2002

Selected Synthetic Studies of NLO pi-Bridges and Thermally Stable Monomers

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SELECTED SYNTHETIC STUDIES OF NLO π-BRIDGES AND THERMALLY STABLE MONOMERS

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

By

STACEY M. FAULEY
B.S., Ohio Northern University, 1999

2002
Wright State University

WRIGHT STATE UNIVERSITY

SCHOOL OF GRADUATE STUDIES

August 23, 2002

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Stacey M. Fauley ENTITLED Selected Synthetic Studies of NLO π-Bridges and Thermally Stable Monomers BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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Signed: Eric Fossum, Ph.D.

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ABSTRACT

Fauley, Stacey M. M.S., Department of Chemistry, Wright State University, 2002.
Selected Synthetic Studies of NLO π-Bridges and Thermally Stable Monomers.

The molecular weights of two series of PEEK polymers were determined using gel permeation chromatography (GPC). The first series contains oxyalkylene linkages. The other series contains oxyethylene linkages.

The synthesis of several thermally stable monomers has been investigated. These monomers include 9,9-dihexylfluorene-2,7-dicarboxaldehyde, 2,7-bis(bromomethyl)-9,9-dibutylfluorene and 2,7-bis(hydroxymethyl)-9,9-diethylfluorene. These monomers can be used to form polymers that will contain short conjugated segments separated by nonconjugated segments.

The synthesis of 50 g of each of the following monomers was accomplished: bis(3-methylphenyl)phenylphosphine oxide, bis(4-methylphenyl)phenylphosphine oxide, bis(3-carboxyphenyl)phenylphosphine oxide and bis(4-carboxyphenyl)phenylphosphine oxide. These monomers will be used in a polymerization to form polybenzoxazoles.

The synthesis of the NLO π-bridge 2,10-dibromo-5,6-diphenyl-11,12-dihydroindeno[2.1-a] was accomplished. Alkylation of this compound was attempted, but the results were inconclusive. This project was abandoned due to the consistently low yields. Another NLO π-bridge that was attempted contained the c-fused system, however, the initial steps also showed consistently low yields. Because of low yields, this project was also abandoned.

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DEDICATION

To my husband, Jason, for his loving support.

ACKNOWLEDGMENTS

I would like to thank my advisor, Dr. William Feld, Department of Chemistry, Wright State University, Dayton, Ohio, for his support, guidance and advice.

INTRODUCTION

Poly(ether ether ketone)s

There is a constant search for materials that exhibit properties such as thermal stability, chemical resistance and thermooxidative resistance while maintaining electrical and mechanical properties. Poly(arylene ether)s, specifically poly(ether ether ketone)s, are a group of materials that exhibit these types of properties. These materials can be used in composite as well as adhesive applications.

Poly(ether ether ketone)s can be prepared by two methods. The first is nucleophilic substitution of a dihalide with an alkali metal bisphenolate. The second method is by Friedel-Crafts acylation.

In the past decade, a relationship between structure and property has been explored. Oxyalkylene units and oxyethylene units have been incorporated into the monomers that undergo polymerization to form poly(ether ether ketone)s. The length of these units causes a change in the glass transition temperature with little affect on the thermal stability of the polymer.

The objective of this project was to determine the molecular weight of a series of poly(ether ether ketone)s using gel permeation chromatography (GPC).

Polybenzoxazoles

Polymers that contain phosphine oxide linkages, like poly(arylene ether phosphine oxide)s (PEPO), are another type of thermoplastic material of interest. These polymers tend to have a high glass transition temperature[1] and thermal stability as well as flame retardency and high energy radiation resistance[2]. Because of these reasons, these materials are being investigated for use in nuclear and or space applications.

The objective of this project was to synthesize significant amounts of each of the following: bis(3-methylphenyl)phenylphosphine oxide, bis(4-methylphenyl)phenylphosphine oxide, bis(3-carboxyphenyl)phenylphosphine oxide and bis(4-carboxyphenyl)phenylphosphine oxide.

Poly(phenylenevinylene)

Poly(phenylene vinylene)s (PPVs) have been popular since the discovery of their electroluminescent properties and their ability to conduct current. The conductivity of these polymers can be altered by doping or by changing the component groups within the polymer[3].

Because there is some control over the conductivity of PPVs, they have become a candidate for use in light emitting diodes (LEDs). These polymers can be made using an assortment of synthetic routes which can lead to a wide variety of polymers.

Much research has focused on developing an efficient, stable organic species that emits in the blue region for use in light emitting diodes (LEDs). Red and green emitters are readily available, but blue emitters have been a synthetic challenge. Among the blue emitting polymers that have been synthesized are poly(2,7-(9,9-dialkylfluorene))s and poly(phenylenevinylene)s[4].

These polymers have been extensively studied for use in light emitting diodes (LEDs) because of their electroluminescent and conductive properties[3]. Derivatives of

PPV have been shown to have emissions in the visible spectrum from green to red[5]. Blue emission is difficult to achieve with these polymers because the conjugation length must be controlled[6].

The objective of this project was to synthesize 9,9-dihexylfluorene-2,7-dicarboxaldehyde and 2,7-bis(bromomethyl)9,9-dibutylfluorene.

Nonlinear Optical Materials

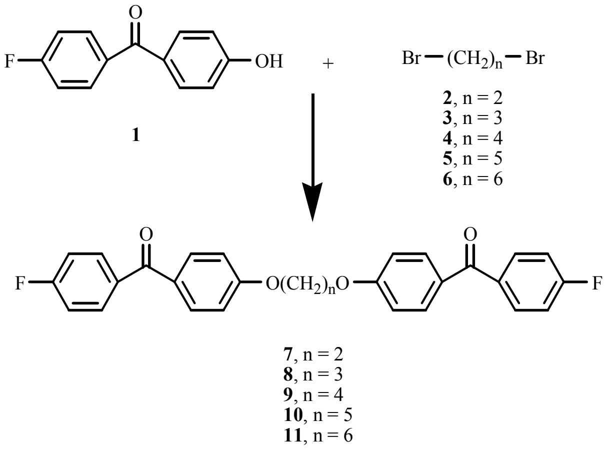
In the past several years, nonlinear optical materials have been a popular research topic. These materials have numerous applications including frequency upconverted lasers[7], optical communication and data storage[8] and optical and sensor limiting. The application focused on in this study is optical and sensor limiting. The nonlinear optical materials that undergo two photon absorption are most important to this study. Two photon absorption occurs when a material is irradiated with infrared radiation. The material absorbs two photons simultaneously, undergoes nonradiative decay and then emits a photon at a frequency higher than that absorbed. In designing nonlinear optical materials, the 9,9-dialkylfluorene bridge has proven the most suitable based on its two photon cross section.[9] This is attributed to the planarity and the conjugation length of the molecule.

The focus of this project was to synthesize an indenofluorene molecule for use as a polarizable π bridge in these chromophores. Using an indenofluorene would maintain the planarity of the bridge, but increase the conjugation length.

