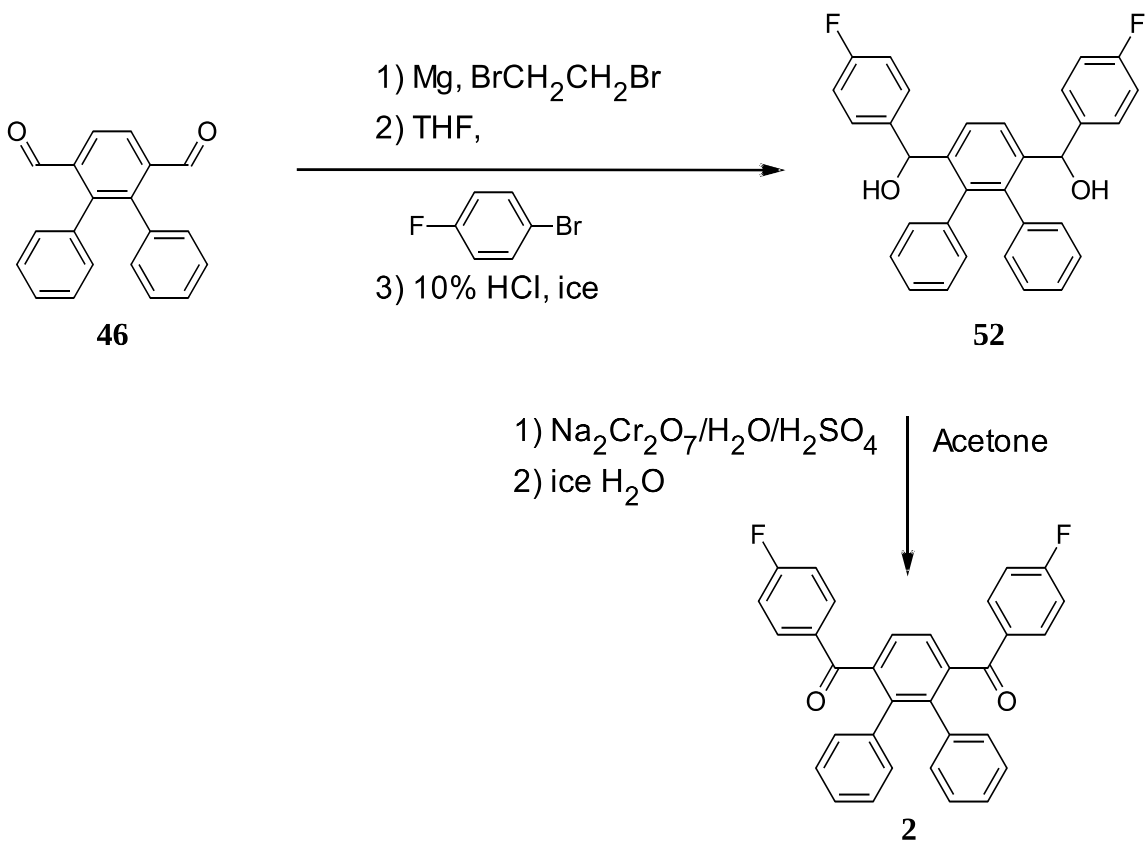
49 **50**

At about this same time, Lorge,[24] who sought a pathway to 2,3 diphenyl-1,4-bis(fluorobenzoyl)benzene **2,** discovered that the Friedel-Crafts reaction of diacid halide **44** with fluorobenzene led to the intramolecular cyclization product, 5,8-dioxo-5,8-dihydroindeno[2,1c]fluorene **51** rather than **2**. Although not initially anticipated, the reaction can be rationalized because of the proximity of the intermediate cation in the Friedel-Crafts reaction to the ortho situated phenyl substituents.



44 **2** **51**

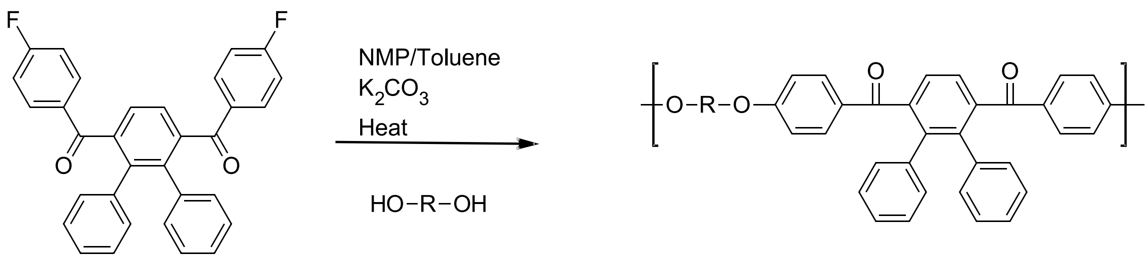
In 2005, Dancevic[3] discovered a method to synthesize 2,3 diphenyl-1,4-bis(fluorobenzoyl)benzene **2**. This was accomplished through a two-step process starting



46 **52** **2**

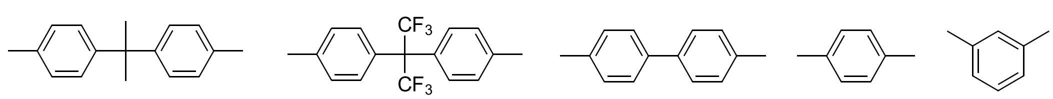
with the reaction of dialdehyde **46** with p-fluorophenylmagnesium bromide to produce the diol intermediate **52** containing two chiral centers. The product was a mixture of stereoisomers resulting in a purification problem. A Jones oxidation reaction was used to convert the chiral secondary alcohols in **52** to ketones, resulting in the product, 2,3-diphenyl-1,4-bis(4-fluorobenzoyl)benzene **2** thus eliminating the stereocenters and the corresponding purification problem.

Monomer **2** was polymerized with various aromatic bisphenols **14, 19, 53a-c** via a nucleophilic aromatic substitution reaction to yield a series of poly(ether ether ketone ketone) polymers **54a-e**. The reaction was carried out in N-methyl-2-pyrrolidone using potassium carbonate as a base. Toluene was also used for azeotropic removal of water from the system with a Dean-Stark trap.[3]



2 **14, 19, 53a-e** **54a-e**

R=



14, 54a **53a, 54b** **53b, 54c** **19, 54d** **53c, 54e**

The resulting polymers were obtained in yields of greater than 90% and were all soluble in chlorinated solvents like chloroform. The polymers could be cast as thin films. The polymers retained excellent thermal stability, which will be discussed later.[3]

The unanticipated intramolecular ring closure of the diacid halide **44** in the Friedel-Crafts reaction with fluorobenzene reported by Lorge,[24] the synthesis of a phenylated dialdehyde **31** by Ganesan,[21] the synthesis of a alkylated/phenylated dialdehyde **50** by Cheek[25] and the success of the use of aromatic dialdehydes in the synthesis of bis(fluorobenzoyl) monomers by Dancevic[3] suggests a variety of additional modifications of monomer **2**.

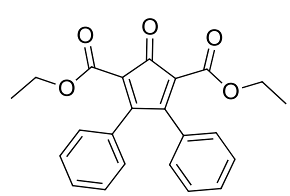
Thus, the objectives of this research were to 1) synthesize and characterize an alkyl substituted phenylated bisfluorobenzoyl monomer by way of dialdehyde **50**, 2) polymerize the new monomer with bisphenols of varying rigidity, 3) characterize the resulting novel poly(ether ether ketone ketone)s (PEEKKs), and 4) compare the physical properties of the unsubstituted **15**, the phenylated **54a**, and the phenylated and alkyl substituted PEEKK.

Experimental

Instrumentation and Chemicals.

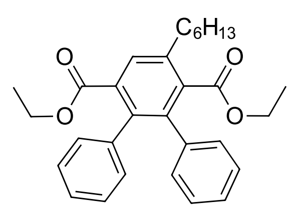
Carbon (^{13}C) and proton (^{1}H) Nuclear Magnetic Resonance (NMR) spectra were obtained using a Bruker Avance 300 NMR Spectrometer. Solvents used were deuterated chloroform ($CDCl_3$) and deuterated acetone (acetone-d_6). Bruker Topspin 3.5 was used to process all NMR spectra. A Thermo Scientific Nicolet 6700 FT-IR was used to acquire the Infrared spectra (IR) employing thin films on a NaCl plate. Polymer IR spectra were obtained by casting thin films. Number-average molecular weights (Mw) and weight-average molecular weights (Mw) were obtained using a Viscotek Triple Detector Array (TDA) Model 300 Gel Permeation Chromatograph (GPC) calibrated with polystyrene. Melting points were determined with a DigiMelt MPA-160 apparatus. Thermal Gravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC) were obtained with a TGA Q 500 and a TA DSC Q 200 in air or nitrogen atmospheres. Elemental analyses were performed by Midwest Micro Laboratories, Indianapolis, Indiana. Starting materials were acquired from Sigma-Aldrich and used without further purification unless otherwise stated.

2,5-Bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone 40



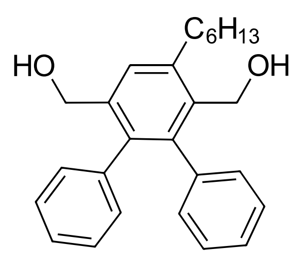
A solution of sodium metal (2.572 g, 0.1118 mol) dissolved in ethanol (50 mL) was added to diethyl 1,3-acetonedicarboxylate (24.2 g, 0.1196 mol) and benzil (21.0 g, 0.0998 mol) dissolved in ethanol (100 mL) heated to reflux (80°) in a 250 mL, three-necked, round-bottomed flask. The initial orange solution then slowly turned yellow and a yellow precipitate rapidly formed. The precipitate was vacuum filtered and washed with ethanol three times. After air drying, the yellow solid was slurried with acetic anhydride (70 mL) in a 500 mL Erlenmeyer flask. Sulfuric acid was added dropwise until the solution was a deep red and the solid had dissolved. Water was added dropwise alternating with drops of sulfuric acid until the temperature had reached 50°. The temperature was maintained by drops of water between 50° and 80° until the addition of water no longer raised the temperature. The red solution was diluted with water and stirred overnight. The orange precipitate was filtered and air dried to yield 16.02g (42.5%) of orange product: mp 117-119° (lit[23] mp 120-121°); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 1.17 (t, 6H, J = 7.1 Hz, CH_3), 4.20 (q, 4H, J = 7.1 Hz, CH_2), 7.00-7.07 (m, 4H, Ar CH), 7.22-7.31 (m, 4H, Ar CH), 7.32-7.41 (m, 2H, Ar CH).

Diethyl 5-hexyl-2,3-diphenyl-1,4-benzenedicarboxylate 48



Into a 35 mL Q-tube® were placed 2,5-bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone (3.136 g, 0.0083 mol), 1-octyne (0.9181 g 0.0083 mol) and toluene (7 mL) and the solution was heated in an oil bath at 120° overnight. The solution was cooled to room temperature and evaporated under vacuum to yield 2.75 g (71.9%) of a dark brown oil: IR (NaCl, cm^{-1}) 3053, 3025 (Ar CH), 2927 (Ali CH), 1724 (C=O Ester); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 0.90 (m, 9H, CH_3), 1.36 (m, 6H, CH_2), 1.72 (m, 2H, CH_2), 2.71 (t, 2H, CH_2), 3.95 (q, 2H, J= 7.1 Hz, CH_2), 3.99 (q, 2H, J= 7.1 Hz, CH_2), 6.92 - 7.17 (m, 10H, Ar CH), 7.67 (s, 1H, Ar CH); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 13.51 (CH_3), 13.58 (CH_3), 14.07 (CH_3), 22.55 (CH_2), 29.29 (CH_2), 31.18 (CH_2), 31.60 (CH_2), 33.50 (CH_2), 60.96 (CH_2), 60.99 (CH_2), 126.46 (Ar, CH), 126.81 (Ar, CH), 127.19 (Ar, CH), 127.21 (Ar, CH), 128.94 (Ar, CH), 129.83 (Ar, CH), 130.17 (Ar, CH), 133.56 (Ar, C), 137.11 (Ar, C), 138.26 (Ar, C), 138.47 (Ar, C), 138.79 (Ar, C), 139.02 (Ar, C), 139.59 (Ar, C), 168.65 (C=O Ester), 168.79 (C=O Ester).

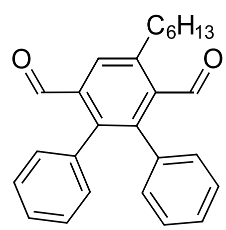
5-Hexyl-1,4-bis(hydroxymethyl)-2,3-diphenylbenzene 49



In a 500 mL, three-necked, round-bottomed flask containing anhydrous tetrahydrofuran (THF) (80 mL) equipped with a nitrogen inlet and outlet, lithium aluminum hydride (1.88 g, 0.046 mol) was added slowly at 0°. A solution of diethyl 5-hexyl-2,3-diphenyl-1,4-benzenedicarboxylate (4.75 g, 0.010 mol) in THF (30 mL) was added dropwise from an addition funnel over 30 min. The solution was stirred at room temperature for 1h after which the heat was increased to reflux (65°) and maintained overnight. The reaction was cooled with an ice bath and treated with 1) H_2O (4 mL) added dropwise and stirred for 15 min, 2) 15% NaOH (12 mL) added dropwise and stirred for 15 min, and 3) H_2O (12 mL) added slowly and stirred for 15 min. The solution was evaporated in a stream of nitrogen and the resulting mixture was stirred overnight in

150 mL of 10% H_2SO_4 to dissolve any aluminum salts. The product was vacuum filtered and recrystallized from aqueous ethanol to yield 3.03 g (78%) of a white powder: mp 142-144° (lit[25] mp 135-136°);IR (NaCl, cm^{-1}) 3313 (OH), 3054 (aromatic CH), 2923 (aliphatic CH); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 0.81-1.93(m, 14H, Ali CH), 2.88 (m, 2H, CH_2), 4.44 (s, 2H, CH_2OH), 4.47 (s, 2H, CH_2OH), 6.92-7.23 (m, 10H, Ar, CH), 7.47 (s, 1H, Ar, CH); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 14.12 (CH_3), 22.66 (CH_2), 29.69 (CH_2), 31.79 (CH_2) 32.13 (CH_2), 33.24 (CH_2), 59.61 (O-CH_2), 63.64 (O-CH_2), 126.44 (Ar, CH), 126.47 (Ar, CH), 127.50 (Ar, CH), 127.59 (Ar, CH), 128.24 (Ar, CH), 130.00 (Ar, CH), 130.11 (Ar, CH), 135.49 (Ar, C), 138.39 (Ar, C), 138.99 (Ar, C), 139.66 (Ar, C), 142.05 (Ar, C), 142.58 (Ar, C); Anal. Calcd. for $C_{26}H_{30}O_2$: C, 83.38%; H, 8.59%. Found: C, 83.93%; H, 8.08%.

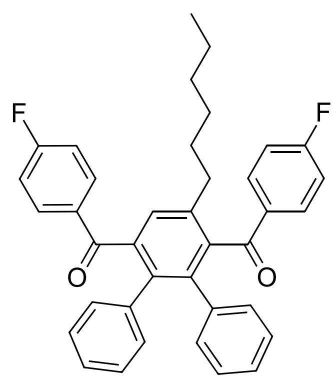
5-Hexyl-2,3-diphenyl-1,4-benzenedicarboxaldehyde 50



In a 500 mL, round-bottomed flask equipped with a drying tube, containing CH_2Cl_2 (175 mL) was added pyridinium chlorochromate (PCC) (10.95 g, 0.051 mol) and 5-hexyl-1,4-bis(hydroxymethyl)-2,3-diphenylbenzene (7.6 g, 0.0203 mol). The mixture was heated to 50° and stirred for 2h. Ethyl ether (175 mL) was added, the mixture was stirred for 20 min and decanted into a 500 mL Erlenmeyer flask. The decanted solution was then filtered through a sintered-glass funnel containing a pad of filter-aid. The yellow filtrate was evaporated under reduced pressure. The product was purified by column chromatography using an eluent of 90% hexane and 10% ethyl acetate on solid silica.

The eluents were evaporated under reduced pressure to yield 6.81g (75%) of a yellow powder: mp 75.5-78.5° (lit[25] mp 73-75°); IR (NaCl, cm^{-1}) 3056 (aromatic CH), 2927 (aliphatic CH), 1693 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 0.93 (t, 3H, J = 6.9 Hz, CH_3), 1.11-2.02 (m, 8H, CH_2), 3.01-3.06 (m, 2H, CH_2), 6.98-7.26 (m, 10H, Ar CH), 7.95 (s, 1H, Ar CH), 9.77 (s, 1H, HC=O aldehyde), 9.80 (s, 1H, HC=O aldehyde); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 31.68 (CH_2), 31.81 (CH_2), 33.62 (CH_2), 127.60 (Ar, CH), 127.67 (Ar, CH), 127.78 (Ar, CH), 127.86 (Ar, CH), 128.43 (Ar, CH), 130.92 (Ar, CH), 131.05 (Ar, CH), 134.82 (Ar, C), 135.85 (Ar, C), 135.99 (Ar, C), 137.54 (Ar, C), 143.02 (Ar, C), 143.61 (Ar, C), 146.02 (Ar, C), 192.33 (CH aldehyde), 194.38 (CH aldehyde). Anal Calcd. for $C_{26}H_{26}O_2$: C, 84.29%; H, 7.07%. Found: C, 84.72%; H 7.17%.

5-Hexyl-2,3-diphenyl-1,4-bis(fluorobenzoyl)benzene 55



The bis(fluorobenzoyl) monomer **2** was synthesized via a two-step process involving a Grignard reaction followed by a Jones oxidation.

Step 1: In a 3-necked, round-bottomed, 250 mL flask equipped with magnetic stir bar, nitrogen inlet, and constant pressure dropping funnel, was placed 1.006 g (0.041 moles) of dried and crushed magnesium. The flask was then flame dried under nitrogen flow. To the magnesium was added a solution of dry tetrahydrofuran (THF) (15 mL) and p-bromofluorobenzene (5.43 g, 0.031 mol). The reaction was initiated by the addition (1-

2 drops) of dibromoethane. The reaction was then left to stir for 1h after which a solution of the dialdehyde **55** (3.80 g, 0.010 mol) in 50 mL of dry THF was added dropwise over 10 min. After the dialdehyde **55** was added, the nitrogen flow was stopped, the dropping funnel was replaced by a condenser equipped with a drying tube, and the temperature was increased to 70° for 2h. The solution was then cooled to room temperature and poured over 10% HCl and ice water (100 mL). The mixture was then extracted with ethyl acetate. The ethyl acetate was evaporated in vacuo and used directly in the next step.

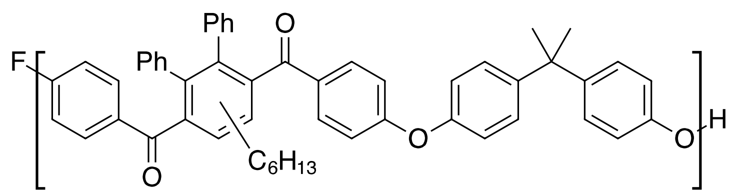
Step 2: The yellowish oil was dissolved in 20 mL of acetone and placed in a three-necked, round-bottomed flask, equipped with a magnetic stir bar, a condenser, drying tube and a constant-pressure dropping funnel. Jones reagent was made by dissolving 10 g of sodium dichromate dihydrate in 30 mL of water, adding 7.3 mL of concentrated sulfuric acid (99%) and diluting further to a total of 50 mL. The Jones reagent (15 mL) was then added dropwise over 10 min. The reaction mixture was then refluxed (70°) overnight. The reaction was cooled to room temperature, poured into 100 mL H_2O, extracted with ethyl acetate, and dried under reduced pressure. The crude product was a yellow oil, which was chromatographed on silica using an eluent of 95% hexane and 5% ethyl acetate. The fractions containing the desired product were located using thin layer chromatography. The combined fractions were then recrystallized from aqueous acetone to yield 4.56 g (63% yield) of colorless crystals: mp 143-144°; IR (NaCl, cm^{-1}) 3058 (aromatic CH), 2929 (aliphatic CH), 1670 (C=O), 1596 (C=C), 1151 (F-C); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 0.84 (t, 3H, J =6.6 Hz, CH_3), 1.15-1.39 (m, 6H, CH_2), 1.47-1.81 (m, 2H, CH_2), 2.57 (d, 1H, J = 9 Hz, Ar-CH_2), 2.63 (d, 1H, J = 9 Hz, Ar-CH_2), 6.21-7.40 (m, 14H, Ar, CH), 7.47 (s, 1H, Ar, CH), 7.58 (d of d, 2H, J_{HH} = 8.8 Hz,

J_{HF} = 5.4 Ar, CH), 7.62 (d of d, 2H, J_{HH} = 8.8 Hz, J_{HF} = 5.4 Ar, CH); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 13.99 (CH_3), 22.43 (CH_2), 29.18 (CH_2), 31.05 (CH_2), 31.42 (CH_2), 33.24 (CH_2), 115.15 (d, 1C, J = 22.0 Hz Ar, CH), 115.33 (d, 1C, J = 22.0 Hz Ar, CH), 126.78 (Ar, CH), 127.36 (Ar, CH), 127.65 (Ar, CH), 130.80 (Ar, CH), 131.38 (Ar, C), 131.88 (d, 1C, J = 9.4 Hz Ar, CH), 132.28 (d, 1C, J = 9.4 Hz Ar, CH), 133.57 (d, 1C, J = 2.8 Hz Ar, C), 133.87 (d, 1C, J = 2.8 Hz Ar, C), 136.97 (Ar, C), 137.21 (Ar, C), 137.38 (Ar, C), 138.89 (Ar, C), 139.37 (Ar, C), 141.00 (Ar, C), 141.15 (Ar, C), 165.44 (d, 1C, J = 254.25 Hz C-F), 165.63 (d, 1C, J = 254.25 Hz C-F), 197.33 (C=O ketone). Anal. Calcd. for $C_{38}H_{32}F_2O_2$: C, 81.70%; H, 5.77%. Found: C, 81.86%; H, 5.75%.

General Polymerization Procedure

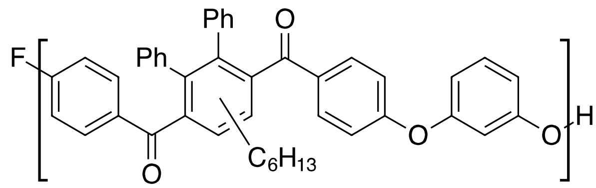
The polymerizations were carried out in a Q-tube™, equipped with a magnetic stir bar. Calculated equimolar quantities of the bis(fluorobenzoyl) monomer **55** (0.966 mmol) and bisphenol-A **14** were charged and dissolved in N-methyl-2-pyrrolidone (NMP) (5 mL). Finely crushed, dry, potassium carbonate (0.0029 mol) was also added. The reaction was then sealed and heated to 170° for 18h. After cooling to room temperature, the reaction mixture was coagulated in methanol-water solution (80/20 v/v) acidified with glacial acetic acid (~ 3 mL). The polymer was collected by filtration. The polymer was then dissolved in NMP, and coagulated in methanol-water solution (80/20 v/v) acidified with glacial acetic acid. The polymer was collected by filtration dissolved in NMP again, and coagulated in methanol-water solution (80/20 v/v) acidified with glacial acetic acid. The polymer was collected by filtration and dried under vacuum overnight at 70°.

Poly(oxy-1,4-phenylene-1-methylethylidene-1,4-phenylene-oxy-1,4-phenylene-carbonyl-(5-hexyl-2,3-diphenyl-1,4-phenylene)-carbonyl-1,4-phenylene) 56a



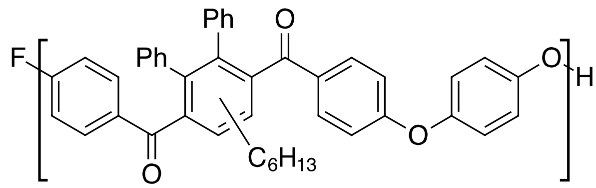
The white paper like substance was obtained in a 57% yield: IR (film) cm^{-1} 3060 (aromatic CH), 2920 (aliphatic CH), 1660 (C=O), 1590 (C=C), 1230, 1160 (C-O-C); ^1H NMR (300 MHz, $CDCl_3$ δ) 0.84 (t 3H CH_3), 1.12-1.36 (m 6H $(CH_2)_3$), 1.48-1.63 (m 2H CH_2), 1.69 (s 6H $(CH_3)_2$), 2.56-2.63 (m 2H CH_2), 6.40-7.35 (m 22H Ar, CH), 7.44 (s 1H Ar, CH), 7.52-7.61 (m 4H Ar, CH); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 14.05 (CH_3), 22.46 (CH_2), 29.20 (CH_2), 31.00 (CH_3), 31.04 (CH_2), 31.47 (CH_2), 33.25 (CH_2), 42.33(quaternary C), 116.90 (Ar, CH), 116.94 (Ar, CH), 119.35 (Ar, CH), 119.47 (Ar, CH), 126.61 (Ar, CH), 126.82 (Ar, CH), 127.25 (Ar, CH), 127.54 (Ar, CH), 128.24 (Ar, CH), 130.89 (Ar, CH), 131.63 (Ar, CH), 131.89 (Ar, C), 132.08 (Ar, CH), 132.22 (Ar, C), 136.93 (Ar, C), 137.55 (Ar, C), 137.72 (Ar, C), 138.85 (Ar, C), 139.13 (Ar, C), 141.13 (Ar, C), 141.30 (Ar, C), 146.63 (Ar, C), 146.74 (Ar, C), 153.24 (OAr, C), 153.40 (OAr, C), 161.67 (OAr, C), 161.92 (OAr, C), 197.43 (C=O), 197.48 (C=O). Anal. Calcd. for $C_{53}H_{47}FO_4$: C, 83.00%; H, 6.18%. Found C, 84.6%; H, 6.48%.

Poly(oxy-1,3-phenylene-oxy-1,4-phenylene-carbonyl-(5-hexyl-2,3-diphenyl-1,4-phenylene)-carbonyl-1,4-phenylene) 56b



The pale brown paper like substance was obtained in a 42% yield: IR (film) cm^{-1} 3057 (aromatic CH), 2926 (aliphatic CH), 1667 (C=O), 1585 (C=C), 1223, 1157 (C-O-C); ^{1}H NMR (300 MHz, $CDCl_3$ δ) 0.85 (t 3H CH_3), 1.11-1.41 (m 6H $(CH_2)_3$), 1.46-1.80 (m 2H CH_2), 2.49-2.70 (m 2H CH_2), 6.27-7.39 (m 18H Ar CH), 7.46 (s 1H Ar CH), 7.46-7.60 (m 4H Ar CH); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 14.03 (CH_3), 22.44 (CH_2), 29.19 (CH_2), 31.06 (CH_2), 31.45 (CH_2), 33.27 (CH_2), 111.11 (Ar, CH), 114.98 (Ar, CH), 115.10 (Ar, CH), 115.24 (Ar, CH), 117.49 (Ar, CH), 117.60 (Ar, CH), 126.65 (Ar, CH), 126.88 (Ar, C), 127.29 (Ar, CH), 127.72 (Ar, CH), 130.77 (Ar, CH), 130.90 (Ar, C), 131.64 (Ar, CH), 132.05 (Ar, CH), 132.54 (Ar, C), 132.79 (Ar, C), 136.92 (Ar, C), 137.46 (Ar, C), 137.64 (Ar, C), 138.82 (Ar, C), 139.34 (Ar, C), 141.09 (Ar, C), 141.31 (Ar, C), 157.02 (Ar, C), 157.07 (Ar, C), 157.29 (Ar, C), 157.35 (Ar, C), 160.65 (OAr C), 160.97 (OAr C), 197.47 (C=O). Anal. Calcd. for $C_{44}H_{37}FO_4$: C, 81.46%; H, 5.75%. Found C, 77.57%; H, 5.58%.

Poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-(5-hexyl-2,3-diphenyl-1,4-phenylene)-carbonyl-1,4-phenylene) 56c

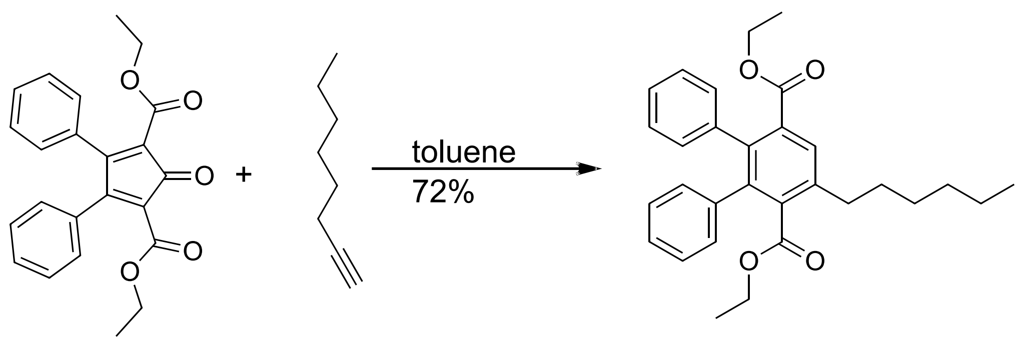


The pale brown, straight, brittle, fibers were obtained in a 51% yield: IR (film) cm^{-1} 3052 (aromatic CH), 2920 (aliphatic CH), 1663 (C=O), 1592 (C=C), 1222, 1159 (C-O-C); ^{1}H NMR (300 MHz, $CDCl_3$ δ) 0.84 (t 3H CH_3), 1.10-1.41 (m 6H $(CH_2)_3$), 1.45-1.8 (m 2H CH_2), 2.57-2.64 (m 2H CH_2), 6.31-7.4 (m 18H Ar CH), 7.46 (s 1H Ar CH), 7.54-7.62 (m 4H Ar CH); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 14.04 (CH_3), 22.45 (CH_2), 29.20 (CH_2), 31.03 (CH_2), 31.46 (CH_2), 33.25 (CH_2), 116.81 (Ar CH), 116.90 (Ar, CH), 121.28 (Ar, CH), 121.44 (Ar, CH), 126.62 (Ar, CH), 126.80 (Ar, CC), 127.25 (Ar, CH), 127.59 (Ar, CH), 130.91 (Ar, CH), 131.69 (Ar, CH), 132.13 (Ar, CH), 132.40 (Ar, C), 136.92 (Ar, C), 137.51 (Ar, C), 137.70 (Ar, C), 138.84 (Ar, C), 139.20 (Ar, C), 141.01 (Ar, C), 141.28 (Ar, C), 151.78 (Ar, C), 151.88 (Ar, C), 151.99 (Ar, C), 152.10 (Ar, C), 161.57 (OAr C), 161.80 (OAr C), 197.42 (C=O). Anal. Calcd. for $C_{44}H_{37}FO_4$: C, 81.46%; H, 5.75%. Found C, 83.69%; H, 5.83%.

RESULTS AND DISCUSSION

Diester Synthesis

The reaction of 2,5-bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone **40** with 1-octyne **47** in toluene at reflux yielded diethyl 5-hexyl-2,3-diphenyl-1,4-benzene-dicarboxylate **48**. Excess solvent, and any unreacted alkyne were removed via reduced pressure and heat.



40 **47** **48**

Diester **48** was characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. The IR spectrum (**Figure 12)** exhibited an absorption at 1724 cm^{-1}, indicating the presence of the conjugated ester carbonyl, at 2927cm^{-1} indicating the presence of aliphatic C-H stretching and at 3053 cm^{-1} signifying the presence of aromatic C-H stretching.

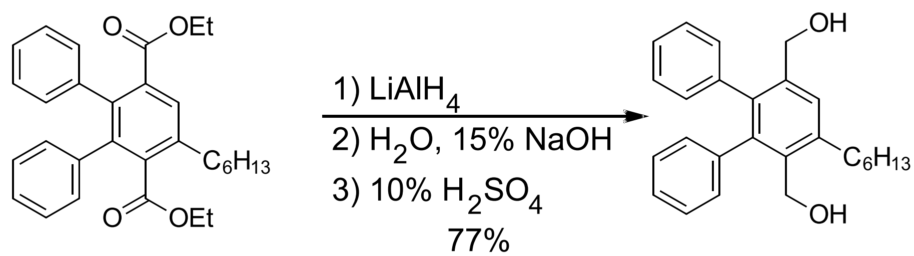
The ^{1}H NMR spectrum of **48** (**Figure 13)** indicated that the reaction between 1-octyne and 2,5-bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone had been successful. The spectrum shows the appearance of multiple aliphatic absorptions between 0.85-1.81 δ, which indicate the inclusion of an alkyl chain in the compound. The multiplet at 2.72 δ integrating to 2H is indicative of the aliphatic methylene closest to the aromatic ring on the pendant chain. The ester methylenes appear at 3.97 δ as a pair of overlapping quartets that together integrate to 4H due to the slightly asymmetric nature of the molecule. In the aromatic region, the proton absorptions appear as two multiplets at δ 6.99 and δ 7.11 that integrate to 4H and 6H, respectively. The only other proton absorption in the aromatic region is a singlet at δ 7.68 integrating to 1H, which represents the lone proton on the center phenyl ring. It is shifted downfield because of its proximity to the carbonyl group.

The ^{13}C NMR spectrum of **48** (**Figure 14**) highlights the asymmetric nature of the molecule as each individual carbon atom gives rise to a unique absorption in the aliphatic region. The two carbon absorptions at 60.96 and 60.99 ppm represent the methylene groups of the ethyl esters. They are shifted downfield due to their proximity to the electron withdrawing oxygen. The methyl group absorptions of the ester appear at 13.51 and 13.59 ppm, which is close to the methyl of the alkyl chain at 14.07 ppm. All of the other absorptions are methylene absorptions according to the DEPT 135 spectrum (**Figure 15**).

The two individual ester carbonyl absorptions appear characteristically at 168.65 and 168.79 ppm. Once again two are observed because the two carbons are not equivalent due to the pendant alkyl chain.

Diol Synthesis

Diester **48** was reduced using lithium aluminum hydride ($LiAlH_4$) in THF to yield 5-hexyl-1,4-bis(hydroxymethyl)-2,3-diphenylbenzene **49**. The diol was purified by aqueous ethanol recrystallization to yield a white powder.



48 **49**

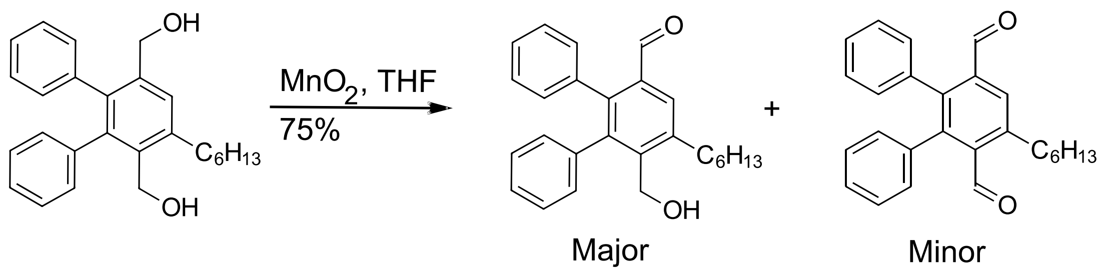
Diol **49** was characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. In the IR spectrum (**Figure 16**), it can be seen clearly that the carbonyl stretching is no longer present and has been replaced with a broad OH absorption at 3313 cm^{-1}. This supports the conversion of the ester groups to the corresponding alcohols.

The ^{1}H NMR spectrum of **49** shows an absorption for the methyl at the end of the alkyl chain as a slightly distorted triplet at 0.94 δ integrating to 3H. At the other end of the alkyl chain, an absorption for the methylene group closest to the aromatic ring can be seen as a more distorted triplet at 2.89 δ integrating to 2H. The methylene groups adjacent to the hydroxyls appear as two singlet absorptions at 4.44 δ and 4.47 δ, each integrating to 2H. The aromatic proton region is split into two absorption areas (**Figure 17**). The first region is in the range 6.94 – 7.23 δ is a broad multiplet absorption and integrates to 10H, the second is a singlet absorption at 7.47 δ integrating to 1H.

The ^{13}C NMR spectrum of **49** (**Figure 18**) showed retention of the six alkyl carbons on the pendant chain, with the addition of two new peaks further downfield at 59.61 ppm, and 63.63 ppm. These two peaks correspond to the benzylic methylenes in **49**. The reason for the separate peaks is that the molecule is asymmetric due to the alkyl pendant chain, and the benzylic methylene groups are not equivalent. There are no absorptions above 150 ppm, which further supports the conversion of the ester groups to primary benzylic alcohols.

Dialdehyde Synthesis

The initial method of oxidizing diol **49** to dialdehyde **50** involved the use of manganese dioxide (MnO_2) in THF. The reaction product was analyzed using ^{1}H NMR spectroscopy and it was discovered that there was incomplete conversion of diol **49** to the



49 **57** **50**

dialdehyde **50**. This can be seen in the ^{1}H NMR spectra (**Figure 1**) by the appearance of a singlet at 9.70 δ, corresponding to the monoaldehyde **57**, and two much smaller peaks of equal integration at 9.77 δ and 9.80 δ indicating a small amount of the dialdehyde **50**.

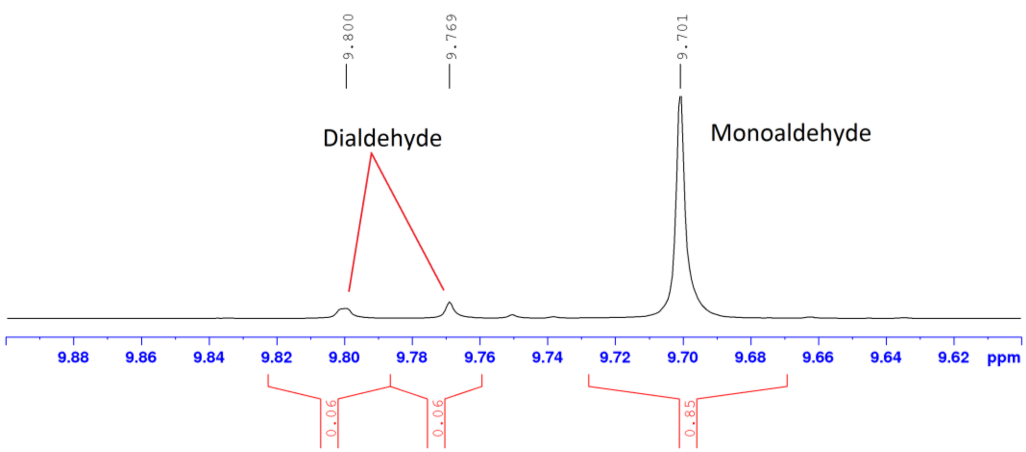


Figure 1. Expanded aldehyde region of the ^{1}H NMR spectrum of MnO_2 oxidation products **50** and **57**.

It was hypothesized that the steric hindrance of the pendant alkyl chain and the phenyl group prevent complete conversion to the dialdehyde (**Figure 2)**. This agrees with the observations of Cheek.[25]

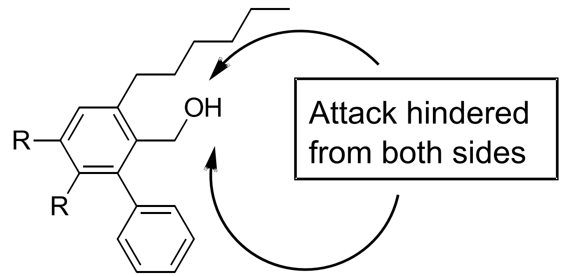
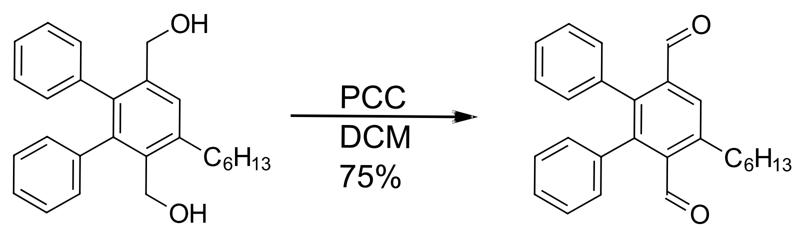


Figure 2. Oxidation Attack Steric Effects.

In order to fully oxidize **49** to **50,** the use of a stronger oxidizing agent was required. The oxidizing agent that was found to yield complete conversion of **49** to **50** was pyridinium chlorochromate (PCC).



49 **50**

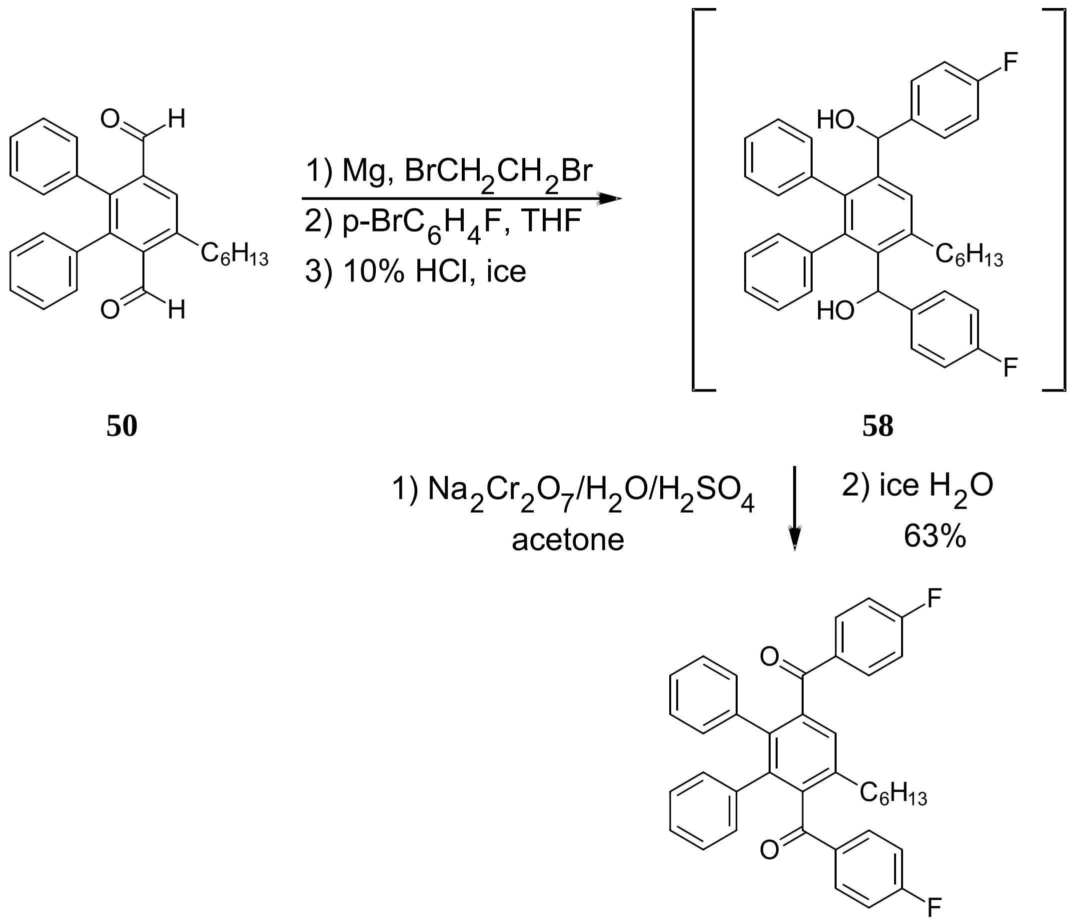
The identity of the dialdehyde compound was confirmed by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. The IR spectrum (**Figure 20**) of **50** exhibited a conjugated aldehyde carbonyl absorption at 1693 cm^{-1}. It was also noted that the alcohol stretching could no longer be observed. The aromatic C-H stretching absorptions were observed at wavenumbers greater than 3000 cm^{-1}, and the aliphatic C-H absorptions were observed at 2950-2850 cm^{-1}. The ^{1}H NMR spectrum (**Figure 21**) clearly exhibited aldehyde hydrogen absorptions at δ 9.77 and δ 9.80. The two distinct absorptions were expected due to the asymmetric molecule. The lone aromatic proton on the center phenyl ring could also be identified by an absorption at δ 7.95. This absorption is in the same general area for all three compounds, the diester **48**, the diol **49**, and the dialdehyde **50**, but is shifted further downfield based on the strength of electron-withdrawing group (EWG) that is adjacent to that proton on the central aromatic ring. The aldehyde group in **50** is the best EWG and **50** has an absorption at δ 7.95, next strongest is the ester group in **48** that gives rise to an absorption at δ 7.68, and finally the hydroxymethylgroup in **49** results in an absorption at δ 7.47. The ^{13}C NMR spectrum (**Figure 22**) showed carbonyl peaks at 192.34 ppm and 194.39 ppm. These peaks were confirmed as aldehyde peaks in the ^{13}C DEPT135 NMR spectra (**Figure 23**).