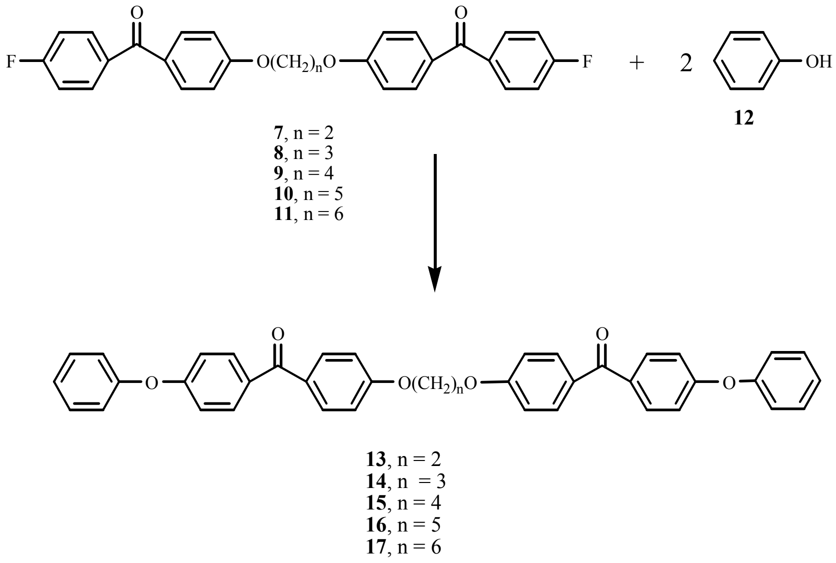
HISTORICAL

Poly(ether ether ketone)s with Oxyalkylene linkages[10]

In 1992, a series of bis(fluorobenzophenone) monomers containing oxyalkylene linkages of varying lengths was synthesized by reacting 4-fluoro-4'-hydroxybenzophenone **1** with 1,2-dibromoethane **2**, 1,3-dibromopropane **3**, 1,4-dibromobutane **4**, 1,5-dibromopentane **5** and 1,6-dibromohexane **6** to form 1,2-bis(4-(4-fluorobenzoyl)phenoxy)ethane **7**, 1,3-bis(4-(4-fluorobenzoyl)phenoxy)propane **8**, 1,4-bis(4-(4-fluorobenzoyl)phenoxy)butane **9**, 1,5-bis(4-(4-fluorobenzoyl)phenoxy)pentane **10** and 1,6-bis(4-(4-fluorobenzoyl)phenoxy)hexane **11**, respectively.



A model study was performed using these oxyalkylene containing monomers.



7, n = 2
8, n = 3
9, n = 4
10, n = 5
11, n = 6

12

13, n = 2
14, n = 3
15, n = 4
16, n = 5
17, n = 6

The monomers **7-11** were reacted with phenol **12** to form 1,2-bis(4-(4-phenoxybenzoyl)phenoxy)ethane **13**, 1,3-bis(4-(4-phenoxybenzoyl)phenoxy)propane **14**, 1,4-bis(4-(4-phenoxybenzoyl)phenoxy)butane **15**, 1,5-bis(4-(4-phenoxybenzoyl)phenoxy)pentane **16** and 1,6-bis(4-(4-phenoxybenzoyl)phenoxy)hexane **17**, respectively.

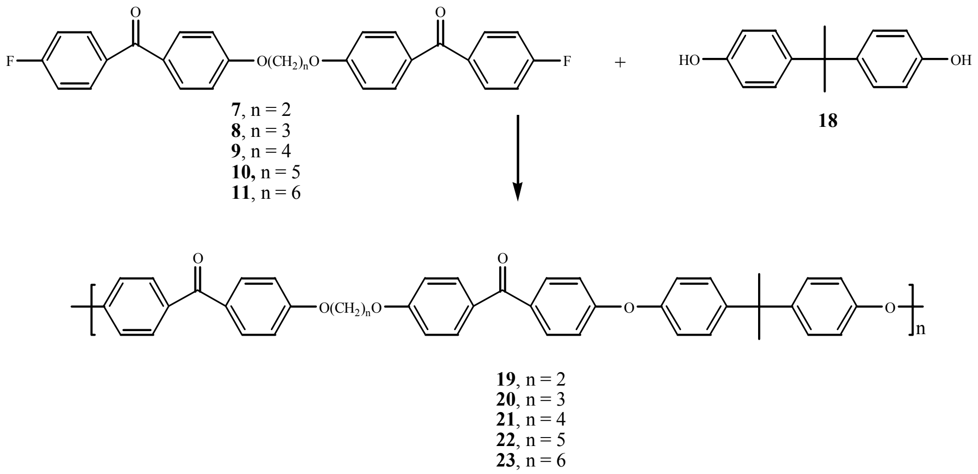
Table 1

Melting Points and Yields of Model Oxyalkylene Containing Compounds

Compound	Number of Carbons in link	Melting Point (^{o}C)	Yield (%)
13	2	215	86
14	3	175	67
15	4	220	53
16	5	177	62
17	6	172	60

The melting point of the compounds containing an oxyalkylene linkage with an even number of carbons decreases while the odd numbered carbon oxyalkylene linkages cause a slight increase in melting point.

The polymerizations were performed in NMP and toluene with potassium carbonate



7, n = 2
8, n = 3
9, n = 4
10, n = 5
11, n = 6

18

19, n = 2
20, n = 3
21, n = 4
22, n = 5
23, n = 6

acting as the base. The monomers **7-11** were reacted with bisphenol-A **18** to yield poly(oxy-1,4-phenylene-1-methylethylidene-1,4-phenylene-oxy-1,4-phenylene carbonyl-1,4-phenylene-1,4-dioxabutylene) **19**, poly(oxy-1,4-phenylene-1-methylethylidene-1,4-phenylene-oxy-1,4-phenylene carbonyl-1,4-phenylene-1,5-dioxapentylene) **20**, poly(oxy-1,4-phenylene-1-methylethylidene-1,4-phenylene-oxy-1,4-phenylene carbonyl-1,4-phenylene-1,6-dioxahexylene) **21**, poly(oxy-1,4-phenylene-1-methylethylidene-1,4-phenylene-oxy-1,4-phenylene carbonyl-1,4-phenylene-1,7-dioxaheptylene) **22** and poly(oxy-1,4-phenylene-1-methylethylidene-1,4-phenylene-oxy-1,4-phenylene carbonyl-1,4-phenylene-1,8-dioxaoctylene) **23**. Incorporation of the longer oxyalkylene units lead to lower glass transition temperatures (**Table 2**) and enhanced solubility with minimal affect on the thermal stability as measured by thermogravimetric analysis (TGA).

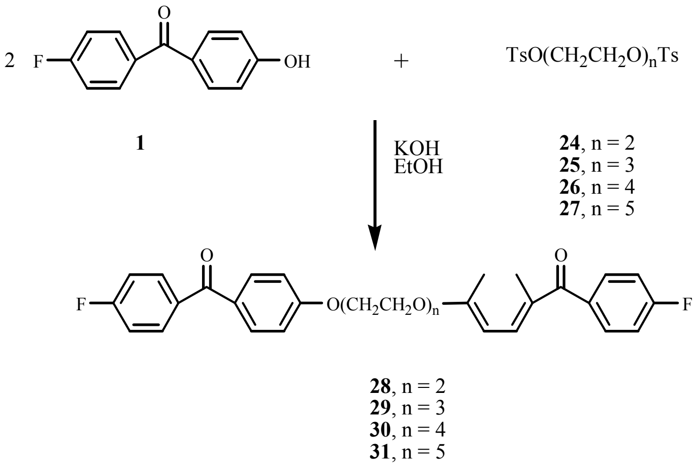
Table 2

Glass Transition Temperatures of PEEK Polymers Containing Oxyalkylene Links

Compound	Number of Carbons in bridge	Tg (^{o}C)	Yield (%)
19	2	136	84
20	3	125	73
21	4	114	82
22	5	108	82
23	6	91	97