The Monomer, 5-Hexyl-2,3-diphenyl-1,4-bis(fluorobenzoyl)benzene

The bis(fluorobenzoyl) monomer **55** was synthesized from the dialdehyde **50** in a two-step process.

The first step involved a reaction of the Grignard reagent formed from *p*-bromofluorobenzene and magnesium in THF, with **50** to yield the diol intermediate **58**. As observed in the synthesis of **2** by Dancevic, the reaction gave a mixture of four stereoisomers by the generation of two new chiral centers. Purification of the mixture was abandoned and it was oxidized with Jones reagent, thus eliminating the chiral centers and the isomer purification problem as shown in step two..

The second step involved converting the two secondary benzylic alcohols into ketones. This was achieved through the use of a Jones oxidation of intermediate **58** in acetone to yield 5-hexyl-2,3-diphenyl-1,4-bis(fluorobenzoyl)benzene **55**. The product was purified by chromatography on silica utilizing ethyl acetate and hexanes (5% /95% v/v) as the eluent to achieve "polymer grade" monomer. The fractions containing monomer **55** were determined using thin layer chromatography. The desired fractions were combined, dried under reduced pressure, and recrystallized from aqueous acetone. The product was dried under vacuum at 70° for 12 hours.



55

Monomer **55** was characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. The IR spectrum of **55 (Figure 24)** exhibited conjugated aryl ketone absorption at 1670 cm^{-1}. The aromatic C-H stretching region showed an absorption at 3058 cm^{-1}, and the aliphatic C-H stretching region showed an absorption at 2927 cm^{-1}. The ^{1}H NMR spectrum (**Figure 7 and 25)** showed the disappearance of the aldehyde proton absorptions. The absorptions that were retained from **50** included all the aliphatic peaks from δ 2.8 – δ 0.80 and the lone aromatic proton on the central phenyl ring at δ 7.47. The spectrum also clearly showed the appearance of the fluorine-coupled aromatic proton absorptions associated with protons adjacent to the carbonyl. These protons experience an H-H ortho coupling of 8.8 Hz, and an H-F meta coupling of 5.4 Hz (**Figure 3)**. This causes each pair of protons to appear as a doublet of doublets, as can be seen in **Figure 4**. The two sets overlap making any additional small para coupling difficult to observe.

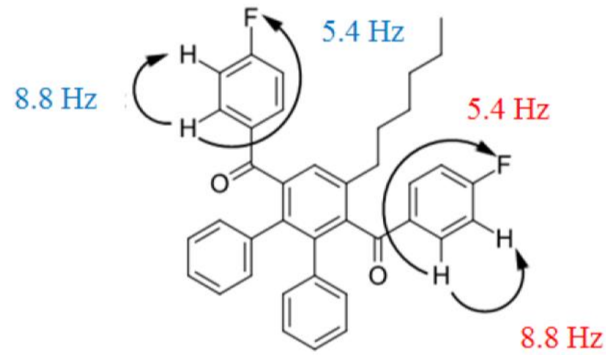


Figure 3. Aromatic H-H and H-F coupling in **55.**

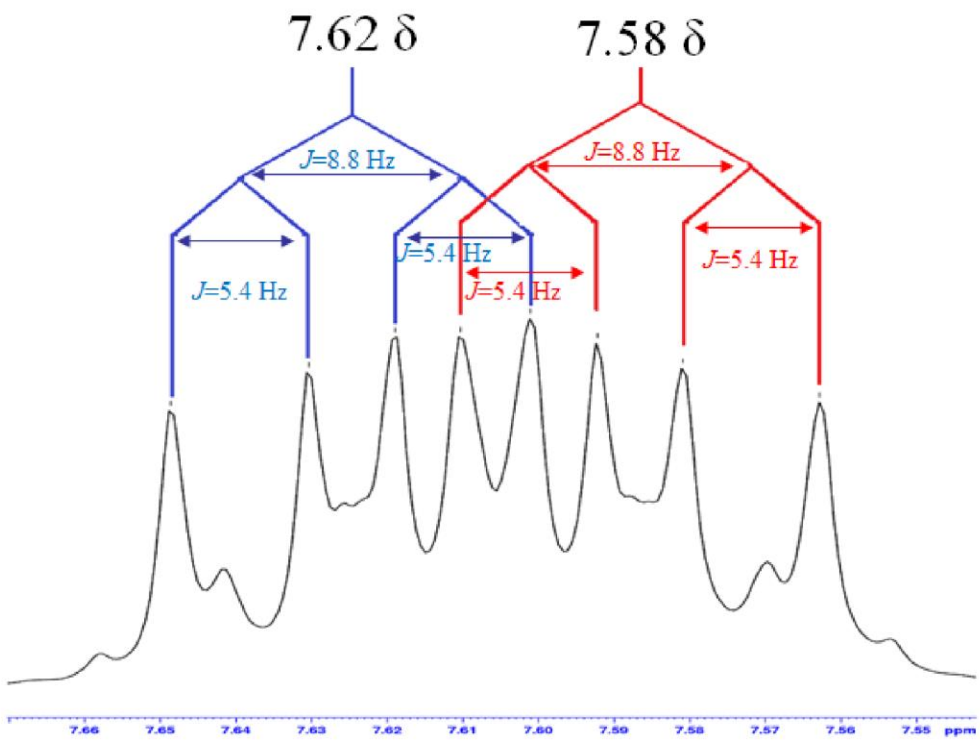


Figure 4. Expansion of aromatic H-F coupling in **55**.

The ^{13}C NMR spectrum (**Figure 26**) of monomer **55** clearly showed six aliphatic carbon absorptions, which corresponds to the six carbons on the alkyl pendant chain. With the introduction of a fluorine atom several of the aromatic carbon absorptions appeared as doublets. Each of the four unique carbons in the phenyl ring with an attached fluorine should exhibit this splitting. This is further complicated by the asymmetric nature of the ring, giving a pair of doublets for each unique carbon in both fluoro substituted rings.[3] The corresponding carbon atoms and the calculated and observed chemical shifts are given below in **Figure 5** and **Table 1).**

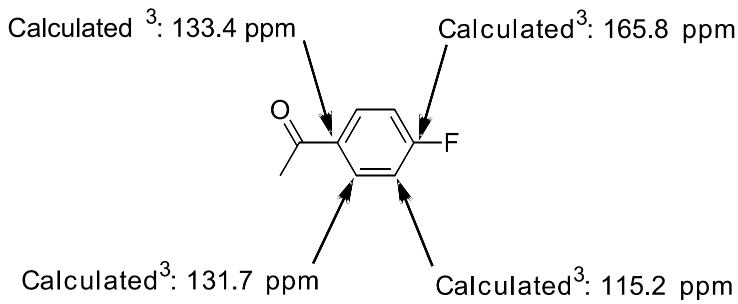
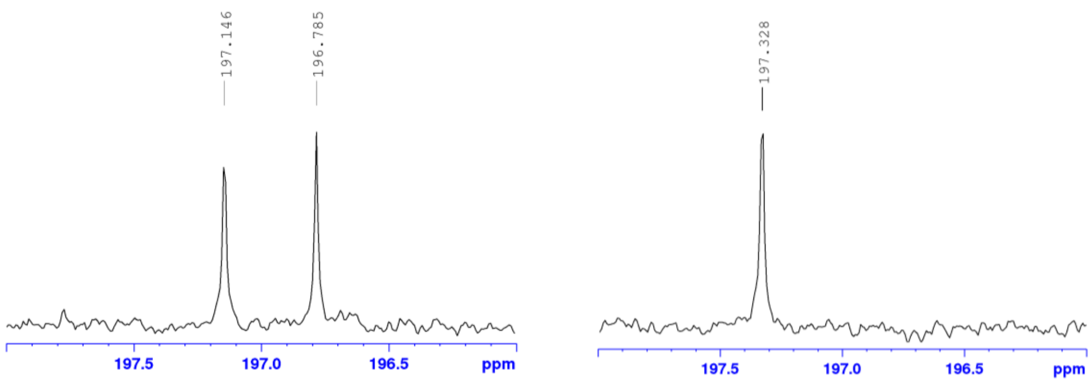


Figure 5. Calculated chemical shifts of carbons in phenyl rings with attached fluorines.

Table 1. Calculated and observed ^{13}C NMR absorptions for phenyl ring bearing F atoms.

Carbon Position relative to F atom	Calculated Chemical Shift[3] (ppm)	Observed Chemical Shift (ppm)
Ipso	165.8	165.62, 165.44
Ortho	115.2	115.32, 115.15
Meta	131.7	132.28, 131.88
Para	133.4	133.87;133.57

The other important absorption is the carbonyl peak at 197.33 ppm (**Figure 26)**. This was confirmed as a ketone absorption by inspection of the ^{13}C DEPT 135 NMR spectra (**Figure 27**) where this absorption is not present, identifying it as a quaternary carbon, in this case a ketone carbonyl carbon. Since the compound is asymmetric, it might be expected that the ketone absorption would appear as two separate peaks. While the peaks appear at the same chemical shift in $CDCl_3$, the spectrum run in acetone-d_6 indicates two ketone absorptions at 197.14 ppm and 196.79 ppm supporting the formation of both ketone functional groups. A comparison of the ketone absorption in the two different solvents is given below in **Figure 6**.



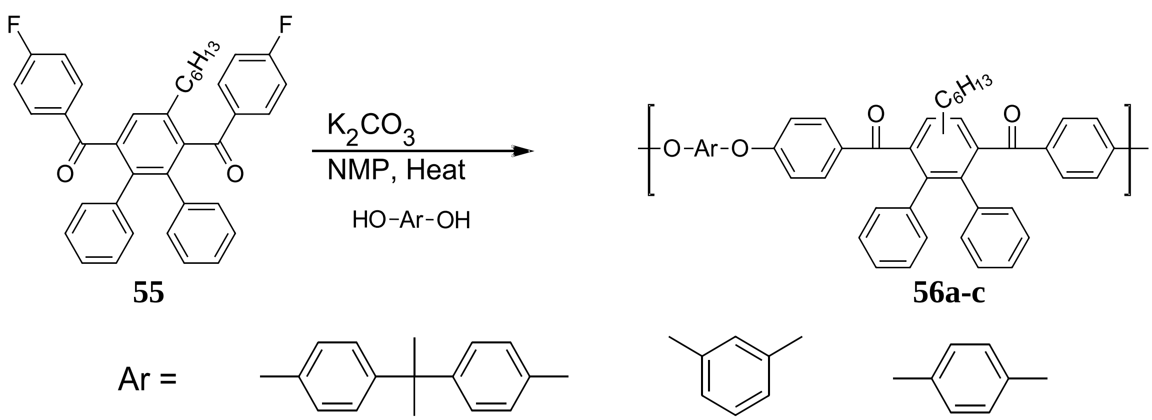
Acetone-d_6 CDCl$_3$

Figure 6. Expanded carbonyl region of ^{13}C NMR of compound **55.**

A composite comparison of the ^{1}H and ^{13}C NMR spectra of compounds **48**, **49**, **50**, and **55** is given in **Figures 7** and **8,** respectively.

Polymerizations

Polymerization reactions of the phenylated, alkyl-substituted bis(fluorobenzoyl) monomer, **55,** with a series of bisphenols were carried out in NMP using potassium carbonate as base.



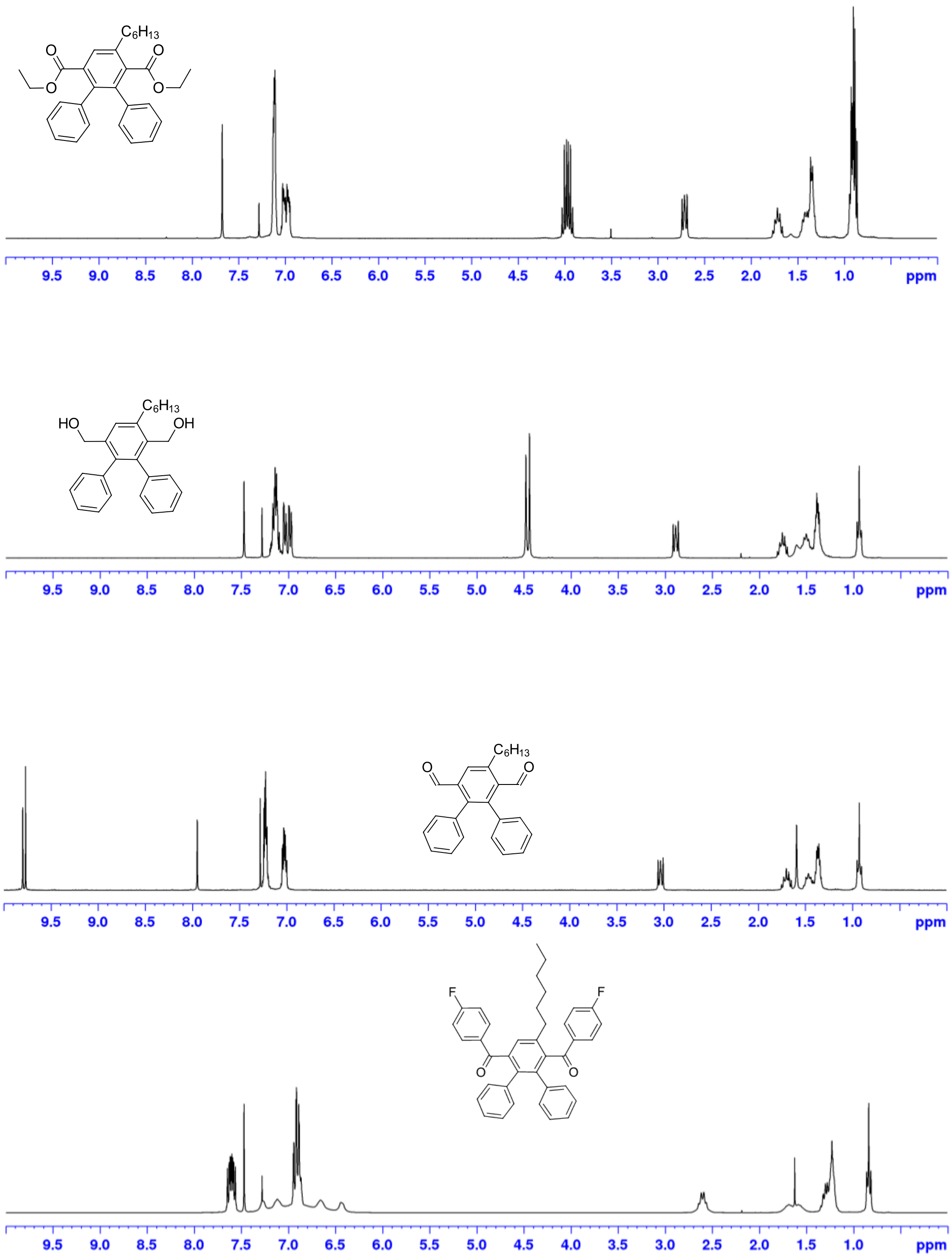


Figure 7. Comparison of the ^{1}H NMR spectra of compounds **48, 49, 50** and **55.**

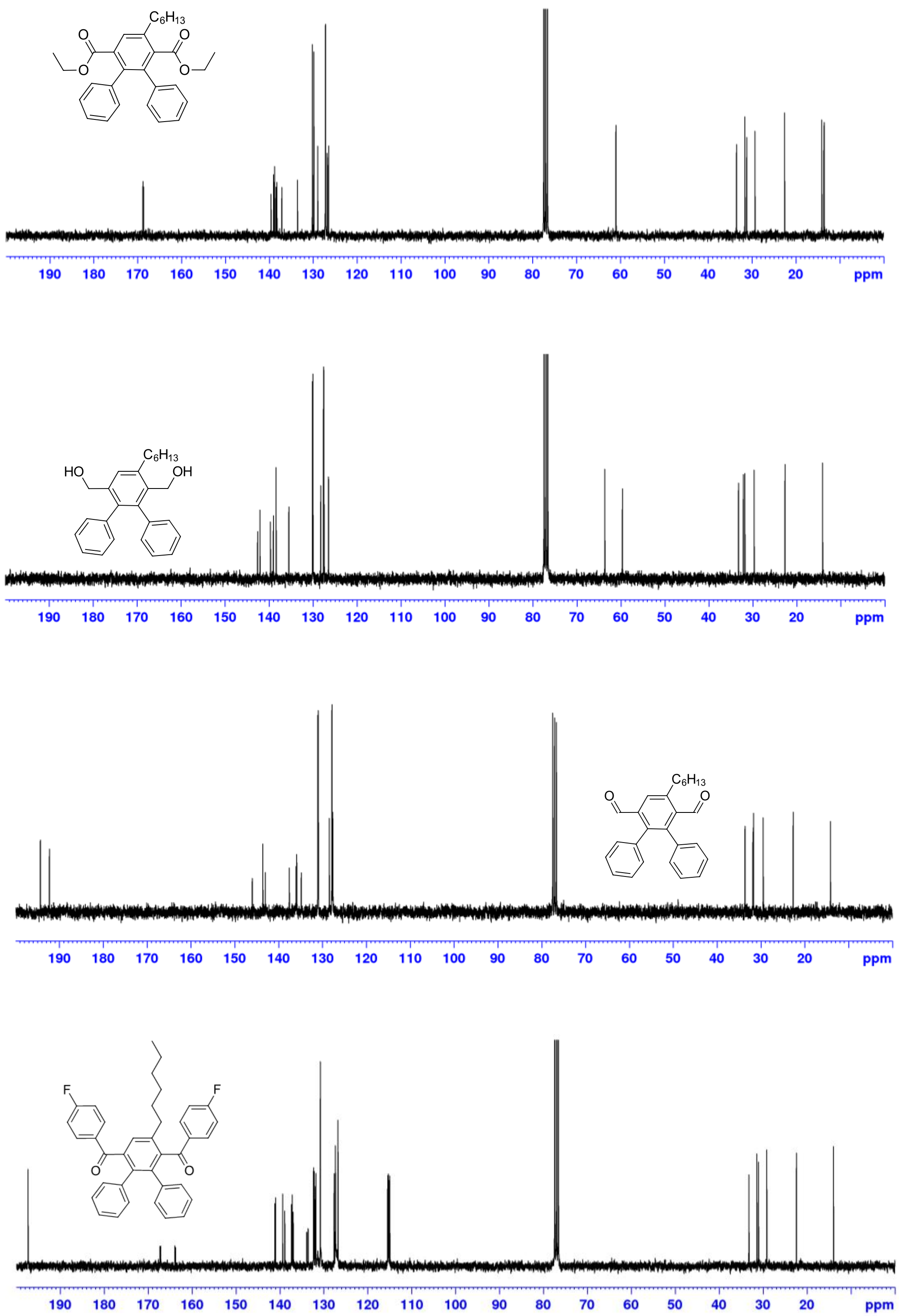


Figure 8. Comparison of the ^{13}C NMR spectra of compounds **48, 49, 50,** and **55**.

All polymers were obtained in yields greater than 40%. They also all showed high solubility in chlorinated solvents such as chloroform and dichloromethane and could be cast as free-standing, thin films. The films were transparent, flexible and did not crack or break when creased. Characterization of polymers **56a-c** was done by a combination of IR, ^{1}H and ^{13}C NMR spectroscopy, GPC, DSC, and TGA analysis.

The infrared spectra for all three new polymers (**Figure 28, 34** and **40)** were very similar and exhibited common absorptions. These are 1) the aromatic C-H stretching absorption at 3057 ± 5 cm^{-1}, 2) the aliphatic C-H stretching absorption at 2920 ± 6 cm^{-1}, 3) the carbonyl absorption (C=O) at 1663 ± 4 cm^{-1}, 4) the aromatic C=C absorption at 1590 ± 5 cm^{-1} and 5) the ether (C-O-C) linkage absorptions at 1223 ± 7 cm^{-1}, and 1159 ± 2 cm^{-1}.

The ^{1}H NMR spectra of the PEEKK polymers, (**Figure 29, 35** and **41)**, were similar in many ways to monomer **55**. The differences observed between the monomer **55** and polymer **56a** were 1) the appearance of a large singlet at δ 1.69 that integrates to six protons, and 2) the appearance of more aromatic proton integration at δ 7.20-7.25. These occur because of the incorporation of the bisphenol-A molecule into the polymer. Another difference is that the absorptions for the group of protons furthest downfield, due to protons adjacent to the carbonyl groups, collapse from eight peaks (two doublet of doublets), to four peaks (two doublets) (**Figure 10**). This is due to the displacement of the fluorine atom during the polymerization and provides evidence that the polymerization did occur. The ^{1}H spectra for polymer **56b** and **56c** show no difference from monomer **55** in the aliphatic region because monomers **53c** and **19** are completely aromatic. In the aromatic region, the resorcinol proton absorptions appear as a broad multiplet centered at δ 6.7. Hydroquinone proton absorptions appear in the aromatic region as a distinct pair of doublets centered at δ 6.8.

In the ^{13}C NMR spectra (**Figure 30, 36** and **42)** of polymers **56a-c**, the absorption pattern is once again very similar to that of the monomer **55.** In the BPA polymer, it can be seen that the absorptions for the two methyl groups from BPA overlap with one of the methylenes from the alkyl chain. This overlap can be clarified by examining the ^{13}C DEPT135 spectrum (**Figure 31)**. In the spectrum of the monomer **55,** all the aromatic carbons in the phenyl ring containing the fluorine exhibited doublet absorptions in the ^{13}C NMR spectra (**Figure 26)**. Once the fluorine has been displaced during the NAS polymerization, the carbon absorptions that previously appeared as doublets now appear as singlets. This is most easily seen in a comparison of polymer **56b** and monomer **55** as seen in **Figure 9**. The pair of doublets at 133.89/133.85 ppm and 133.59/133.55 ppm

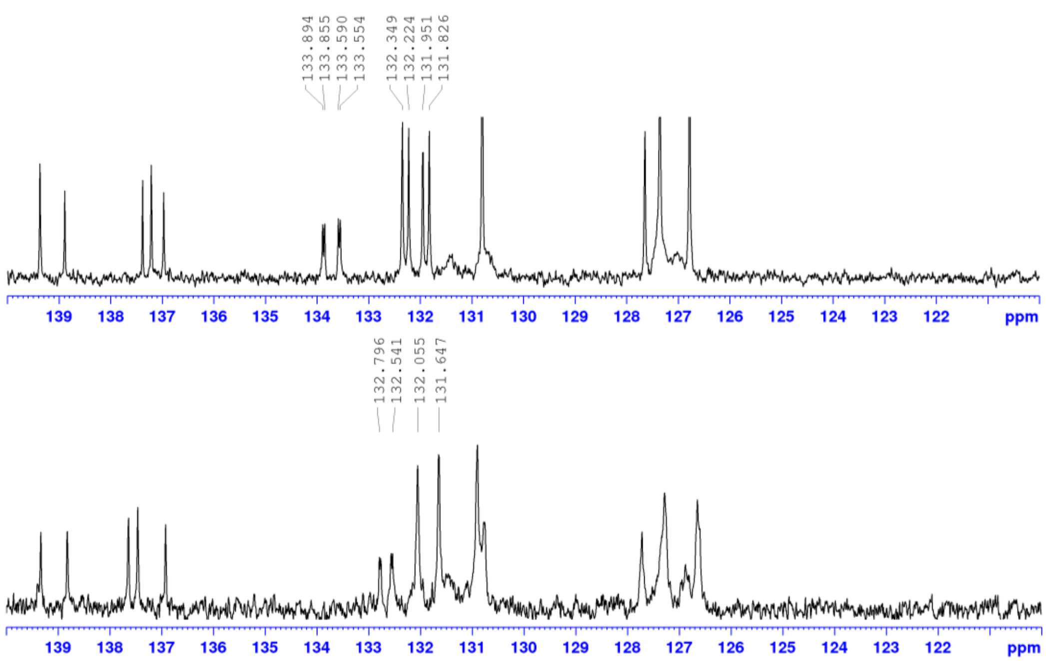


Figure 9. ^{13}C NMR comparison of monomer **55** (top) and polymer **56b** (bottom).

become two singlets at 132.80, and 132.54 ppm, respectively. Also, the pair of doublets at 132.35/132.22 ppm and 131.95/131.82 ppm become two singlets at 132.05 ppm and 131.64 ppm, respectively.

The ^{1}H and ^{13}C NMR spectra both suggest that the polymerization reaction was successful. The aromatic region in the ^{1}H NMR spectrum of **55** (**Figure 4**) has eight peaks, a pair of doublet of doublets. The same region in polymer **56a-c** has only four peaks, a pair of doublets **(Figure 10)**. This is due to the displacement of the fluorine atom during the polymerization. In the ^{13}C NMR spectra of polymers **56a-c**, the fluorine splitting seen in monomer **55** is no longer present. In monomer **55**, the fluorine ipso absorptions appear as two doublets with chemical shifts of 165.62 and 165.44 ppm ($^{1}J_{CF}$ = 255 Hz). In the same region in polymers **56a-c**, four absorptions appear but cannot be absorptions due to fluorine coupling. The absorptions are shifted significantly further upfield, and the distance between the peaks is either too great or too small to be fluorine coupling. Thus, both the ^{1}H and ^{13}C NMR spectra support the successful polymerization of monomer **55** with **14, 19,** and **53c**, respectively.

The incorporation of the corresponding parts of monomers **14** and **55** into polymer **56a** can be seen in **Figure 10** (^{1}H) and **Figure 11** (^{13}C). In **Figure 10** the aliphatic region of polymer **56a** clearly shows the four absorptions from the hexyl chain of **55.** It also clearly shows the singlet absorption of the two chemically equivalent methyl groups of **14.** In the aromatic region, the singlet from the proton ortho to the hexyl group in **55** is apparent in polymer **56a** as well as the doublet further downfield due to the aromatic para substitution in monomer **14.** In **Figure 11** the aliphatic region shows seven different absorptions. While it is expected that the aliphatic region would have eight absorptions, two from **14** and six from **55**, only seven are observed because two absorptions overlap at 31.0 ppm in **14** and **55**. Both of these peaks can be seen in the ^{13}C DEPT135 spectra of polymer **56a** (**Figure 31**).

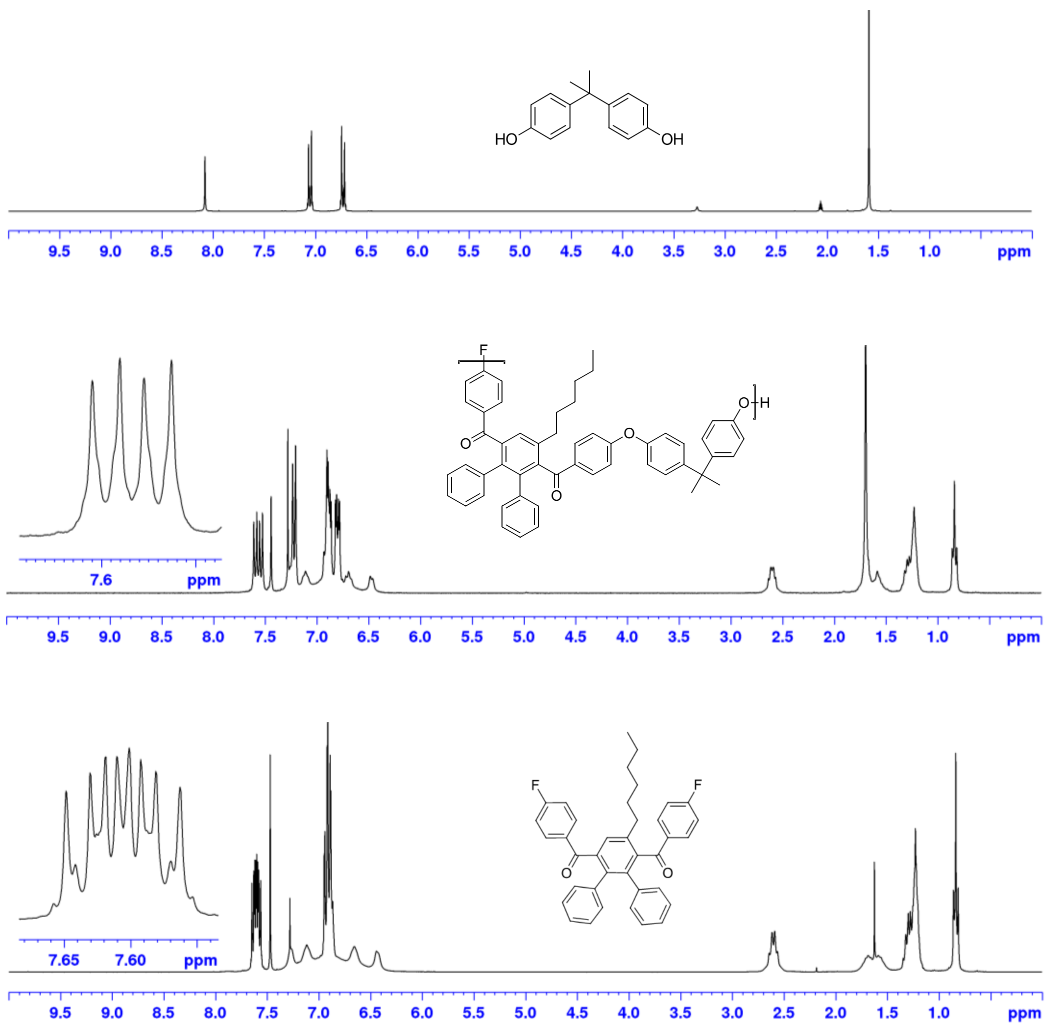


Figure 10. Comparison of ^{1}H NMR spectra of bisphenol-A **14**, polymer **56a**, and bis(fluorobenzoyl) monomer **55**.

The IR, ^{1}H NMR, and ^{13}C NMR spectral data for polymer **56b** can be seen in **Figures 34, 35, 36** and the IR, ^{1}H NMR, and ^{13}C NMR spectral data for polymer **56c** can be seen in **Figures 40, 41, 42**. These spectra are very similar to that of **56a.** The biggest difference in the ^{13}C NMR spectra is that polymers **56b** and **56c** only have six aliphatic

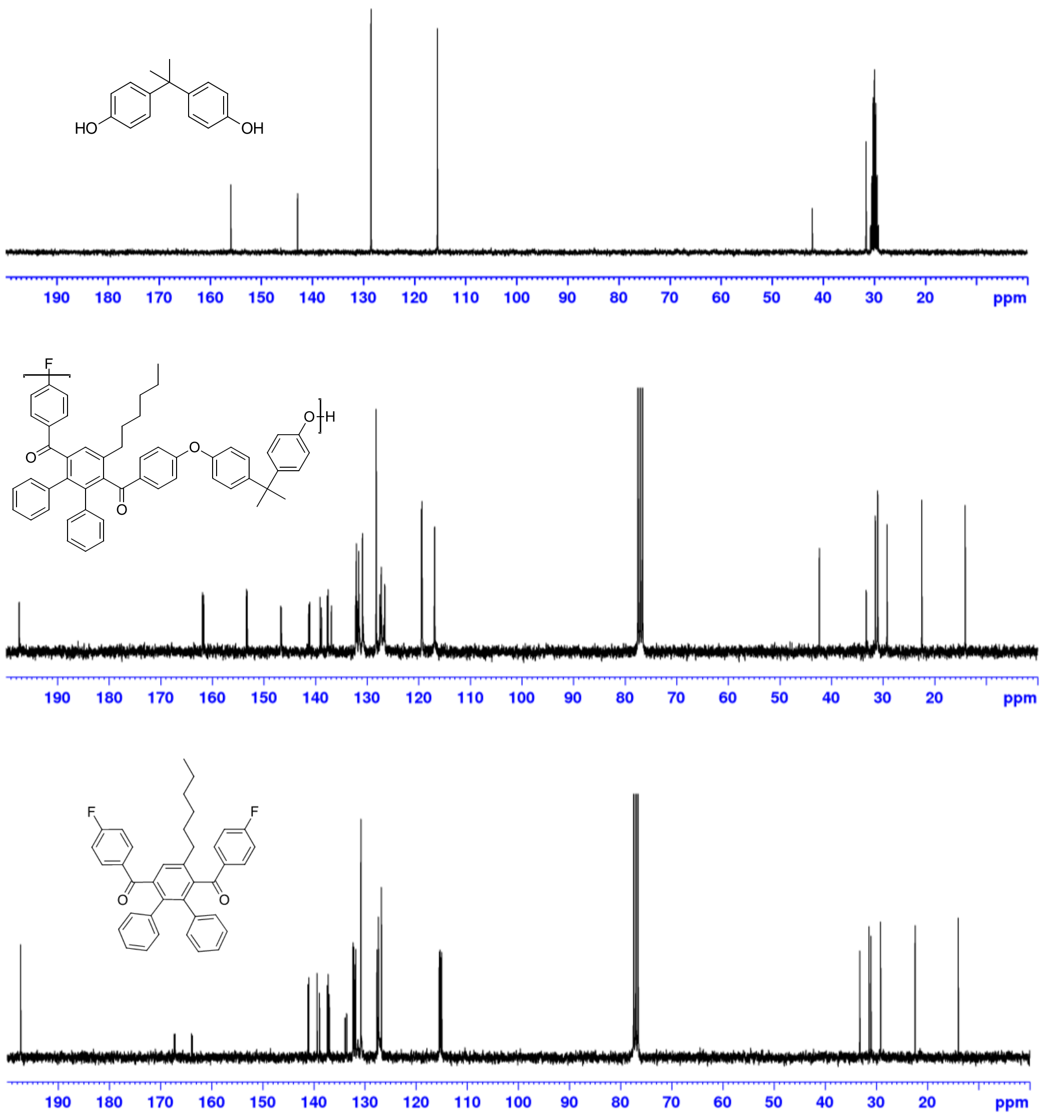


Figure 11. Comparison of ^{13}C NMR spectra of bisphenol-A **14**, polymer **56a**, and bis(fluorobenzoyl) monomer **55**.

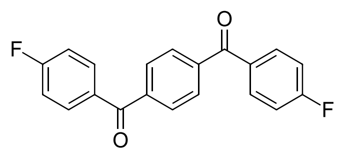
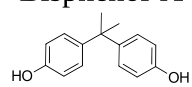
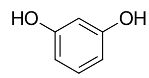
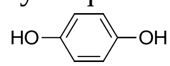
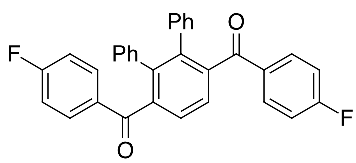
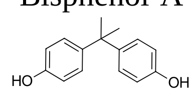
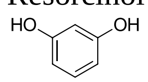
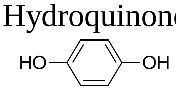
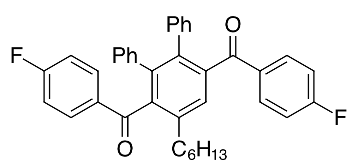
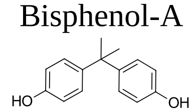
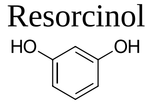
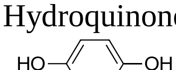
absorptions, as opposed to the seven of **56a.** The monomers **14** and **19** are completely aromatic and thus the ^{13}C NMR spectra of **56b** and **56c** have only aliphatic absorptions from the hexyl chain in monomer **55.** Polymers **56b** and **56c** differ from each other in the aromatic region of the ^{1}H NMR. This is due to the difference in substitution pattern of the bisphenol. In polymer **56b** the bisphenol is meta substituted, and in polymer **56c** the bisphenol is para substituted.

The molecular weight and thermal characteristics for polymers **56a-c** were determined by GPC, DSC, and TGA analysis. The analysis of polymers **56a-c** by GPC resulted in M_w values of 63,000 g/mol, 85,100 g/mol, 55,600 g/mol, respectively and M_n values of 35,700 g/mol, 34,800 g/mol, 28,000 g/mol, respectively with corresponding dispersity values of 1.8, 2.4, and 2.0. The calculated number of repeating units (n) for **56a-c** was calculated to be 46, 53, and 43, respectively. Compared to literature values for PEEK polymers **15** (M_n = 85-125,000 g/mol[13]) the molecular weights achieved for polymers **56a-c** are modest but well into the critical entanglement region for these systems. Even with their modest molecular weights, the polymers could be cast as thin, flexible, free-standing films from chloroform or dichloromethane.

The DSC analysis of polymers **56a-c** revealed glass transition temperatures (T_g) of 164° (**Figure 32)**, 148° (**Figure 38)**, and 162° (**Figure 44)**, respectively. A composite DSC trace is shown in **Figure 46**. Through TGA analysis, polymers **56a-c** exhibited 5% weight loss under nitrogen ($T_{d5\%}$) of 460° (**Figure 33)**, 448° (**Figure 39)**, 458° (**Figure 45)**, respectively. A composite DSC trace is shown in **Figure 47**.

A comparison of various PEEKK polymers representing the phenylated and alkyl substituted monomer, the phenylated monomer, and the unsubstituted monomer is given in **Table 2.**[3,13] From the data it can be seen that while the addition of the phenyl rings to polymers **54a-e** made the polymers more soluble it also increased the glass transition temperatures significantly, 38° for the BPA derivative and 25° for the hydroquinone derivative. This is not surprising as the addition of bulky side groups will often increase the glass transition temperature. This is because the bulky side groups inhibit the rotation

Table 2. Physical data for polymers **15, 54a, 54e, 54d** and **56a, 56b, 56c**.

Difluoro Monomer	**Bisphenol**	**M_n (g/mol)**	**M_w (g/mol)**	**T_g (°C)**	**$T_{d5\%}$ (°C)**
 **13**	Bisphenol-A  (**15a**)	95,000	161,500	160	450
	Resorcinol 	-	-	-	-
	Hydroquinone  (**15b**)	32,800	61,500	154	-
 **2**	Bisphenol-A  (**54a**)	8,700	20,700	198°	496°
	Resorcinol  (**54e**)	5,100	7,900	171°	521°
	Hydroquinone  (**54d**)	4,800	9,300	179°	532°
 **55**	Bisphenol-A  (**56a**)	35,700	63,000	164°	460°
	Resorcinol  (**56b**)	34,800	85,100	148°	448°
	Hydroquinone  (**56c**)	28,000	55,600	162°	458°

of the molecule and thus require more energy before the polymer chains can slide past one another as is characteristic of the glass transition region. It can also be seen in the data from polymers **56a-c** that the alkyl chain effectively lowered the glass transition temperature compared to polymers **54a-e**. The reason that the alkyl chain lowers the glass transition temperature so effectively is that the chain increases the free volume of the polymer, which keeps the polymer chains from packing close together. Since there is more space between the polymer chains it requires less energy before the chains can slide past one another. It can also be seen that the polymers **56a-c** are less thermally stable. This can be accounted for by the addition of the thermally vulnerable aliphatic substituents. Since polymers **15** and **54c-e** are completely aromatic it is not surprising that they exhibit the highest thermal stability. This would also explain that as more aliphatic character is introduced in the polymer, the lower the thermal decomposition temperature.

CONCLUSIONS

The monomer, 5-hexyl-2,3-diphenyl-1,4-bis(fluorobenzoyl)benzene **55,** can be prepared using a four-step process in ?% yield in spite of using a final chromatographic purification. A general sequence of steps starting with 2,5-bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone **40** and involving, sequentially, a Diels-Alder cycloaddition, a diester reduction to a diol, oxidation of the diol to a dialdehyde, addition of a fluorinated aromatic Grignard to the dialdehyde and finally a Jones oxidation provided the monomer.

The sequence appears to be easily modifiable to allow a variety of substituents to be present in the phenyl pendants or as part of the hexyl chain. These might include azo compounds, stilbenes and acid/base active materials.

Polymerization of monomer **55** with bisphenol-A **14**, resorcinol **53c**, and hydroquinone **19**, by a typical NAS polymerization in a Q-tube™ without azeotropic distillation of water gave amorphous polymers **56a-c** of moderate molecular weight (M_w/M_n of 63,000 g/mol/35,700 g/mol with Đ = 1.8, 85,100 g/mol/34,800 g/mol with Đ = 2.4 and 55,600 g/mol/28,000 g/mol with Đ = 2.0, respectively) that were highly soluble in chlorinated solvents, thermally stable ($T_{d5\%}$ of 460°, 448°, 458°, respectively), and formed free-standing, thin, transparent films. Thermal analysis revealed T_gs of 164° 148°, 162°, respectively.

The goal of controlling and correlating T_g, $T_{d5\%}$ and solubility with added pendent phenyl and alkyl substituents was achieved.

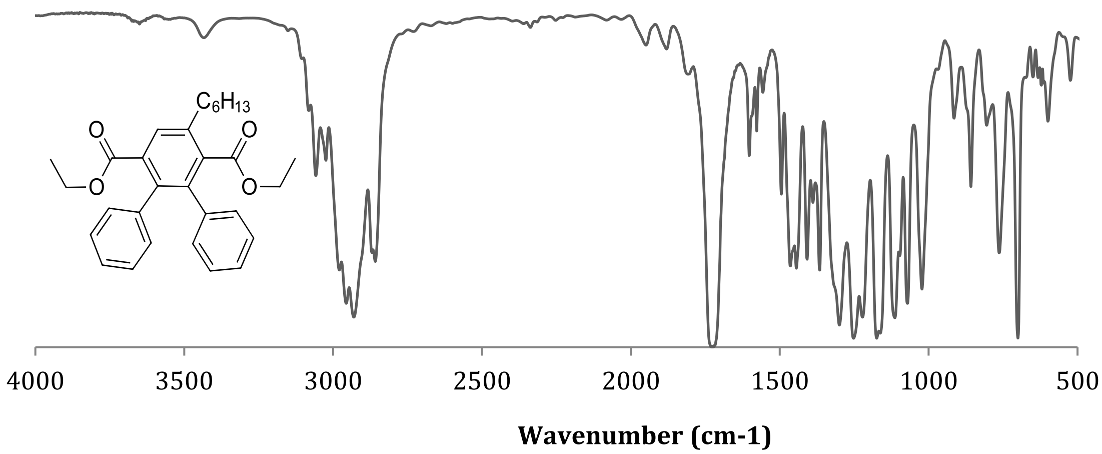


Figure 12. IR spectrum (NaCl) of diester **48**.