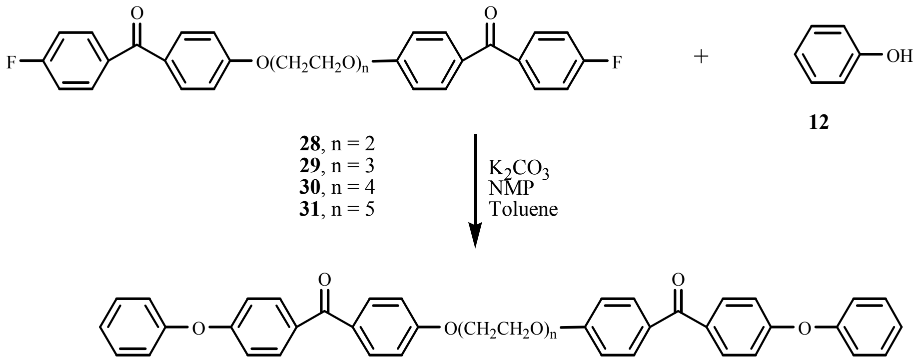
Poly(ether ether ketone)s with Oxyethylene Linkages[11]

In 1992, a related series of bis(fluorobenzophenone) monomers containing oxyethylene linkages of varying lengths was synthesized by reacting 4-fluoro-4'-hydroxybenzophenone **1** with diethylene glycol ditosylate **24**, triethylene glycol ditosylate **25**, tetraethylene glycol ditosylate **26** and pentaethylene glycol ditosylate **27** to form bis(4-(4-fluorobenzoyl)phenoxy)ethyl)ether **28**,



1,2-bis(4-(4-fluorobenzoyl)phenoxy)ethoxy)ethyl)ethane **29**, bis(4-(4-fluorobenzoyl)phenoxy) ethoxy)ethyl)ether **30** and 1,2-bis(4-(4-fluorobenzoyl)phenxy)ethoxy)ethoxy)ethane **31**, respectively.

A model study was performed using these oxyethylene containing monomers. The monomers **28-31** were reacted with phenol **12** to produce bis(4-(4-phenoxybenzoyl)phenoxy) ethyl)ether **32**, 1,2-bis(4-(4-phenoxybenzoyl)phenoxy)ethyl)ethane **33**, bis(4-(4-phenoxybenzoyl) phenoxy)ethoxy)ethyl)ether **34** and 1,2-bis(4-(4-phenoxybenzoyl)phenoxy)ethoxy)ethoxy)ethane **35**, respectively.



28, n = 2
29, n = 3
30, n = 4
31, n = 5

32, n = 2
33, n = 3
34, n = 4
35, n = 5

This study showed that the melting point of these compounds decreased as the length of the oxyethylene unit increased (**Table 3**).

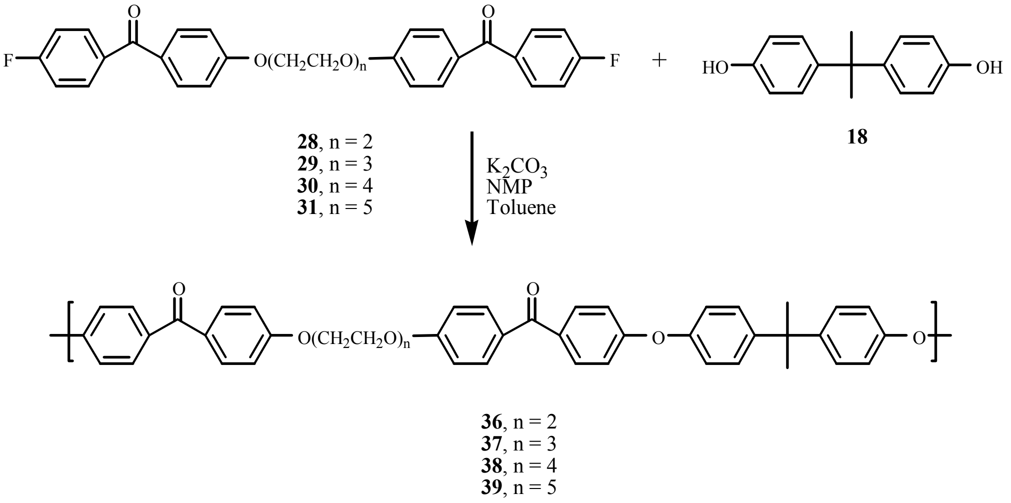
Table 3

Melting Points and Yields of Model Oxyethylene Containing Compounds

Compound	Number of Carbons in bridge	Melting Point (^oC)	Yield (%)
32	2	177-179	82.0
33	3	148-150	86.6
34	4	108-110	89.0
35	5	91-93	98.0

This is an indication that the length of the oxyethylene unit will affect the glass transition temperature of the polymers in a manner similar to the incorporation of oxyalkylene units.

The polymerizations were performed in NMP and toluene with potassium carbonate acting as the base. The monomers **28-31** were reacted with bisphenol-A **18** to yield



poly(oxy-1,4-phenylene-1-methylethylidene-1,4-phenylene-oxy-1,4-phenylene carbonyl-1,4-phenylene-1,4,7-trioxaheptylene **36**, poly(oxy-1,4-phenylene-1-methylethylidene-1,4-phenylene-oxy-1,4-phenylene carbonyl-1,4-phenylene-1,4,7,10-tetraoxadecylene **37**, poly(oxy-1,4-phenylene-1-methylethylidene-1,4-phenylene-oxy-1,4-phenylene carbonyl-1,4-phenylene-1,4,7,10,13-pentaoxatridecylene **38** and poly(oxy-1,4-phenylene-1-methylethylidene-1,4-phenylene-oxy-1,4-phenylene carbonyl-1,4-phenylene-1,4,7,10,13,16-hexaoxahexadecylene **39**. Incorporation of the longer oxyethylene units lead to a lower glass transition temperature (**Table 4**) and enhanced solubility with minimal affect on the thermal stability.

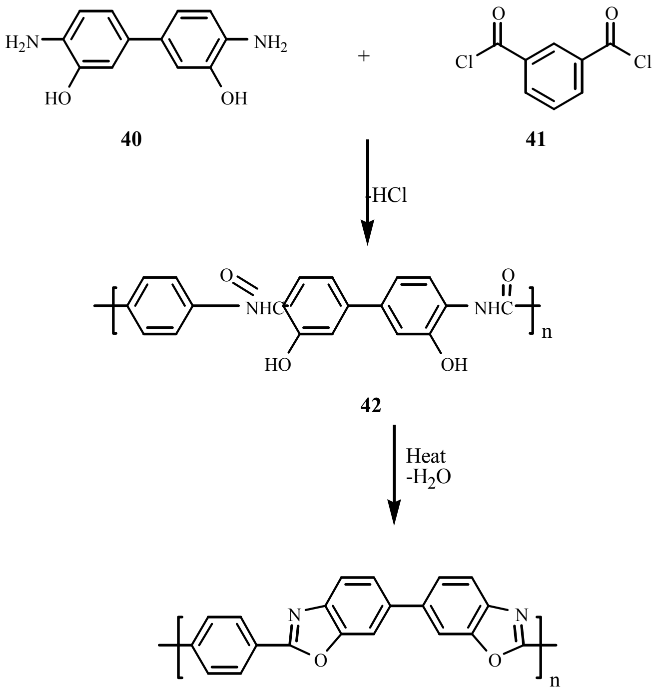
Table 4

Glass Transition Temperatures of PEEK Polymers Containing Oxyethylene Links

Compound	Number of Carbons in link	Tg (^oC)	Yield (%)
36	2	104	88
37	3	87	97.8
38	4	73	98.7
39	5	63.8	97.9

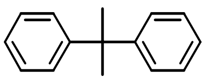
Polybenzoxazoles

Polybenzoxazoles are thermally stable polymers. The first main chain polybenzoxazole reported was made by a polycondensation reaction of 3,3'-dihydroxybenzidine **40** and isophthaloyl chloride **41** to form the polyamide **42**.[12] Heating of the polyamide **42** affords the polybenzoxazole **43**.