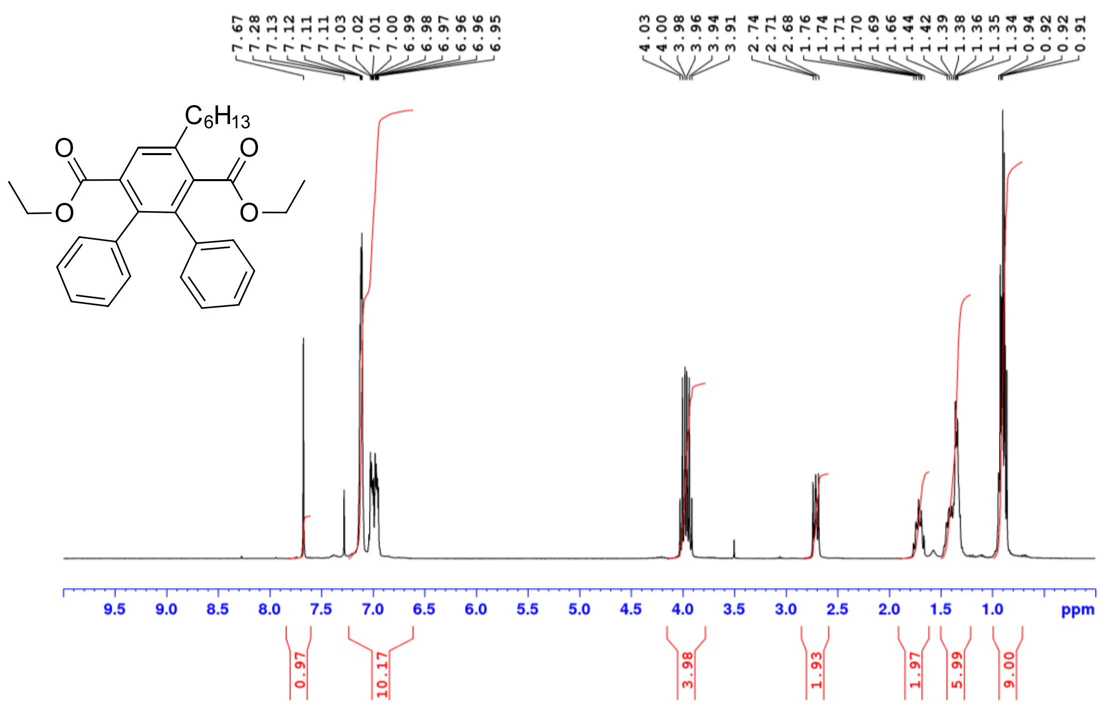


Figure 13. [1]H NMR spectrum (300 MHz, $CDCl_3$) of diester **48**.

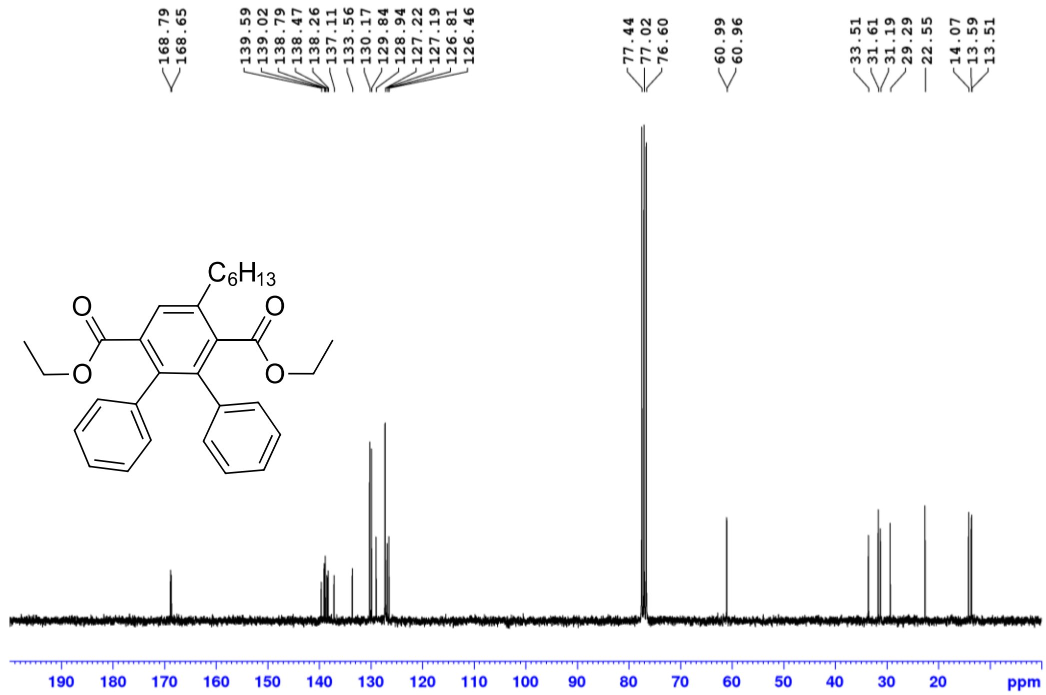


Figure 14. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of diester **48**.

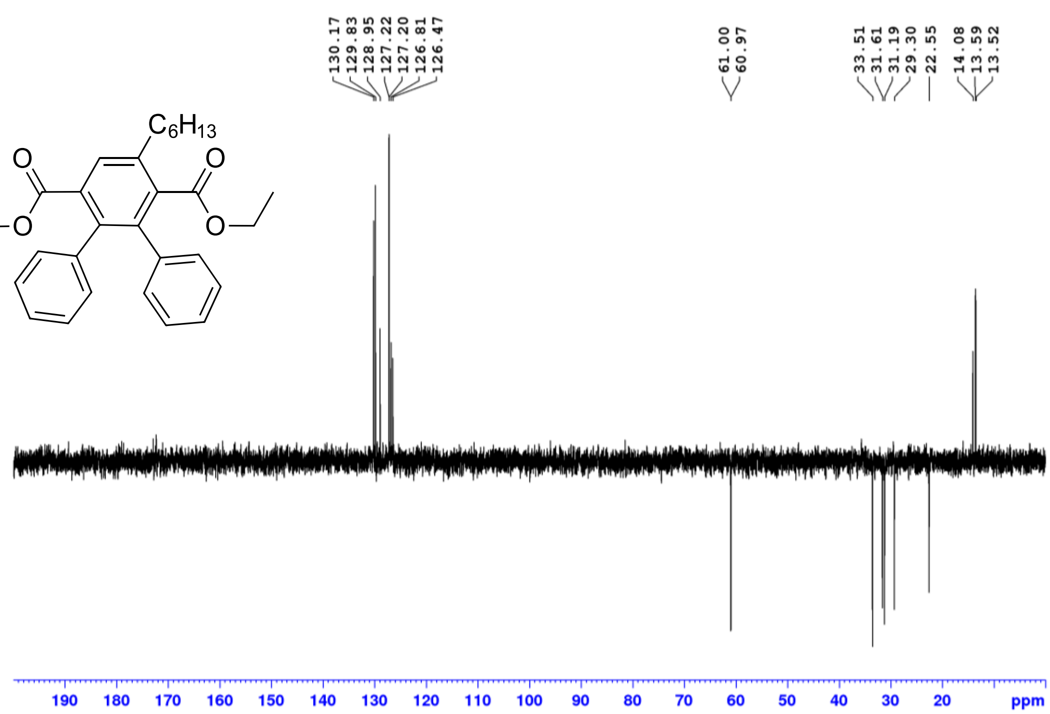


Figure 15. ^{13}C DEPT135 NMR spectrum (75 MHz, $CDCl_3$) of diester **48**.

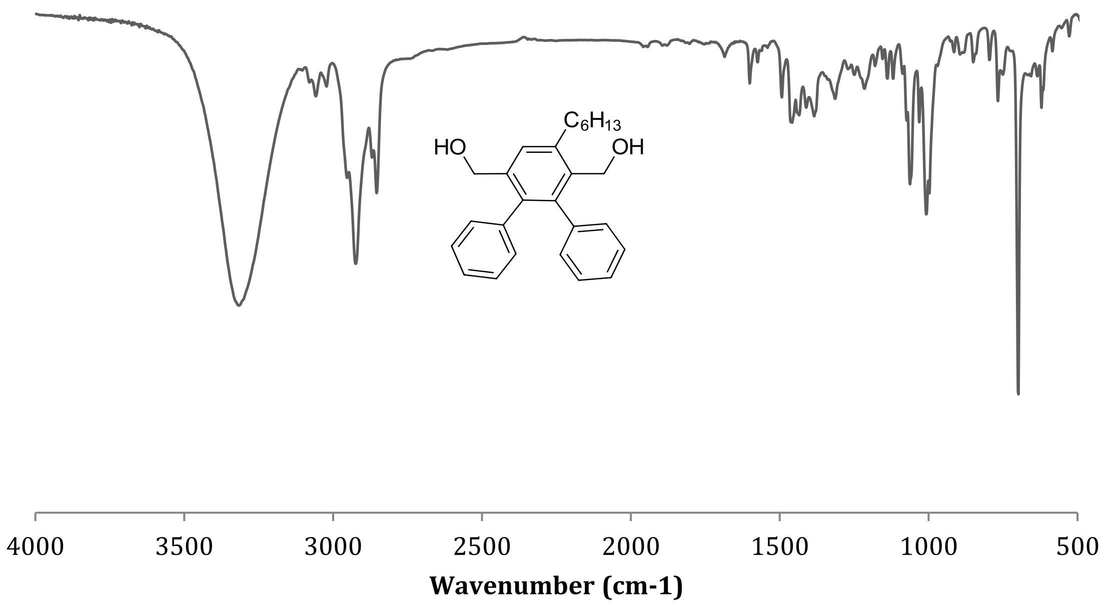


Figure 16. IR spectrum (NaCl) of diol **49**.

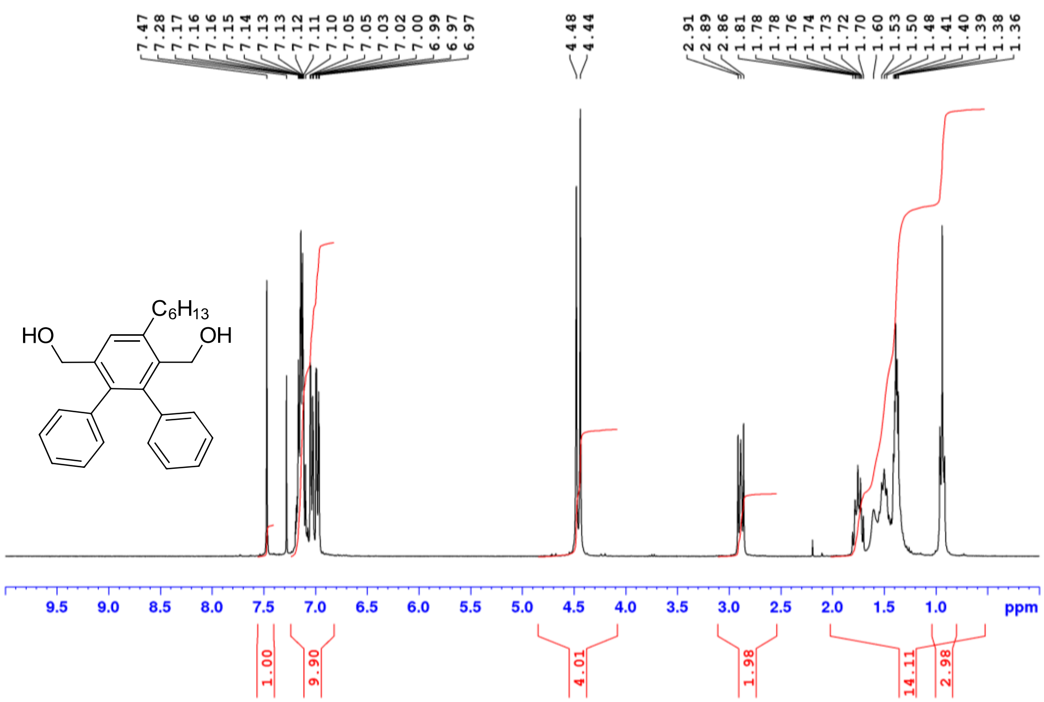


Figure 17. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of diol **49**.

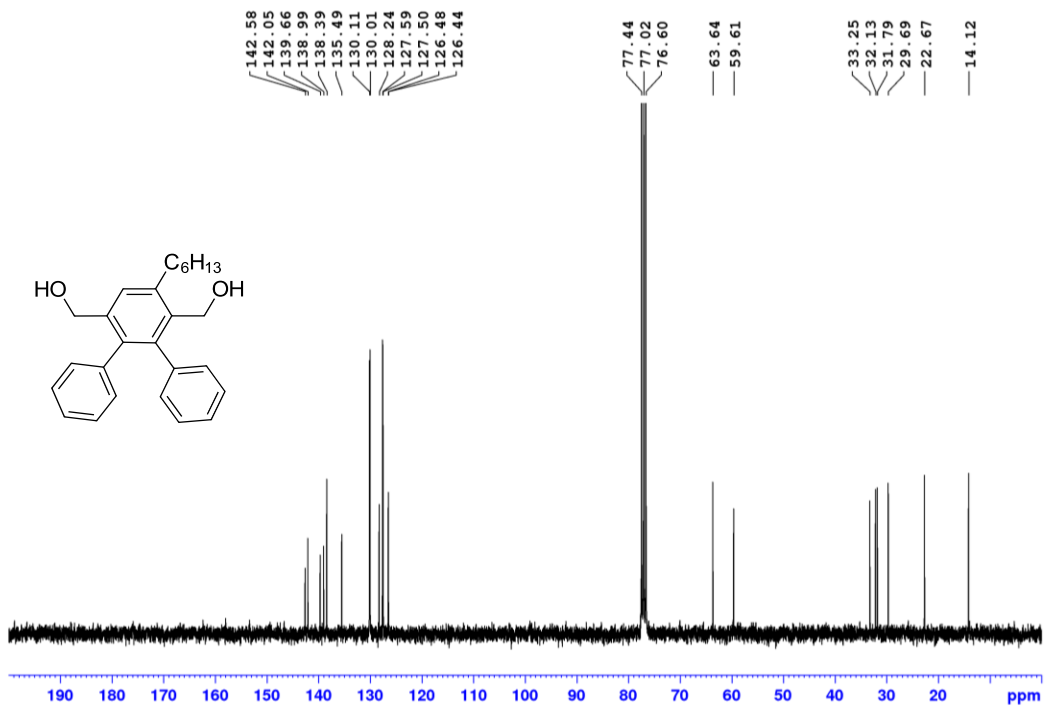


Figure 18. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of diol **49**.

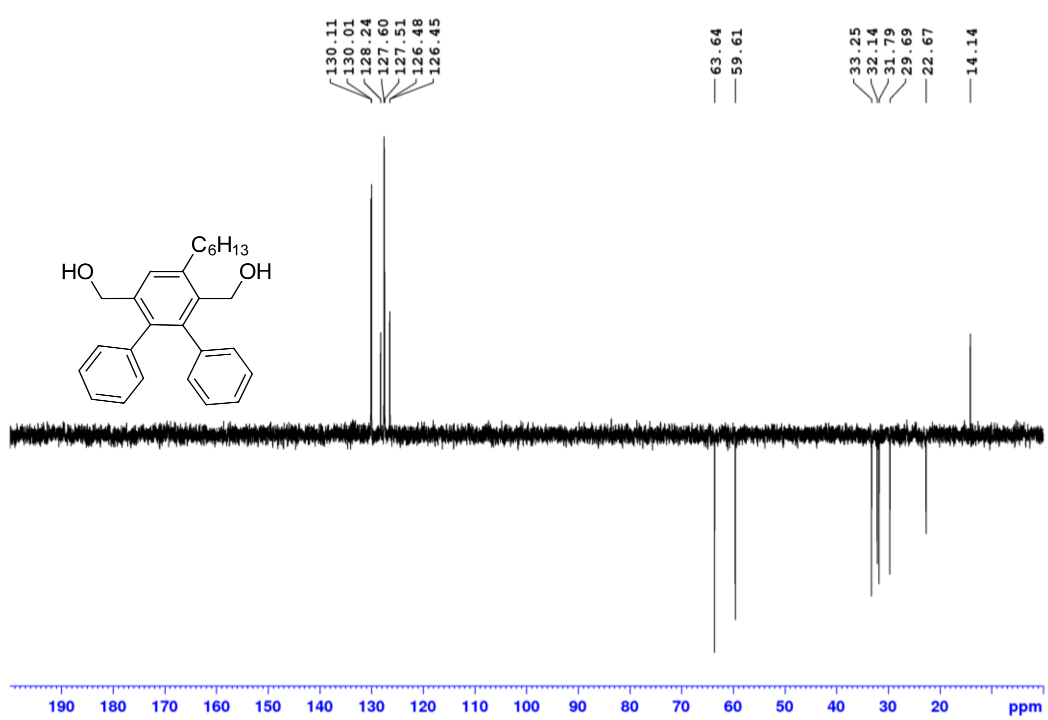


Figure 19. ^{13}C DEPT135 NMR spectrum (75MHz, $CDCl_3$) of diol **49**.

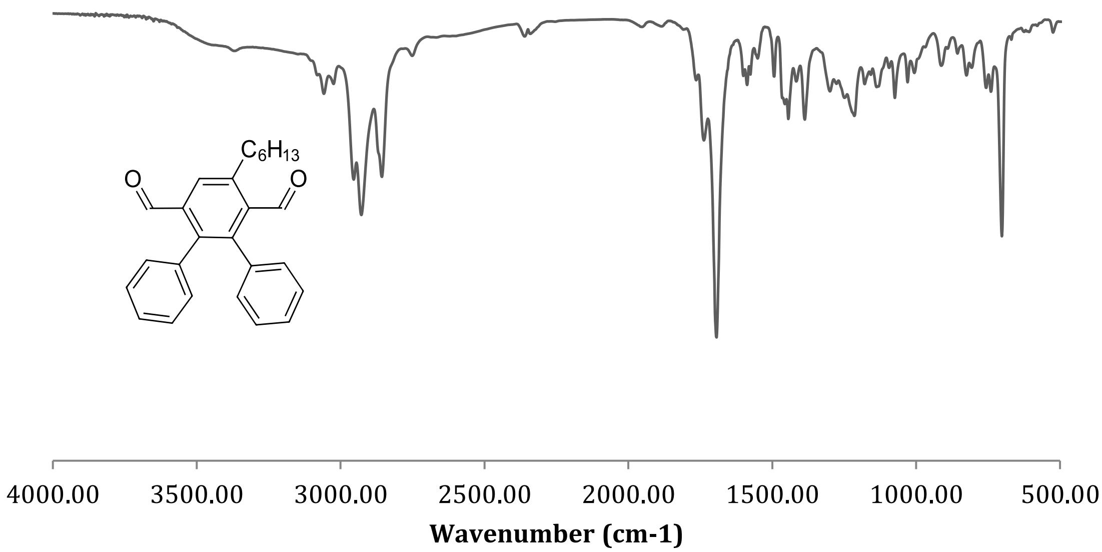


Figure 20. IR spectrum (NaCl) of dialdehyde **50**.

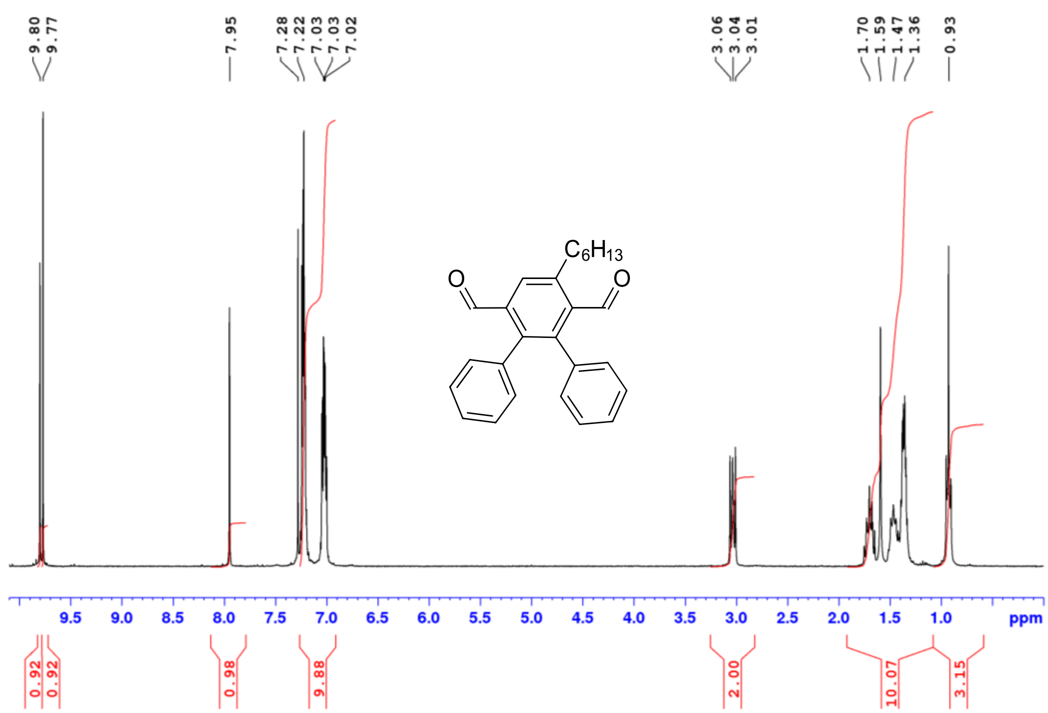


Figure 21. [1]H NMR spectrum (300 MHz, $CDCl_3$) of dialdehyde **50**.

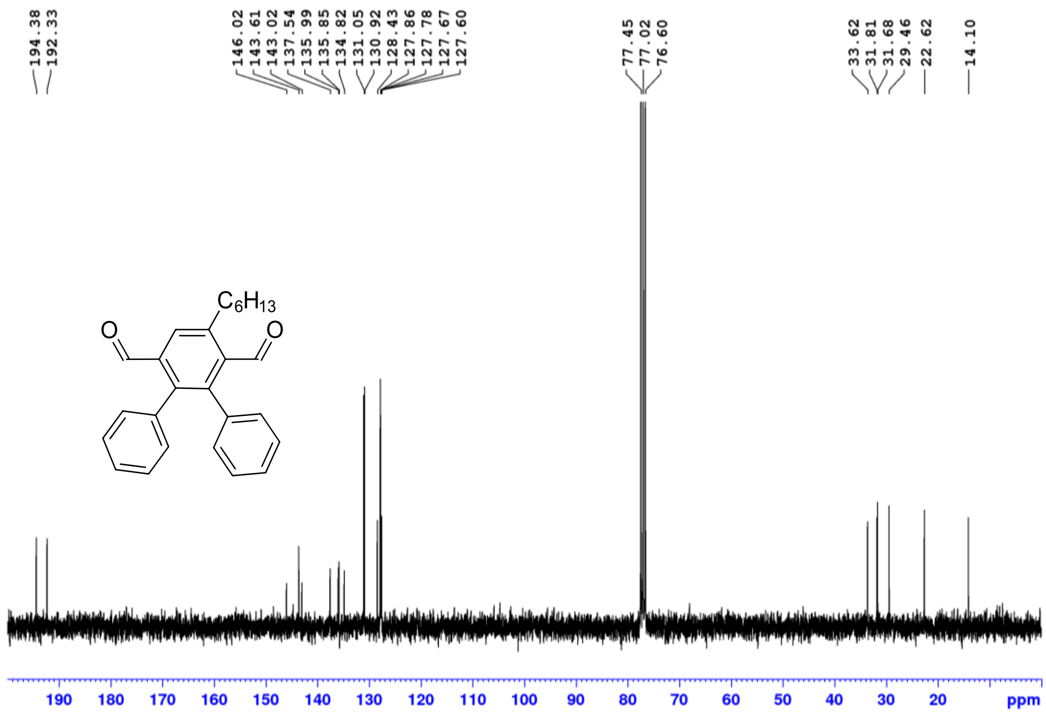


Figure 22. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of dialdehyde **50**.

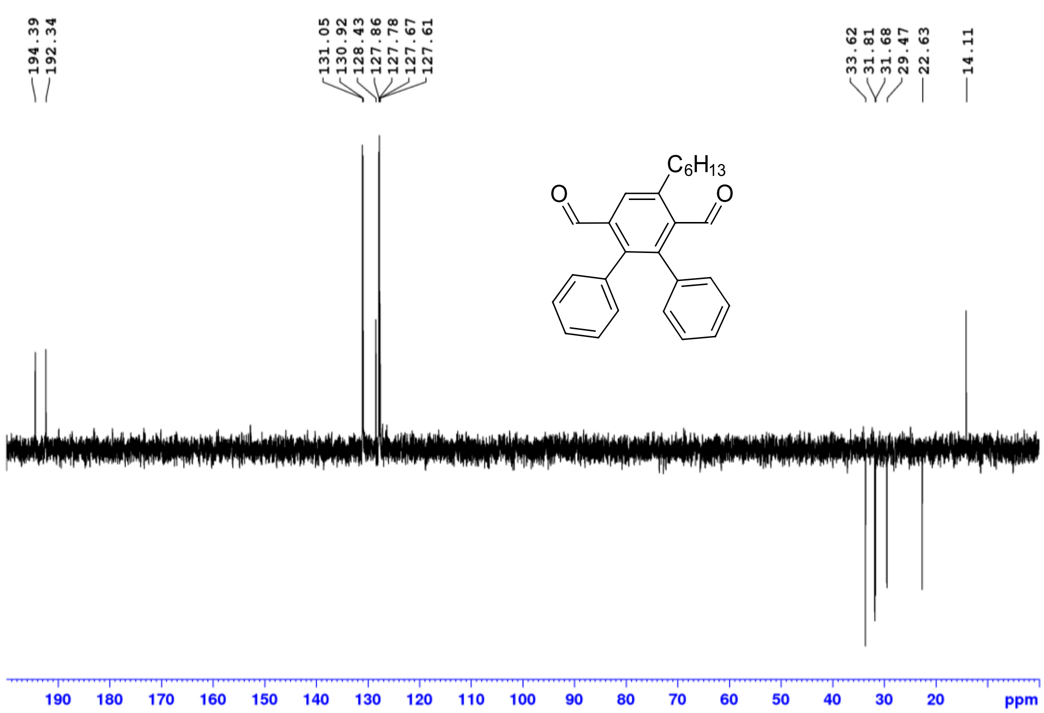


Figure 23. ^{13}C DEPT135 NMR spectrum (75 MHz, $CDCl_3$) of dialdehyde **50**.

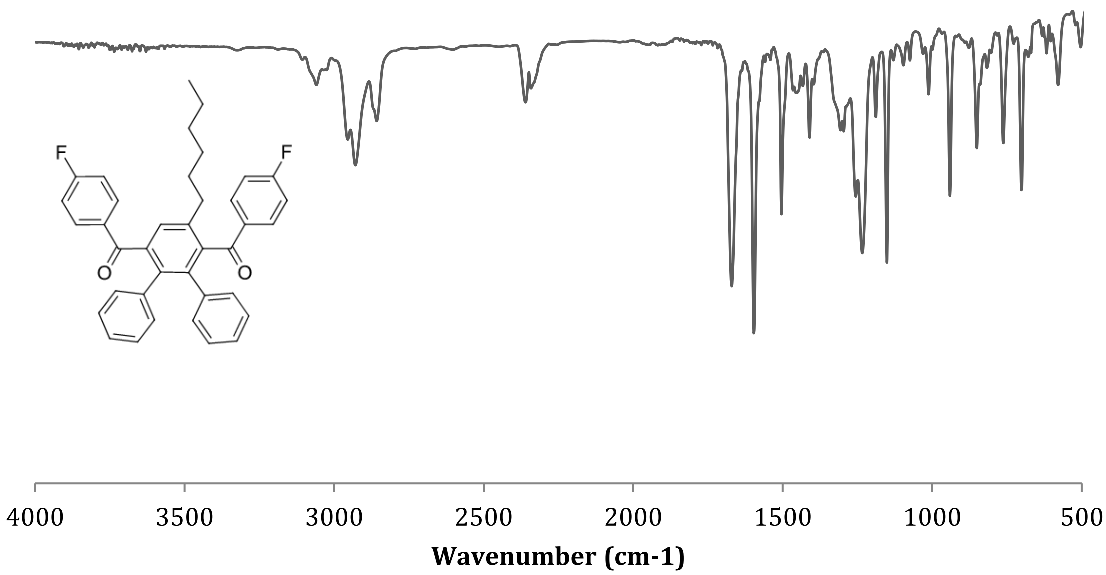


Figure 24. IR spectrum (NaCl) of bis(fluorobenzoyl) monomer **55**.

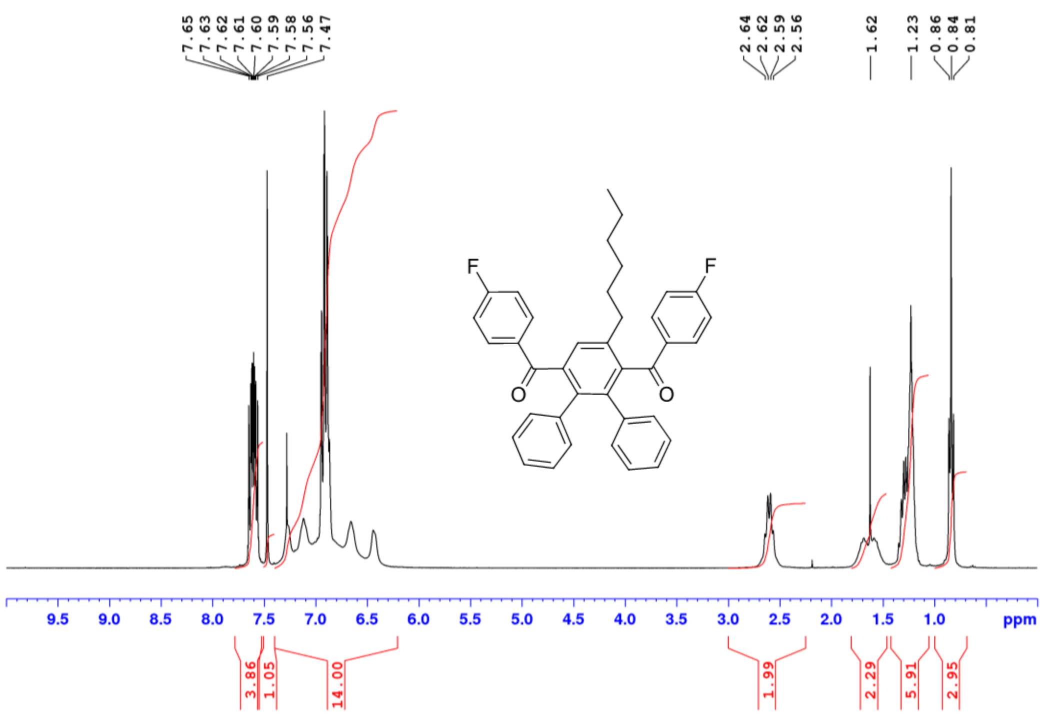


Figure 25. [1]H NMR spectrum (300 MHz, $CDCl_3$) of bis(fluorobenzoyl) monomer **55**.

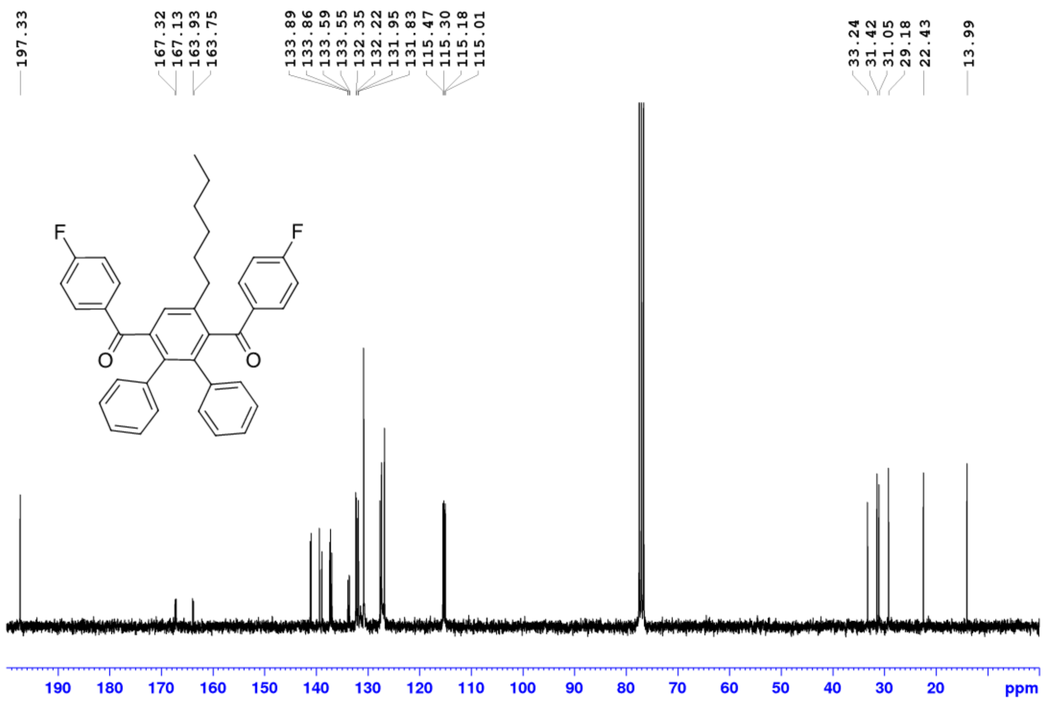


Figure 26. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of bis(fluorobenzoyl) monomer **55**.

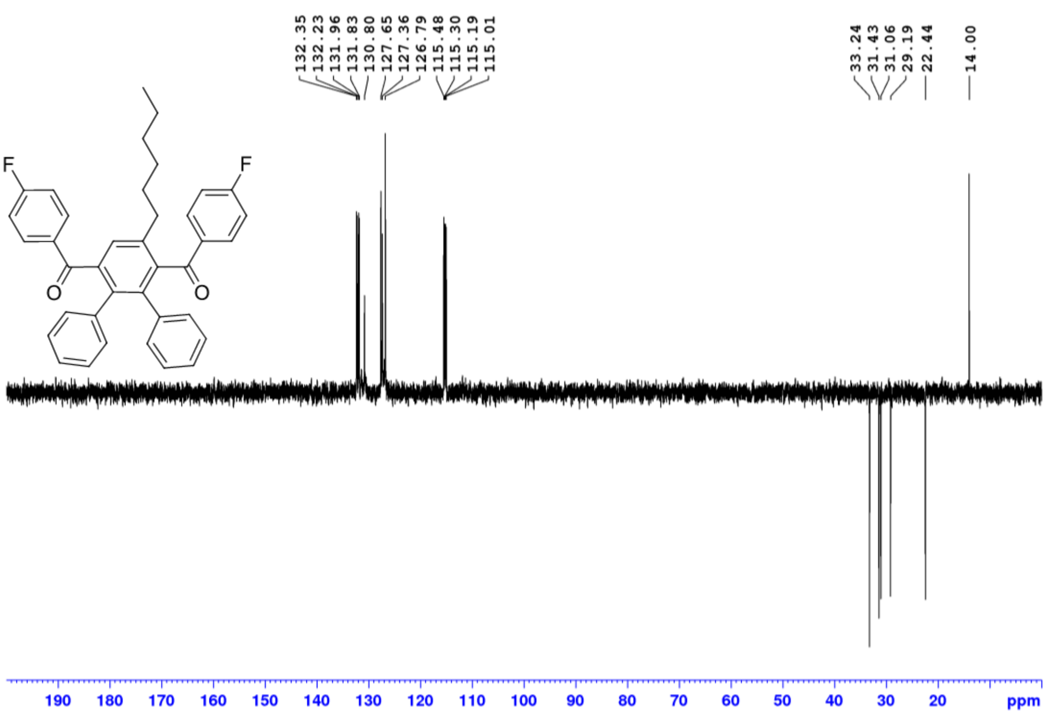


Figure 27. ^{13}C DEPT135 NMR spectrum (75 MHz, $CDCl_3$) of bis(fluorobenzoyl) monomer **55**.

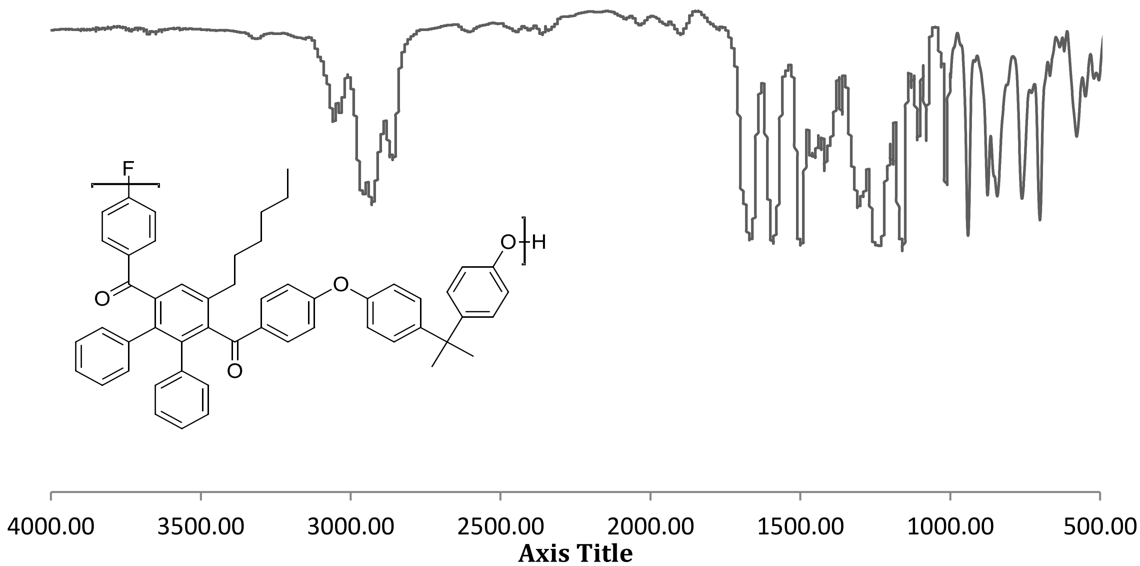


Figure 28. IR spectrum (NaCl) of polymer **56a**.

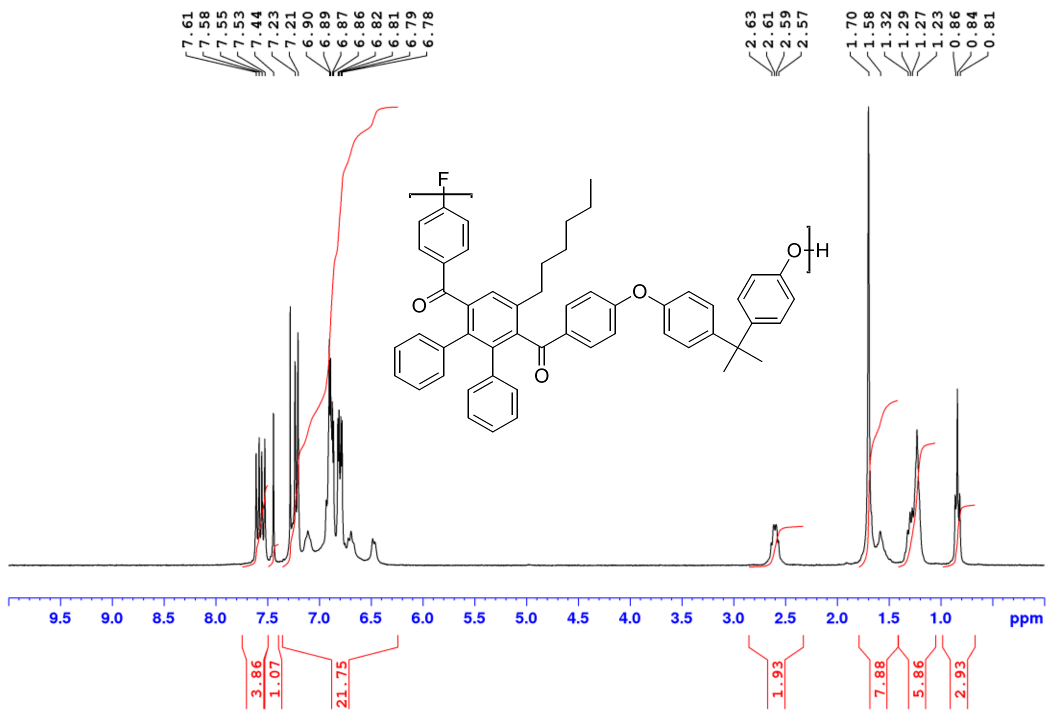


Figure 29. [1]H NMR spectrum (300 MHz, $CDCl_3$) of polymer **56a**.

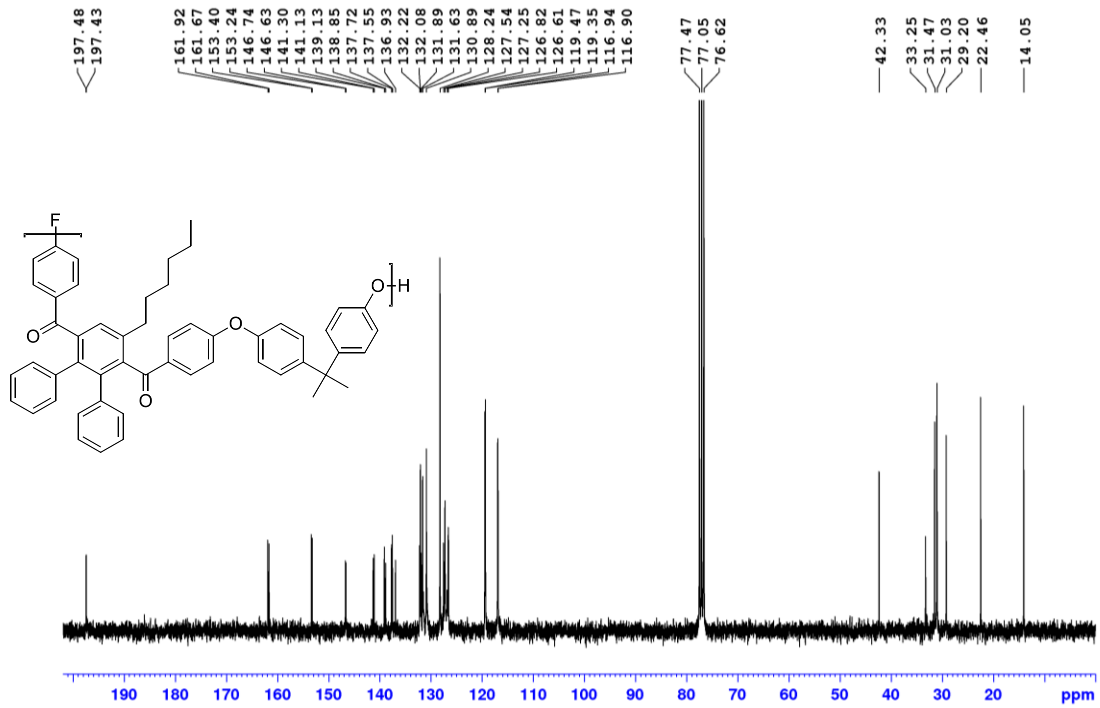


Figure 30. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of polymer **56a**.