43

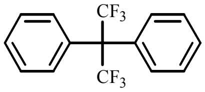
Polyphosphoric acid has been useful in polymerizations of diacids with bis(o-aminophenol)s by acting as a solvent and a dehydrating agent.[13] The problem with most of these is that the resulting polymers are not soluble in common solvents. One solution to this problem was to incorporate isopropylidene units between the aromatic rings **44**.[14]



44

The benefits of incorporating isopropylidene units are three-fold. First, the polymer chain is more flexible. Second, the methyl groups will aid in solubility. Finally, the polymer chain remains thermally stable. These polymer are slightly more soluble, but still not practical enough for many applications.

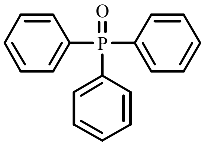
Incorporation of the 1,1,1,3,3,3-hexafluoroisopropylidene (6F) unit in polybenzoxazoles instead



45

of the isopropylidene unit solved the solubility issue **45**.[15] Some of the other benefits of using the 6F unit are high T_g and oxidative resistance.

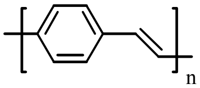
Triphenylphosphine oxide **46** is another unit that may be incorporated into polybenzoxazoles while maintaining thermal stability and oxidative resistance.[2]



46

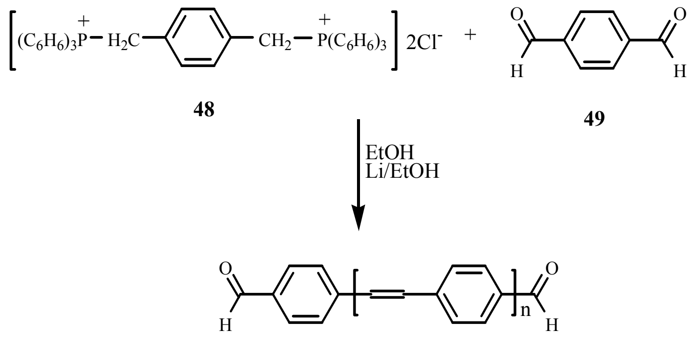
Poly(phenylene vinylene)

Poly(phenylene vinylene) (PPV) **47** is an alternating copolymer of acetylene and benzene.



47

The first synthesis of PPV was reported in 1960 by McDonald and Campbell using a Wittig reaction[16]. An aryl bis-phosphorane was reacted with an aromatic dialdehyde compound to form a PPV.

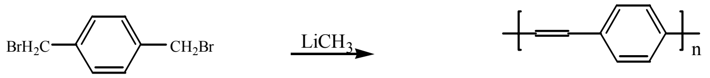


48 **49**

50

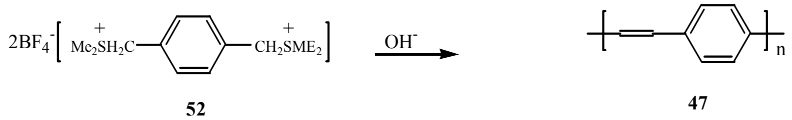
A reaction of p-xylylene bis(triphosphonium chloride) **48** with terephthalaldehyde **49** produced an insoluble, intensely yellow polymer **50** with a melting point of 158-159 ^{o}C and a number average molecular weight (M_w) of about 1200. The polymer was converted to the all trans system by refluxing in toluene with iodine.

PPV was also prepared by the reaction of α,α,α’,α’ tetrabromo-p-xylene **51** with methyl lithium[17].



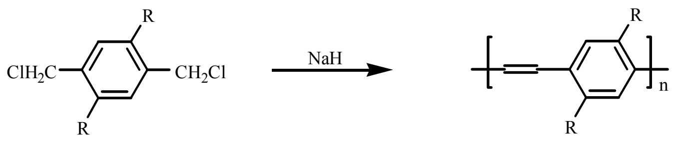
51 **47**

Kanbe and Okawara prepared PPV by the polymerization of p-xylylene bis(dimethylsulfonium tetrafluoroborate) **52**[18].



52 **47**

PPV was also synthesized using a dehydrohalogenation reaction[19]. A reaction of

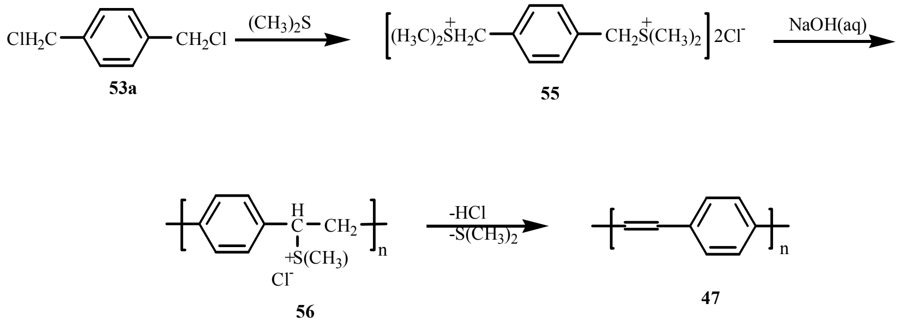


53a, R = H
53b, R = OCH_3

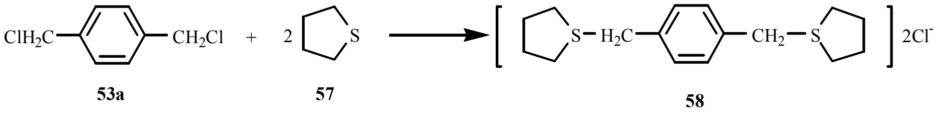
47, R = H
54, R = OCH_3

p-xylylidene dichloride **53a** with sodium hydride formed PPV **47** This reaction was also used to produce the methoxy substituted PPV **54** starting with the methoxy substituted p-xylylene dichloride **53b**.

The problem with each of these reaction schemes is that although many derivatives can be made, the polymers that formed were insoluble with low molecular weights and conductivities. A solution to this would be to form a film from a polymer precursor, then proceed with the polymerization[20]. There are several successful routes to obtaining high molecular weight PPV films using this idea. The first is the polymerization of the monomer p-xylylene bis(dimethylsulfonium chloride) **55**. This monomer is prepared from the reaction of p-xylylidene dichloride **53a** with excess dimethyl sulfide.Electrical conductivities of the PPVs were similar to those of highly doped poly(acetylene) and the molecular weight of the polyelectrolyte **56** was found to be 993 Kilodaltons[20].

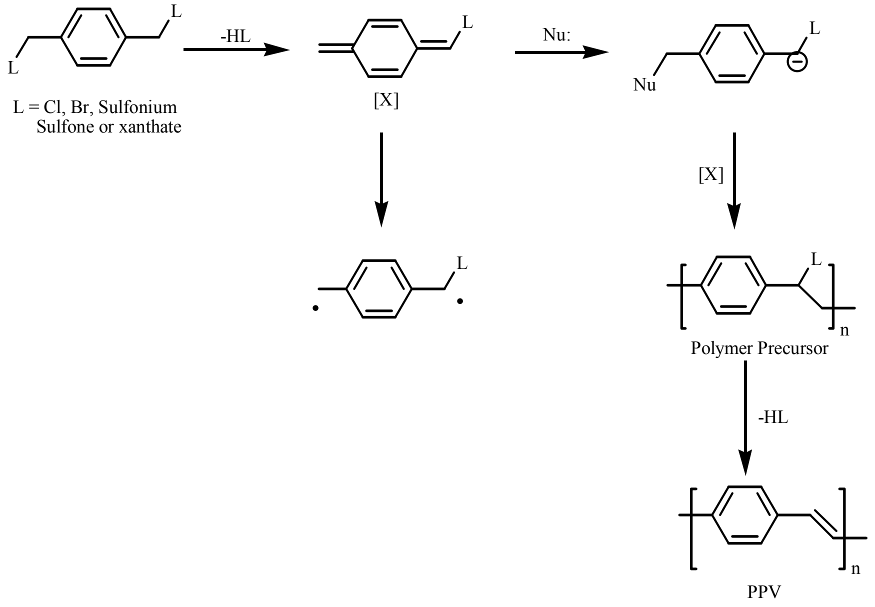


Another route involves the formation of **58** from tetrahydrothiophene **57** and p-xylylidene dichloride **53a**.Under the same conditions as the previous reaction scheme, **58** forms a PPV[20].

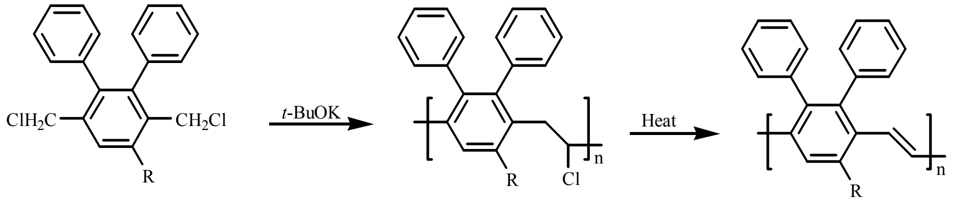


There are currently many synthetic routes to make PPV substituted with different groups. A 1,6-polymerization of *p*-xylylenes will form PPV[21]. This method has been shown to work with bis-halomethyl, bis-sulfonium, sulfone and xanthate type monomers (**Scheme 1**). This method

Scheme 1[21]



has been used to make insoluble polymer thin films[21]. The polymer precursor is cast into a film then treated with heat or light to eliminate HL and form PPV[22]. Using this method, poly(2,3-diphenyl-*p*-phenylene vinylene) **61** and its derivatives were made.

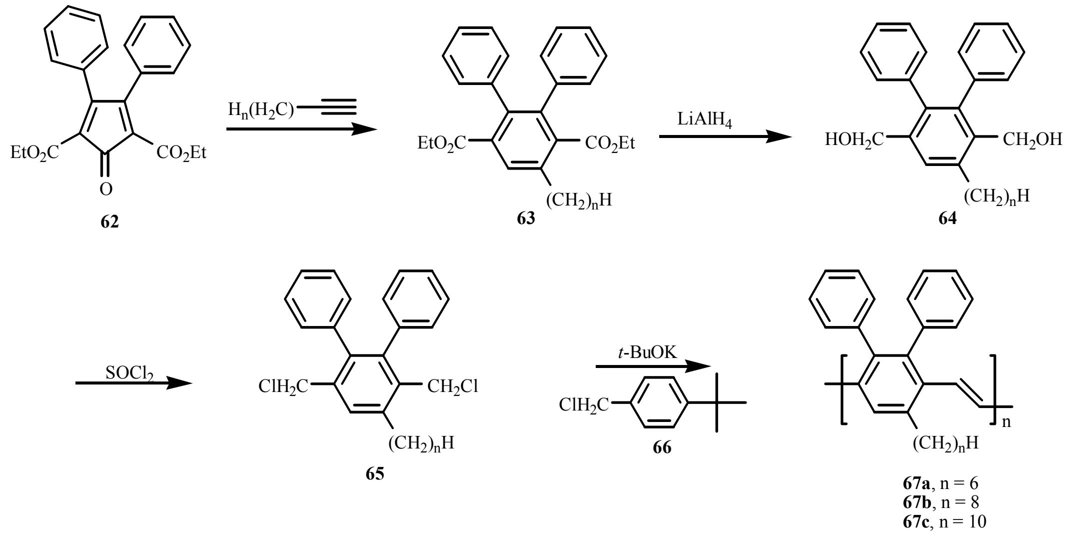


59a, R = H
59b, R = 4-biphenyl

60a, R = H
60b, R = 4-biphenyl

61a, R =H
61b, R = 4-biphenyl

Diels-Alder reactions were used to make the monomers that would become a series of poly(2,3-diphenyl-5-alkyl-*p*-phenylene vinylene)s **65a-c**.[21] The Diels-Alder reaction occurs between the alkyne and the 2,5-bis-(ethoxycarbonyl)-3,4-diphenylcyclopentadienone **62**. Lithium aluminum hydride is then used to reduce the ester **63** to the alcohol **64**. Reaction of **64** with thionyl chloride produces the monomer **65**. This monomer is combined with a base and 4-*t*-butylbenzyl chloride to produce the polymer **67**. The use of 4-*t*-butylbenzyl chloride generally allows formation of high molecular weight polymers with a narrow range of molecular weights.[21] The importance of this route is that virtually any flexible side chain can be introduced into a monomer.[20]



Nonlinear Optical Materials

Design of Nonlinear Optical Materials

The focus of much research in this area is structure property relationships. Generally, the chromophores are separated into two groups (Type I or Type II) based on structure.[9] Type I chromophores consist of a polarizable π bridge linked on both sides to pi electron donors or pi electron acceptors (**Figure 1**). Type II chromophores also contain a polarizable π bridge, but it is linked on one side to an acceptor and on the other to a donor (**Figure 1**).