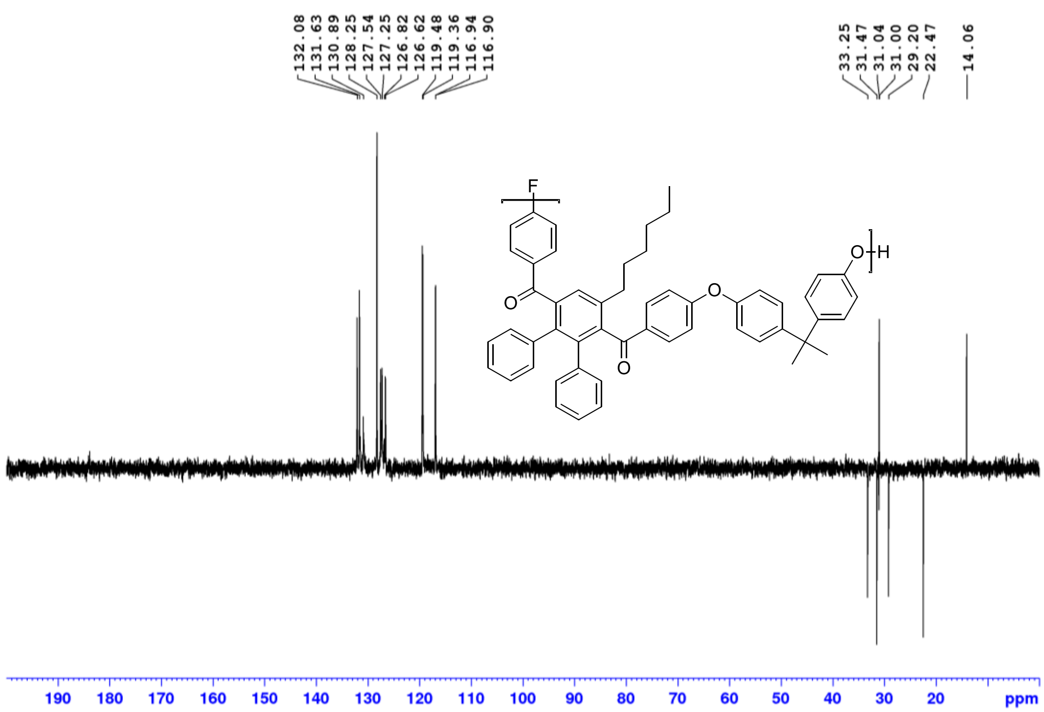


Figure 31. ^{13}C DEPT135 NMR spectrum (75 MHz, $CDCl_3$) of polymer **56a**.

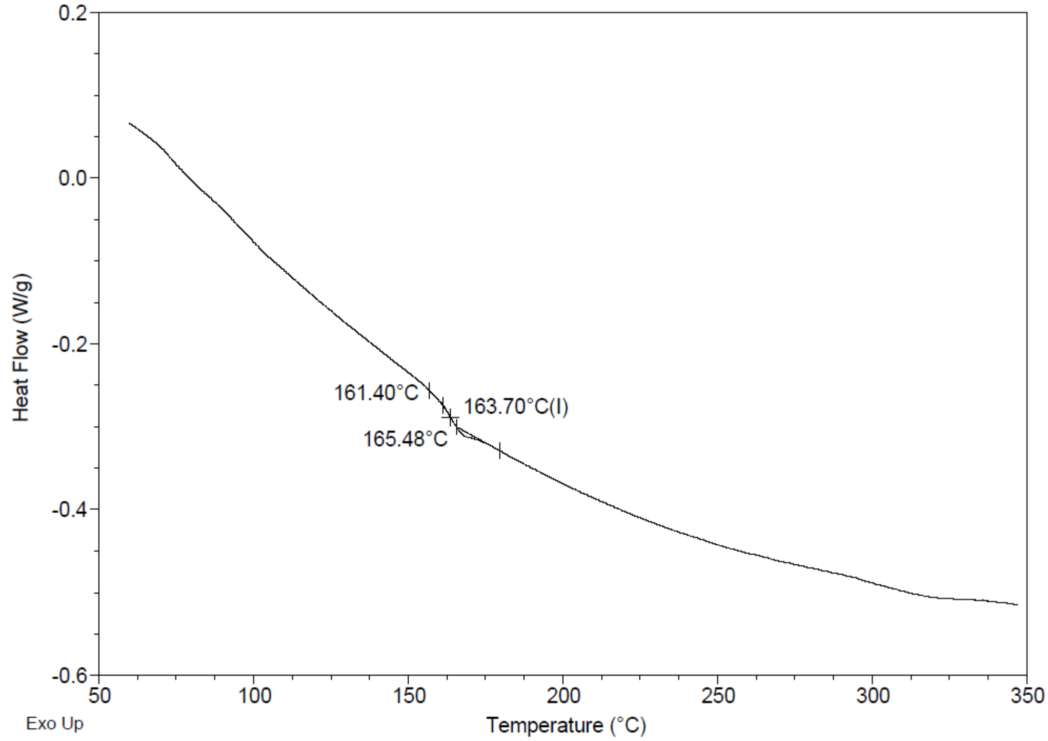


Figure 32. DSC spectrum of polymer **56a**.

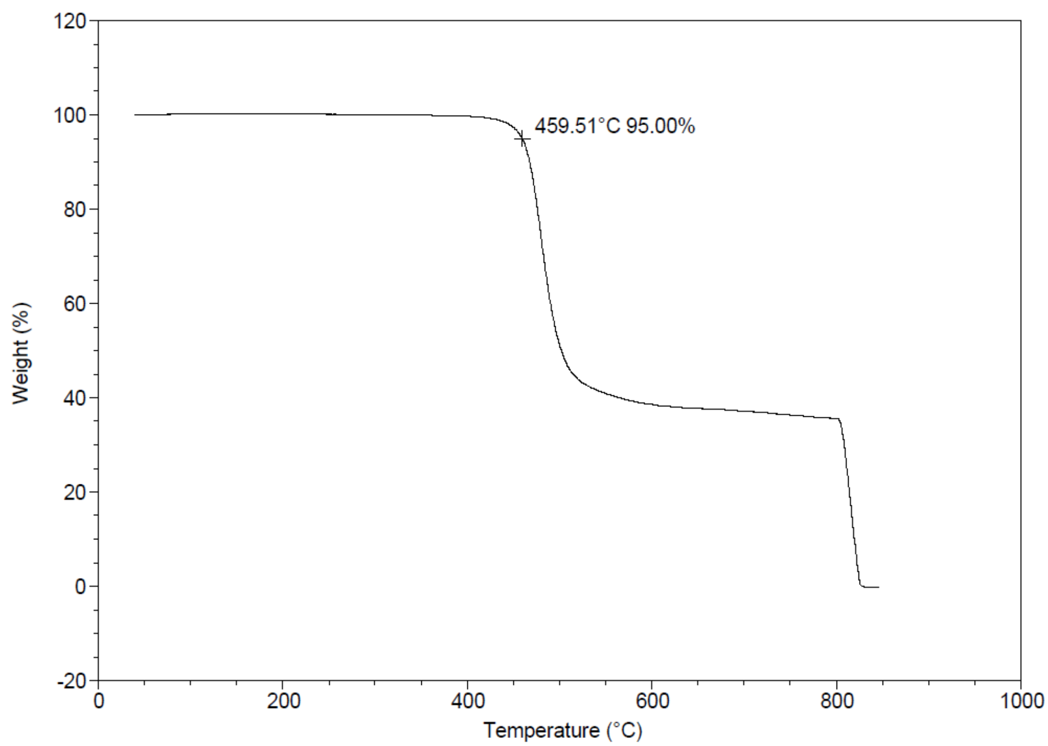


Figure 33. TGA spectrum (nitrogen) of polymer **56a**.

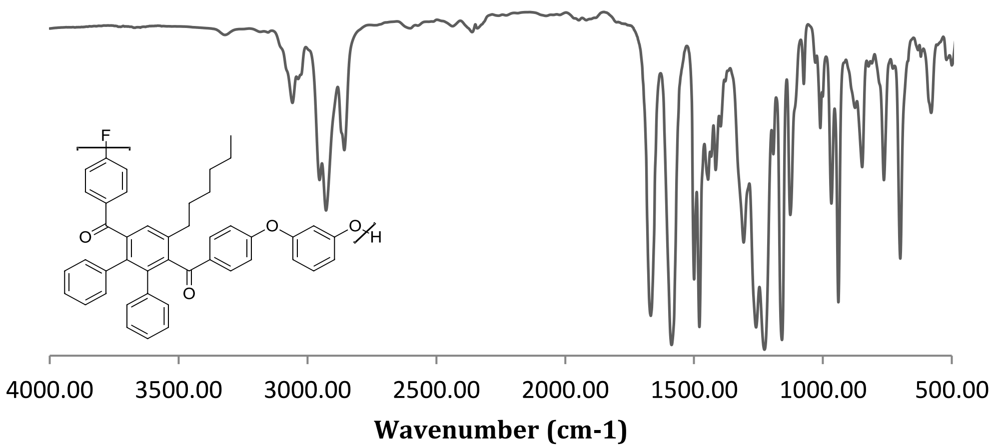


Figure 34. IR spectrum (NaCl) of polymer **56b**.

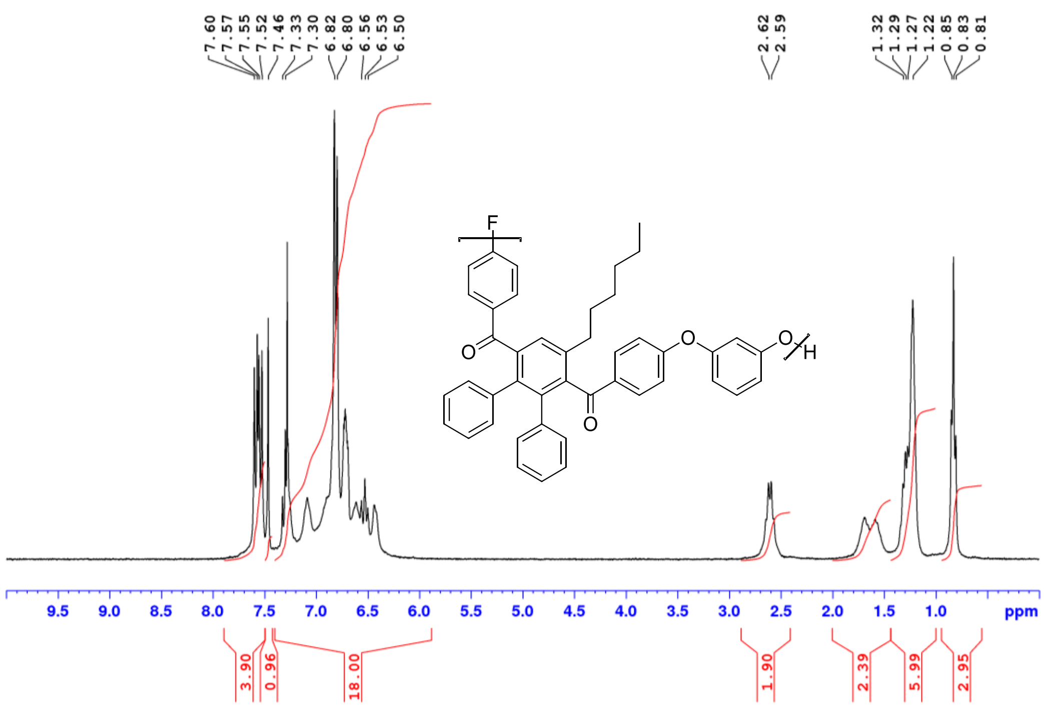


Figure 35. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of polymer **56b**.

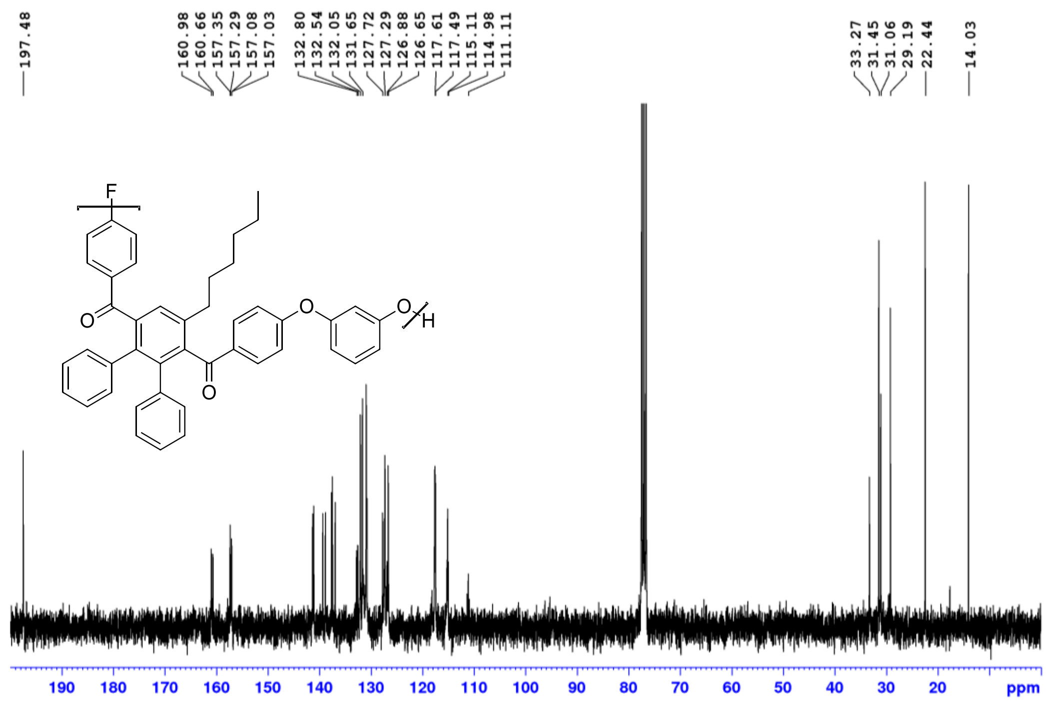


Figure 36. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of polymer **56b**.

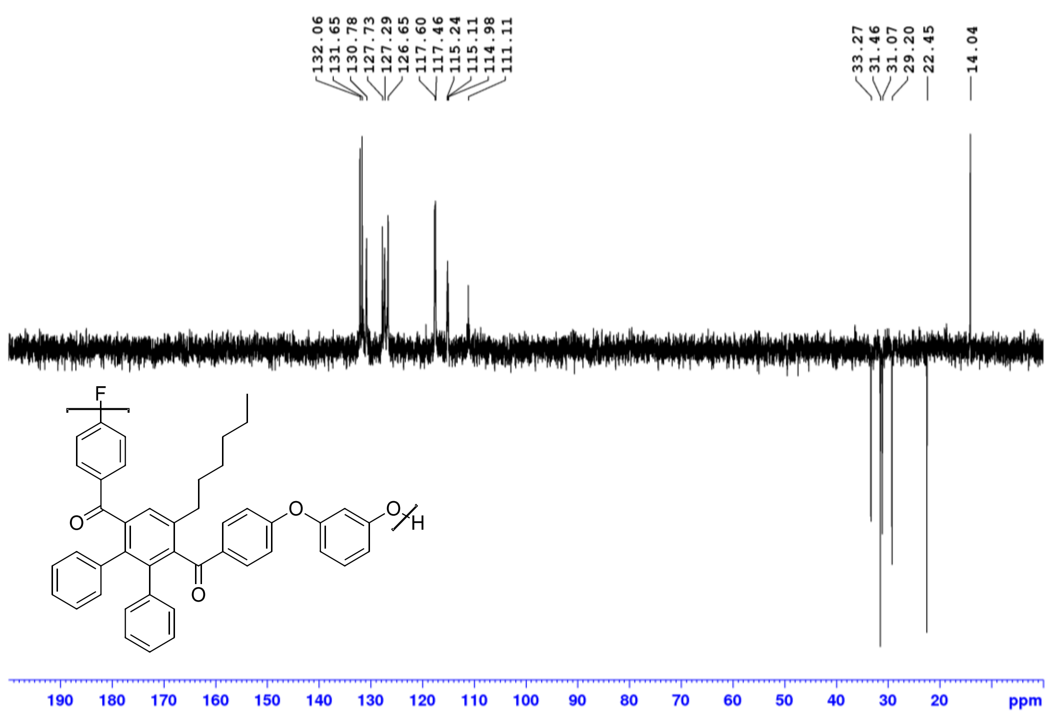


Figure 37. ^{13}C DEPT135 NMR spectrum (75 MHz, $CDCl_3$) of polymer **56b**.

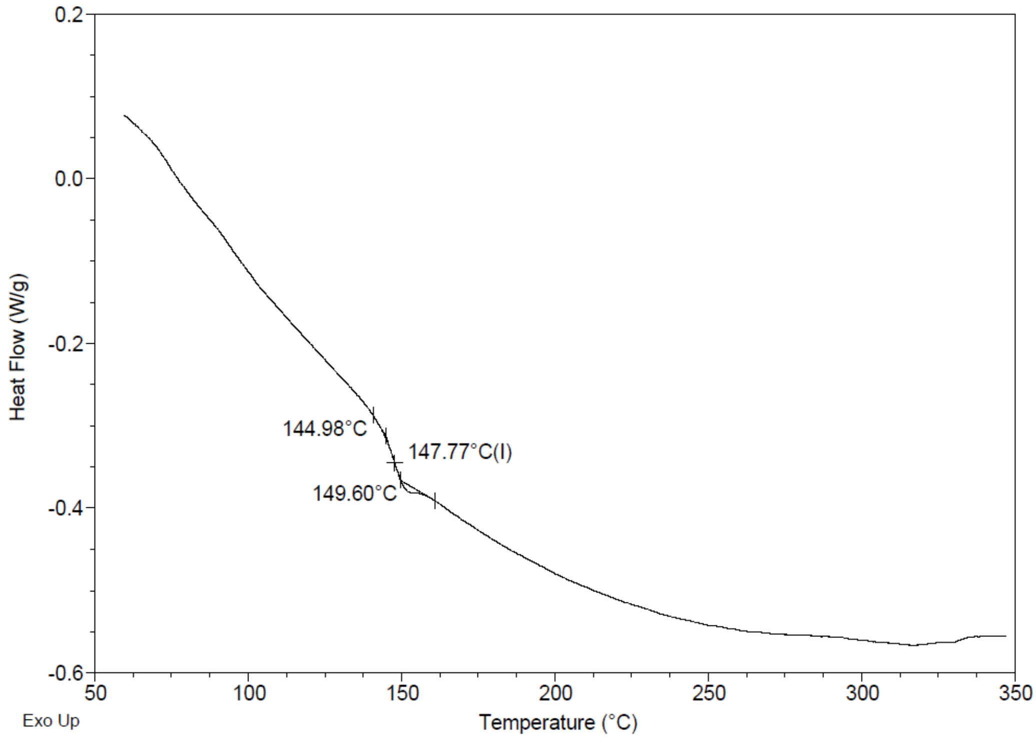


Figure 38. DSC spectrum of polymer **56b**.

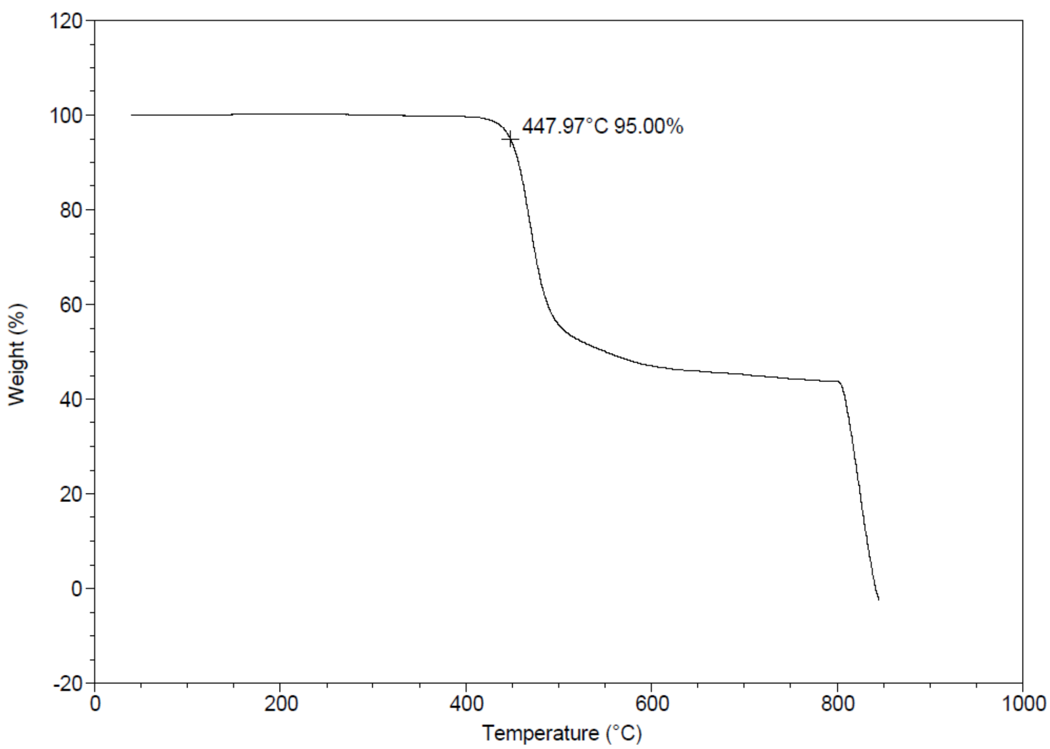


Figure 39. TGA spectrum (nitrogen) of polymer **56b**.