Type I Chromophores

π Donor --- Polarizable π Bridge --- π Donor

π Acceptor --- Polarizable π Bridge --- π Acceptor

Type II Chromophores

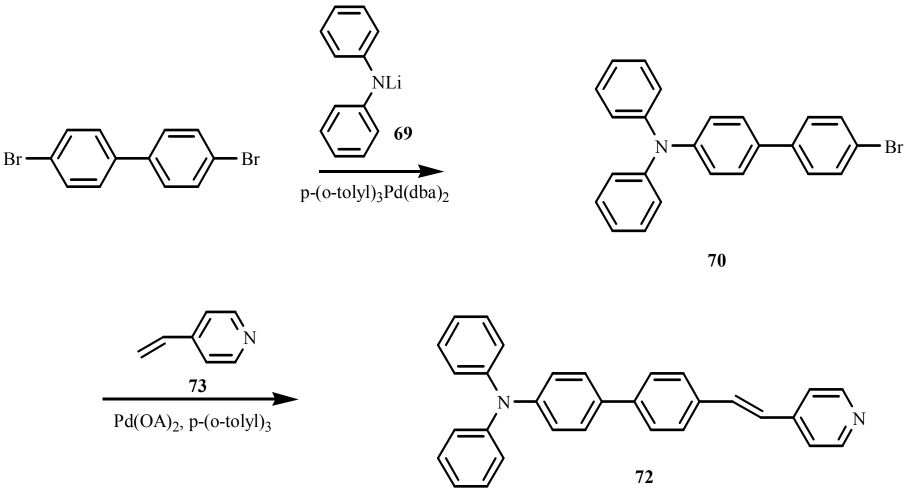
π Donor --- Polarizable π Bridge --- π Acceptor

Figure 1 Type I and Type II Chromophores

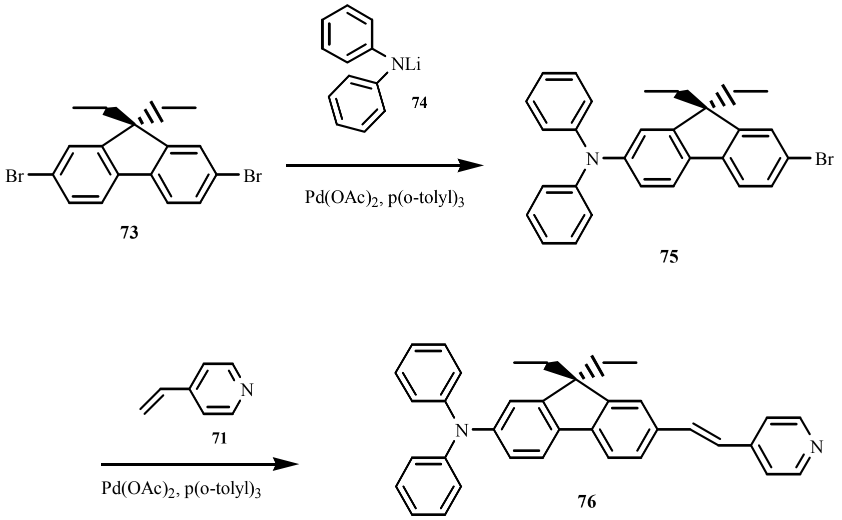
The requirement of these chromophores is that they continue to absorb in the 600 – 800 nm range in order to emit in the visible region.

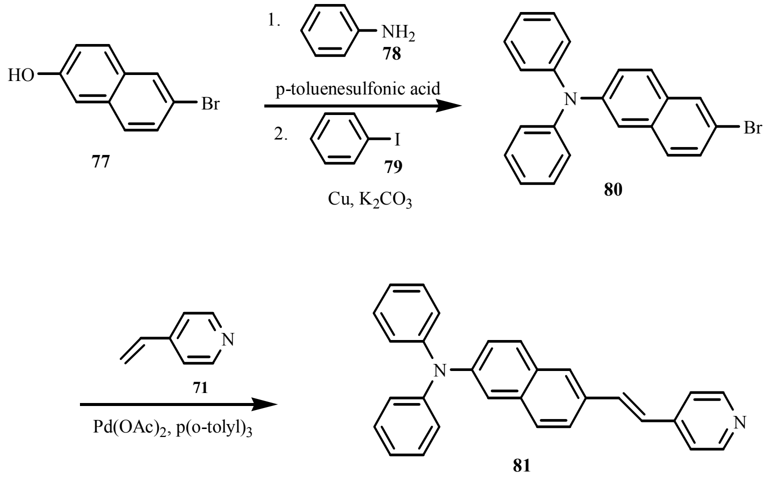
The Polarizable π Bridge

Several molecules have been examined for use as a bridge. These include 2,6-naphthyl, 4,4'-biphenyl, 2,7-fluorene and 7,7'-bifluorene.[9] In order to compare the effect as a bridge, each of these groups was modified to incorporate a diphenylamine group and a 4-vinyl pyridine group. N,N-diphenyl-N-[4-[4-[2-(4-pyridyl)ethenyl]phenyl]phenyl]amine **72** was made by monosubstitution of 4,4'-dibromobiphenyl **68** with the lithium salt of diphenylamine **69**. The result, N,N-diphenyl-N-[4-(4-bromophenyl)phenyl]amine **70** was then reacted with vinyl pyridine **71** under Heck conditions to yield **72**.

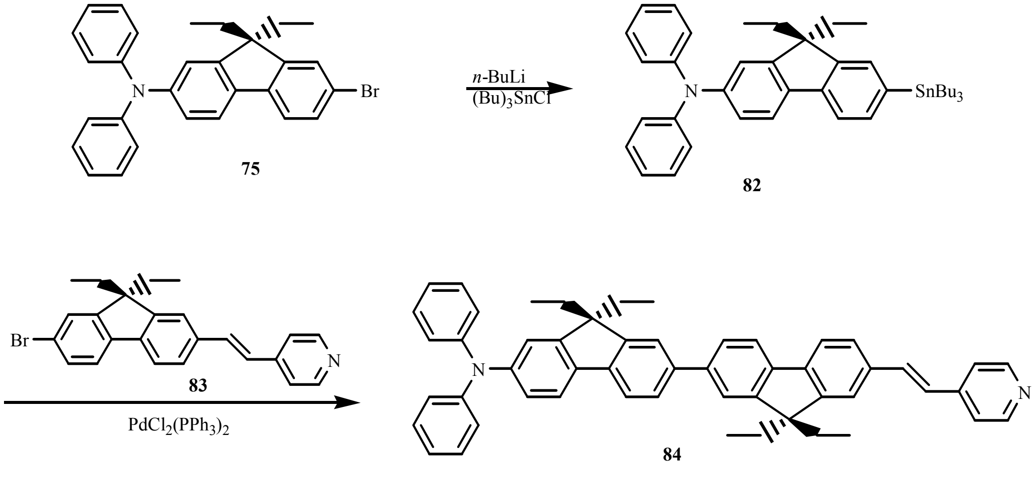


Starting with 2,7-dibromo-9,9-diethylfluorene **73**, N,N-diphenyl-N-[7-[2-(4-pyridyl)ethenyl]-9,9-diethyl-2-fluorenyl]amine **76** was made by the same reaction scheme**.** Formation of N,N-diphenyl-N-[6-[2-(4-pyridyl)ethenyl]2-naphthyl]amine **81** was accomplished by a condensation reaction of 2-bromo-6-hydroxynaphthalene **77** with aniline **78** which was then arylated with iodobenzene **79**. Reaction of 6-bromo-N,N-diphenyl-2-naphthylamine **80** with 4-vinyl pyridine **71** under Heck conditions gives **81**.





Preparation of N,N-diphenyl-N-[7-[7-[2-(4-pyridyl)ethenyl]-9,9-diethyl-2-fluorenyl]-9,9-diethyl-2-fluorenyl]amine **84** was accomplished from the tri-*n*-butyl tin derivative of N,N-diphenyl-N-[4-(4-bromophenyl)phenyl] amine **75** by coupling it with 7-bromo-9,9-diethyl-2-[2-(4-pyridyl)ethenyl]fluorene **83**.



Examination of compounds **72**, **76**, **81** and **84** shows they vary only by the polarizable π bridge. Any difference in the optical properties of these compounds would be attributable to the bridges. The optical measurements are listed in **Table 5**.[9]

Table. 5

Nonlinear Optical Measurements of Various Polarizable Bridges

Chromophore	σ_{max} (nm) Linear Abs.	σ cm/GW at 0.02 mol/L	σ_2' (x10^{-48}) cm^4 sec ph molecule	σ_2'/MW (x10^{-50}) cm^4 sec mol ph molecule g
72	367	1.9	39.0	9.2
76	388	4.7	97.0	19.7
81	388	3.3	68.4	17.2
84	383.5	3.8	79.4	11.1

Sigma, σ, is the two photon absorption coefficient. σ_2 is the molecular two photon cross section. σ_2' is a reproducible coefficient of the material's two photon activity.[9] Comparing the values for compounds **72** and **76**, it is apparent that **76** is a better choice for the bridge. This is due to the planarity of the fluorene molecule. Compounds **76** and **81** both contain a planar bridge, but the conjugation length of the fluorene molecule is longer making **76** the better choice as a polarizable bridge. Comparison of compounds **76** and **84** shows that again **76** is superior as a bridge. The conjugation length of the bridge is longer in **84**, but the molecule loses some of its planarity due to the rotation of the second fluorene molecule.

Using a system that contained indenofluorene instead of fluorene would allow extension of the polarizable bridge while maintaining the planarity of the bridge. Several indenofluorene monomers were synthesized for this reason.

EXPERIMENTAL

Instrumentation and Chemicals

An Electrothermal capillary melting point apparatus equipped with a thermocouple was used to obtain melting points. Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker DMX 300 spectrometer (^{1}H and ^{13}C), with tetramethylsilane (TMS) as an internal standard. Infrared spectra (IR) were recorded with a Perkin Elmer 1600 Series FTIR spectrometer using KBr pellets. Mass spectra were collected on a Hewlett-Packard 5970B gas chromatogram-mass spectrometer. GPC traces were collected using a Viscotek 300 TDA. All reagents were purchased from Aldrich Chemical Company and used without further purification.

Bis(3-methylphenyl)phenylphosphine oxide 87

Magnesium (3.65 g, 0.150 mol) was mixed in tetrahydrofuran (25 mL) under nitrogen at 10^{o}C. A solution of m-bromotoluene (25.67 g, 0.150 mol) in tetrahydrofuran (25 mL) was added dropwise to maintain a gentle reflux. Additional tetrahydrofuran (100 mL) was added. The mixture was warmed to room temperature and stirred overnight. The solution was cooled to 5^{o}C, and phenylphosphonic dichloride (10.4 mL, 0.073 mol) was added dropwise. The solution was stirred overnight at room temperature. The mixture was cooled to 10^{o}C and acidified with 10% sulfuric acid (5 mL). The organic phase was isolated and washed with water (50 mL), 10% bicarbonate (25 mL) and water (50 mL), dried over magnesium sulfate and evaporated. Recrystallization of the residue from heptane yielded a white solid (13.9 g, 90.7%): mp 92.8 –

94.0°C (lit. mp 108.5-109 °C)[23]; ^{1}H NMR δ 2.3 (s, 6H, CH_3), 7.5 (m, 13H, Ar-H); ^{13}C NMR ppm 21.5, 128.6, 129.2, 131.7, 132.1, 132.7, 133.1, 138.4

Bis(4-methylphenyl)phenylphosphine oxide 88

Magnesium (7.1 g, 0.292 mol) was mixed in tetrahydrofuran (50 mL) under nitrogen at 10°C. A solution of p-bromotoluene (50.0 g, 0.292 mol) in tetrahydrofuran (50 mL) was added dropwise. Additional tetrahydrofuran (100 mL) was added. The mixture was warmed to room temperature and stirred overnight. The solution was cooled to 5°C, and phenylphosphonic dichloride (20.3 mL, 0.143 mol) was added dropwise. The solution was stirred overnight at room temperature. The mixture was cooled to 10°C and acidified with 10% sulfuric acid (10 mL). The organic phase was isolated and washed with water (50 mL), 10% bicarbonate (50 mL) and water (50 mL), dried over magnesium sulfate and evaporated. Recrystallization of the residue from hexane yielded a white solid (28.9 g, 96.7%): mp 85.0 – 85.9°C (lit. mp 79.5 °C)[24]; ^{1}H NMR δ 2.2 (s, 6H, CH_3), 7.9 (m, 13H, Ar-H); ^{13}C NMR ppm 21.6, 128.7, 129.1, 129.3, 131.8, 132.2, 132.4, 142.4

Bis(3-carboxyphenyl)phenylphosphine oxide 89

Potassium hydroxide (19.2 g, 0.342 mol), **87** (21.6 g, 0.070 mol) and pyridine (59.8 g, 0.756 mol) were combined and heated to 95°C. A solution of potassium permanganate (128.0 g, 0.810 mol) in water (1000 mL) was added over 2 h maintaining a temperature between 90 – 100°C. This solution was stirred at 95°C overnight. Additional potassium permanganate (10.66 g, 0.067 mol) was added. The mixture was refluxed for 4 h, cooled to room temperature and poured into ethanol (100 mL). The precipitate was filtered and discarded. The aqueous phase was extracted with methylene chloride (3 x 200 mL) and acidified with hydrochloric acid to pH 2. This was stirred overnight. The white precipitate was filtered and dried (22.0 g, 85.1%). ^{1}H

NMR δ 7.6-8.2 (m, 15H, Ar-H); ^{13}C NMR ppm129.8, 130.5, 132.4, 132.8, 134.9, 136.9, 138.3, 167.5

Bis(4-carboxyphenyl)phenylphosphine oxide 90

Potassium hydroxide (26.7 g, 0.476 mol), **88** (30.0 g, 0.98 mol) and pyridine (83.1 g, 1.051 mol) were combined, and heated to 95°C. A solution of potassium permanganate (178.0 g, 1.126 mol) in water (1200 mL) was added over 2 h maintaining a temperature between 90 – 100°C. This solution was stirred at 95°C overnight. Additional potassium permanganate (14.83 g, 0.094 mol) was added. The mixture was refluxed for 4 h, cooled to room temperature and poured into ethanol (150 mL). The precipitate was filtered and discarded. The aqueous phase was extracted with methylene chloride (3 x 200 mL) and acidified with hydrochloric acid to pH 2. This was stirred overnight. The white precipitate was filtered and dried (28.0 g, 78.0%). ^{1}H NMR δ 7.7-8.2 (m, 15H, Ar-H); ^{13}C NMR ppm 129.9, 130.4, 132.4, 132.8, 133.3, 167.3, 207.5

2,7-Dibromofluorene 92

Fluorene **91** (80.01 g, 0.481 mol) and iodine (1.41 g, 0.006 mol) were dissolved in methylene chloride (508 mL). Bromine (50.7 mL, 0.984 mol) in methylene chloride (75 mL) was added dropwise over 2h. Sodium bicarbonate (4.06 g, 0.048 mol) in water (130 mL) was added. The mixture stirred overnight. Methylene chloride was evaporated and water was slowly added. The precipitate was filtered (149.7 g, 95.9%): mp 162.8 – 163.3°C (lit. mp 215 °C)[26]