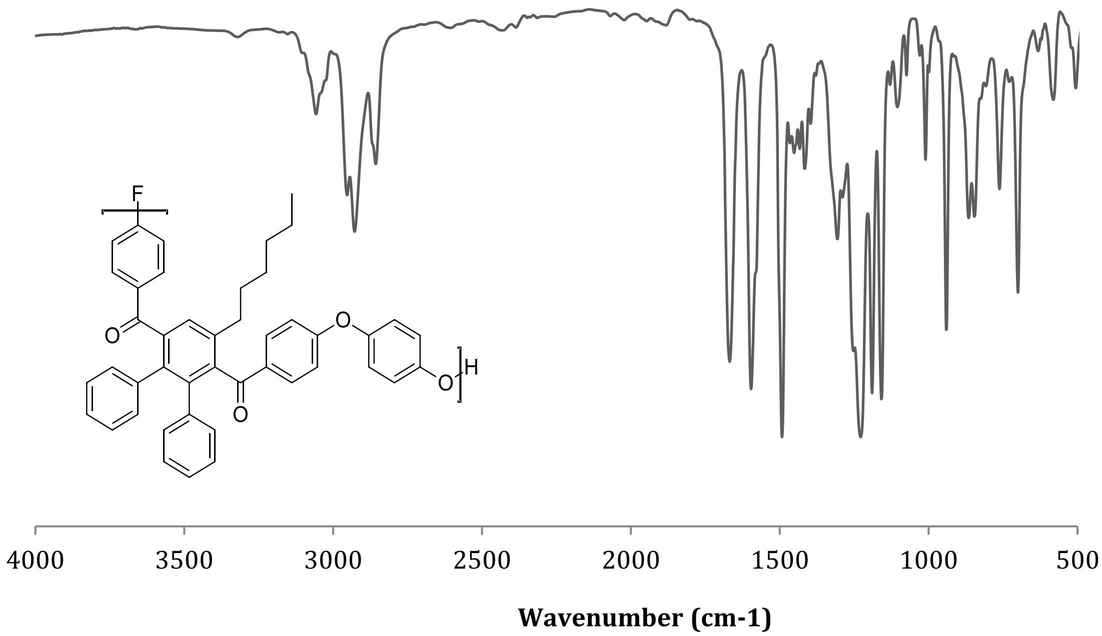


Figure 40. IR spectrum (NaCl) of polymer **56c**.

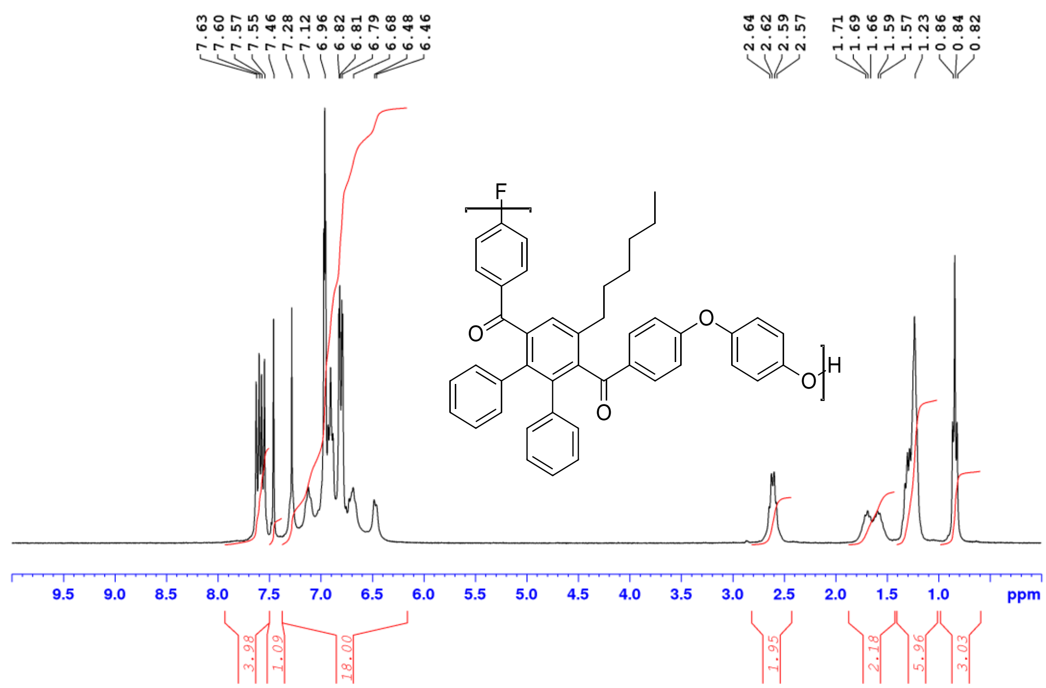


Figure 41. [1]H NMR spectrum (300 MHz, $CDCl_3$) of polymer **56c**.

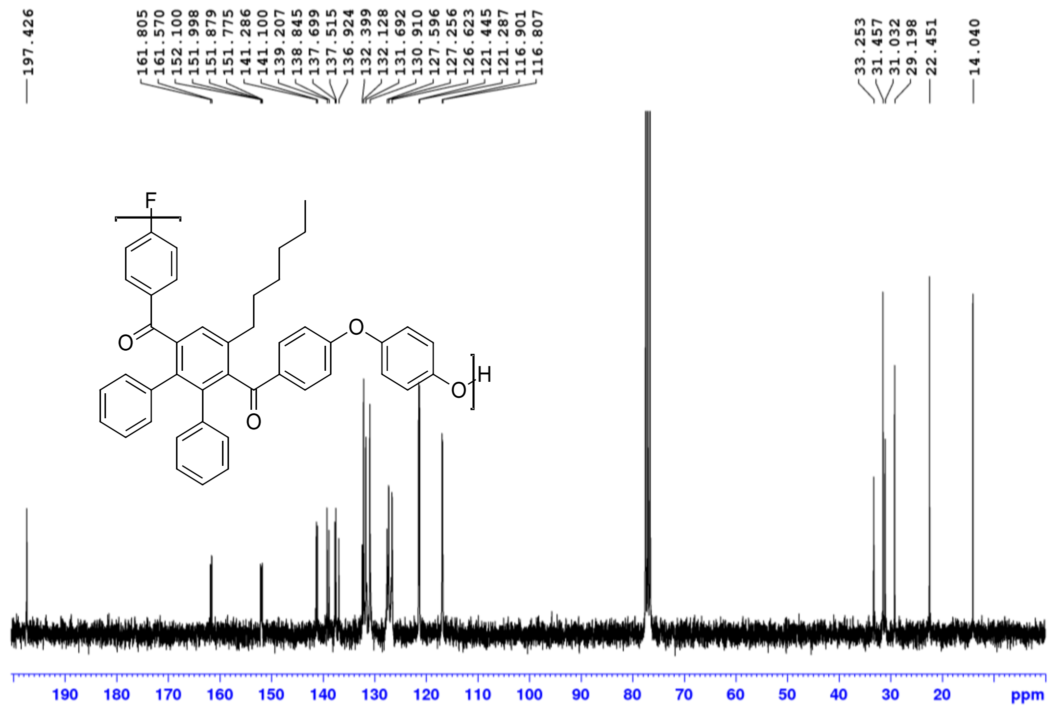


Figure 42. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of polymer **56c**.

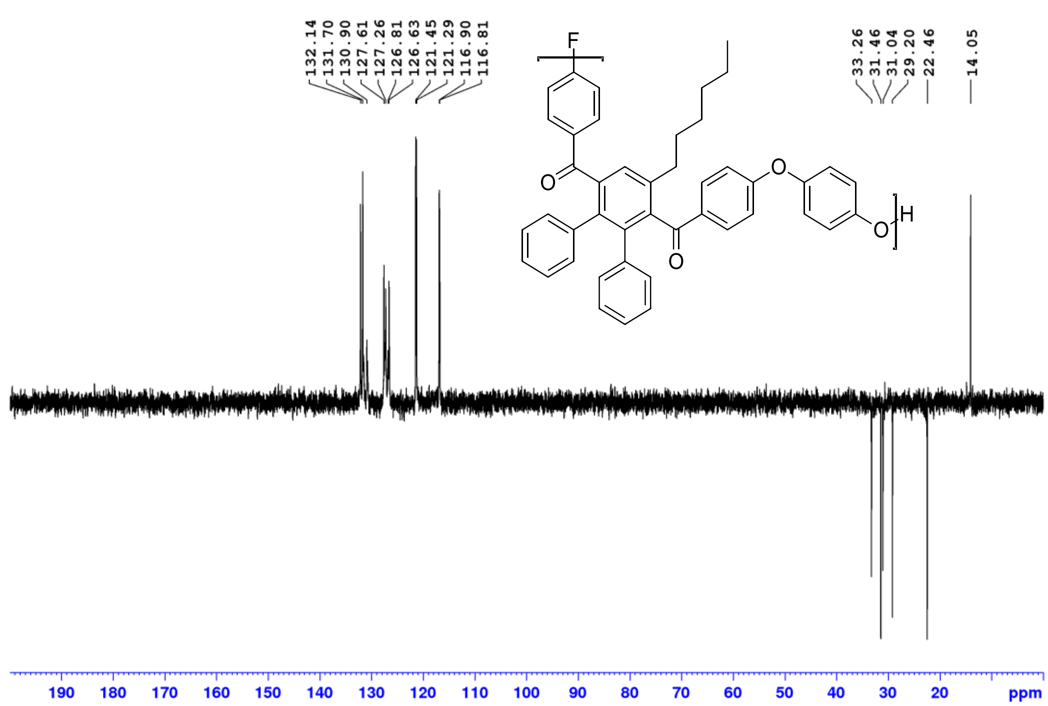


Figure 43. ^{13}C DEPT135 NMR spectrum (75 MHz, $CDCl_3$) of polymer **56c**.

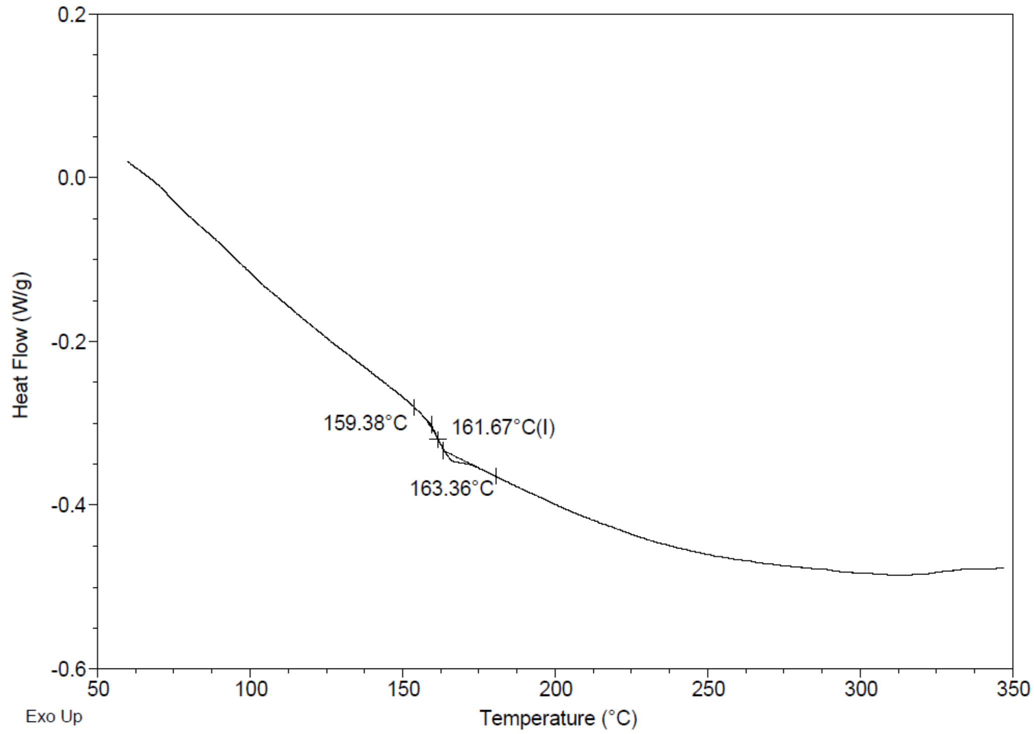


Figure 44. DSC spectrum of polymer **56c**.

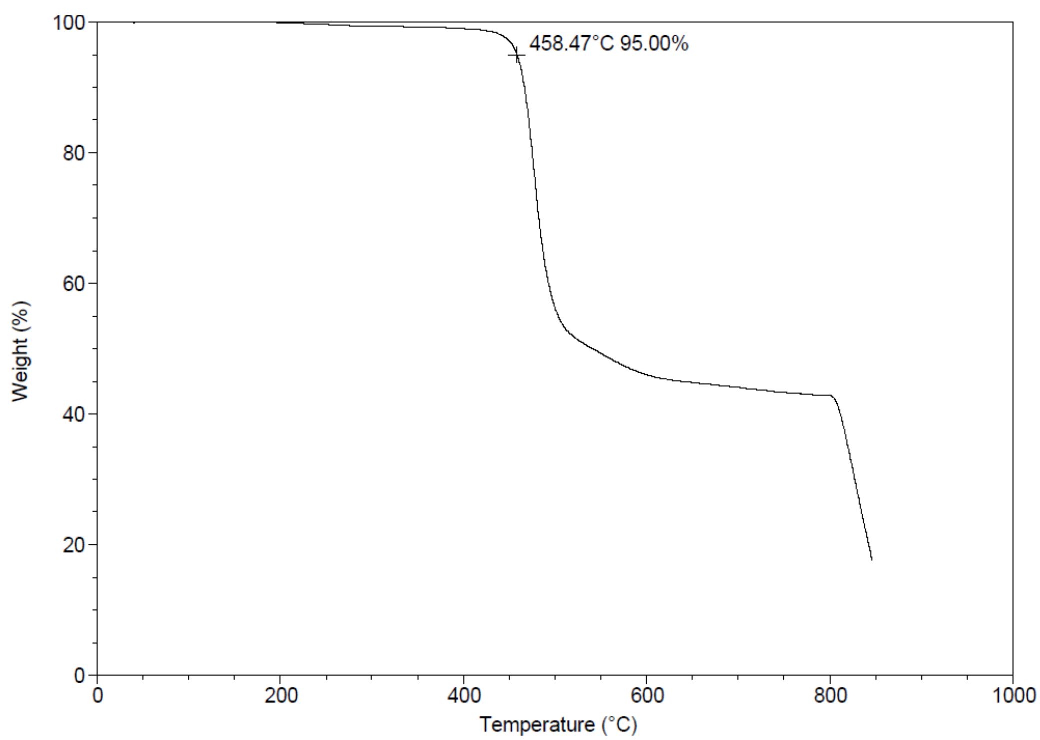


Figure 45. TGA spectrum (nitrogen) of polymer **56c**.

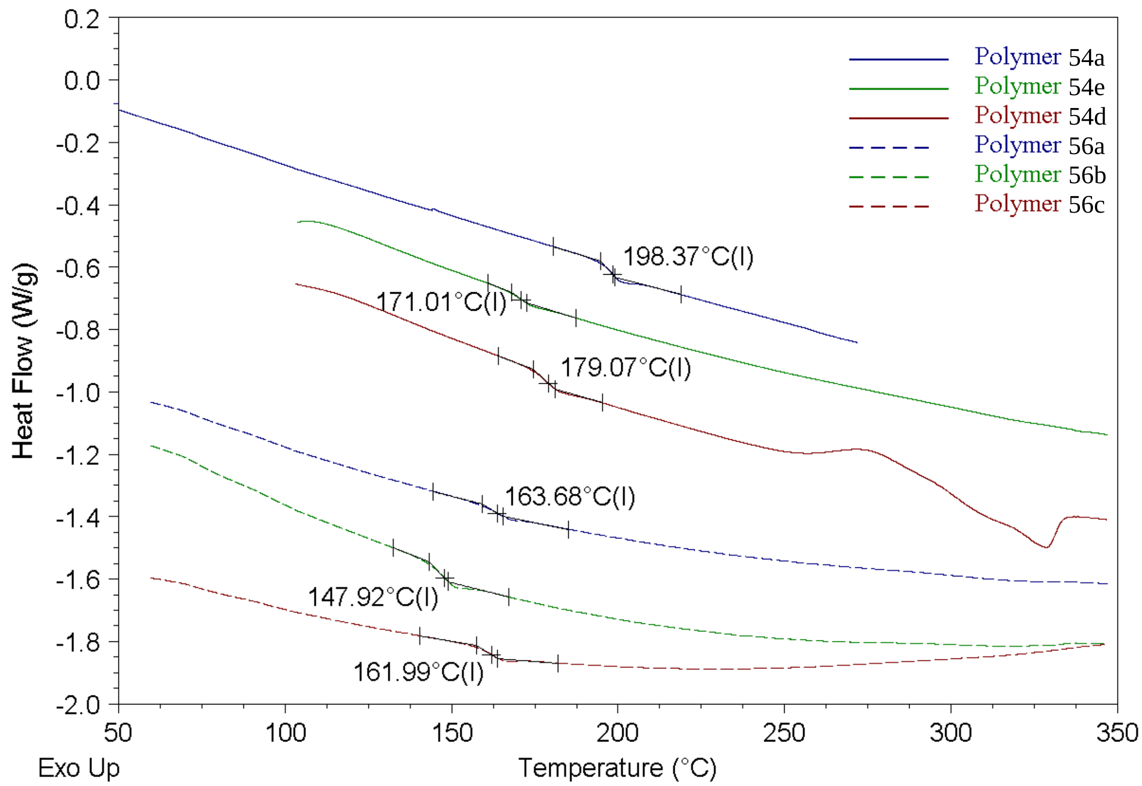


Figure 46. Composite DSC trace for polymers **54a, 54e, 54d, 56a, 56b** and **56c**.

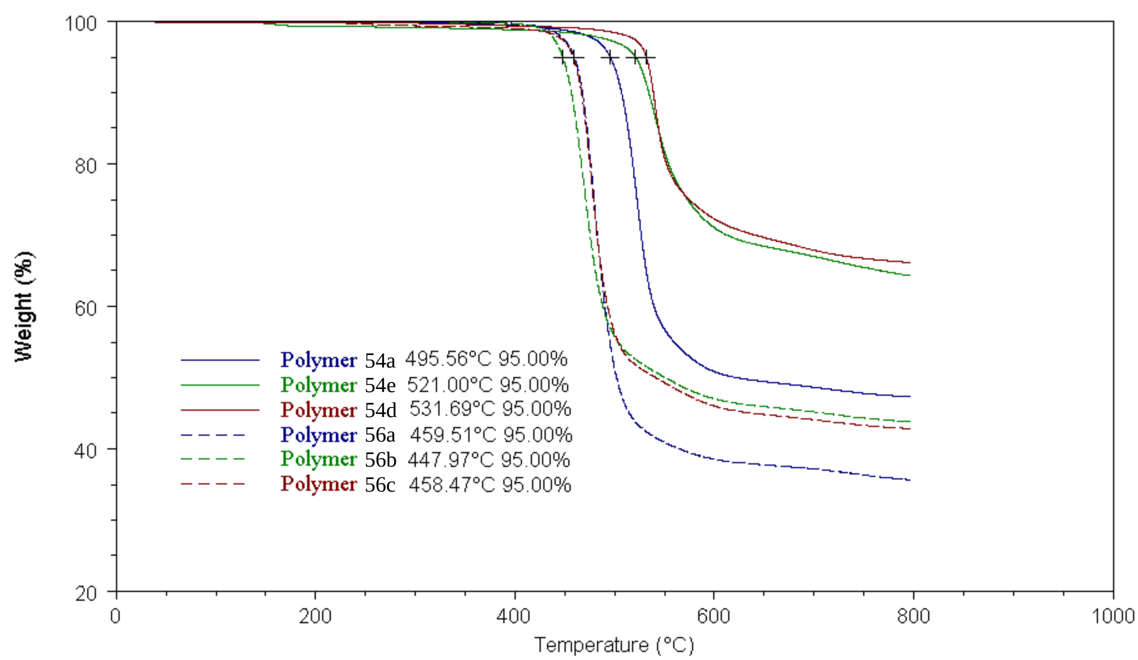


Figure 47. Composite TGA trace for polymers **54a, 54e, 54d, 56a**, **56b** and **56c**.

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VITAE

Matthew Cerone was born December 1, 1988. He graduated from The Ohio State University where he earned his Bachelor of Science in Chemical and Biomolecular Engineering in 2012. He expects to receive his Masters of Science Degree in Chemistry in April 2017.