2,7-Dibromo-9,9-dihexylfluorene 93

Potassium iodide (3.03 g, 0.018 mol), potassium hydroxide (49.43 g, 0.881 mol), **92** (58.5 g, 0.181 mol) and dimethylsulfoxide (130 mL) were combined. The solution was cooled to 5°C. Hexyl bromide (60 mL, 0.427 mol) was added dropwise. The solution was stirred overnight at room temperature, poured into water (200 mL) and extracted with chloroform (3 x 50 mL). The chloroform was evaporated. The residue was recrystallized in hexane to yield brown crystals (73.0 g, 82.1%): mass spectrum, m/z (relative intensity) 492 (M+, 87)

9,9-dihexylfluorene-2,7-dicarboxaldehyde 94

All glassware was dried in the oven overnight. Anhydrous tetrahydrofuran (80 mL) was added to **93** (4.00 g, 0.008 mol). After dissolution, the solution was cooled to –78°C. n-butyl lithium (10.2 mL, 0.016 mol) was added dropwise. The solution was stirred for 20 min. A white precipitate formed. Dimethylformamide (1.5 mL, 0.019 mol) was added dropwise.The mixture was warmed to room temperature and stirred overnight. Water (25 mL) was added, and the solution was extracted with diethyl ether (3 x 75 mL). The extracts were dried and the solvent removed to yield a yellow oil. The oil was purified by chromatography (20% ethyl acetate in hexane) (2.59 g, 81.6%): mass spectrum, m/z (relative intensity) 390 (M+, 43); ^{1}H NMR δ 0.6 (m,6H, CH_3), 0.8 (t, 4H, CH_2), 1.0 (m, 4H, CH_2), 2.1 (m, 4H, CH_2), 7.4 (m, 4H, Ar-H), 7.9 (s, 2H, Ar-H), 10.2 (s, 2H, CHO); ^{13}C NMR ppm 14.4, 22.9, 24.1, 26.0, 30.0, 31.9, 40.5, 121.7, 123.8, 130.8, 136.9, 146.0, 153.3, 192.6

9,9-dibutylfluorene 95

All glassware was dried in the oven overnight. Fluorene **91** (10.0 g, 0.060 mol) was dissolved in anhydrous diethyl ether (150 mL). The solution was then cooled to –78°C. n-Butyl lithium (75.3 mL, 0.120 mol) was added dropwise. After addition was complete, the solution was stirred for 1 h. Butyl iodide (13.8 mL 0.120 mol) was added dropwise, and the solution was stirred for 2 h. Water (100 mL) was added, the organic phase was separated, washed with water (2 x 100 mL) and dried over magnesium sulfate. The solvent was removed to yield an oil (20.0 g, 119.4%): mass spectrum, m/z (relative intensity) 278 (M+, 45); ^{1}H NMR δ 0.7 (t, 6H, CH_3), 0.9

(m, 4H, CH_2), 1.4 (m, 4H, CH_2), 2.1 (m, 4H, CH_2), 7.4 (m, 6H, Ar-H), 7.8 (m, 2H, Ar-H); ^{13}C NMR ppm 14.5, 23.1, 26.3, 40.6, 55.3, 120.0, 123.2, 127.3, 141.5, 151.0.

2,7-Bis(bromomethyl)-9,9-dibutylfluorene 96

Paraformaldehyde (5.40 g, 0.179 mol) and **95** (4.98 g, 0.018 mol) were combined. The mixture was cooled to 0°C while 30% hydrogen bromide in acetic acid (150 mL) was added slowly. The mixture was stirred overnight at a temperature between 60°C – 70°C. The mixture was extracted with methylene chloride. The solvent was removed to produce a brown oil (3.38 g, 40.7%): mass spectrum, m/z (relative intensity) 464 (M+, 8); ^1H NMR δ 0.6 (m, 6H, CH_3), 1.3 (m, 4H, CH_2), 2.0 (m, 4H, CH_2), 2.1 (s, 4H, CH_2), 4.7 (s, 4H, CH_2Br), 7.5 (m, 6H, Ar-H); ^{13}C NMR ppm 23.4, 26.3, 34.8, 40.3, 55.5, 120.5, 124.1, 125.6, 128.5, 137.4, 141.2, 152.1

2,7-Bis(hydroxymethyl)-9,9-diethylfluorene 98

Ethanol (5 mL) and tetrahydrofuran (1 mL) were added to 9,9-diethylfluorene-2,7-dicarboxyaldehyde **97** (0.25 g, 0.900 mmol). After dissolution, the solution was cooled to 0°C while sodium borohydride (0.051 g, 1.35 mmol) was added over 15 min. The mixture was stirred overnight at room temperature. Additional sodium borohydride (0.05 g,1.32 mmol) was added to ensure complete reduction. The mixture stirred for an additional 2 h. The solvent was evaporated, and the residue was dissolved in water (20 mL). Acetic acid (0.1 mL) was added to remove excess sodium borohydride. This solution was stirred for 30 min then extracted with methylene chloride (3 x 10 mL). The methylene chloride was collected, dried, filtered and evaporated to yield the diol. Recrystallization from ethanol:water (8 mL : 2 mL) yielded a white solid (0.25 g, 97.3%): mass spectrum, m/z (relative intensity) 282 (M+, 57), ^1H NMR δ 0.4 (m, 6H, CH_3), 2.0 (m, 4H, CH_2), 4.8 (s, 4H, CH_2), 7.3 (m, 4H, Ar-H), 7.7 (d, 2H, Ar-H); ^{13}C NMR ppm 8.8, 33.0, 56, 66, 120, 122, 126.3, 140.2, 141.2, 150.9

2,2-Bis[4-(bromomethyl)phenyl]propane 100

Phosphoric acid (5 mL), paraformaldehyde (1.98 g, 0.066 mol), 30% hydrogen bromide in acetic acid (12 mL) and 2,2-diphenylpropane (2.5 g, 0.013 mol) were combined. The mixture was heated at 110°C for 6 h. While the mixture was heated, an additional amount of 30% hydrogen bromide in acetic acid (12 mL) was added dropwise. The mixture was then poured into water (150 mL) and stirred overnight. The solid was filtered and dissolved in methylene chloride (50 mL). The methylene chloride was washed with water (3 x 20 mL), dried over magnesium sulfate and evaporated to yield a white wax. The wax was purified by column chromatography using methylene chloride as the eluant and recrystallized three times from hexane to yield a pure product (3.93 g, 80.7%): mp: 76.5 – 78°C (lit mp 116.5-117.5°C)[27]; mass spectrum, m/z (relative intensity) 382 (M+, 9); ^{1}H NMR δ 1.65 (d, 6H, CH_3), 4.5 (s, 4H, CH_2), 7.3 (m, 8H, Ar-H); ^{13}C NMR ppm 31.0, 34.0, 43.3, 126.2, 127.2, 127.7, 128.5, 129.2, 135.6, 151.1

1,3-Bis(4-bromophenyl)-2-propanone 103

Magnesium oxide (4.12 g, 0.102 mol) and 4-bromophenyl acetic acid (20.0 g, 0.093 mol) were combined, crushed with a mortar and pestle, and mixed for 30 min. The mixture was packed into a 25 mL round bottom flask fitted with a distillation apparatus and placed under vacuum. The system was heated to 250°C for 30 min, then to 350-360°C for 4 h. The system was cooled overnight and extracted with methylene chloride. The methylene chloride was slowly removed to yield yellow crystals (5.47g, 32.0%): mp 106.9 – 108.1°C (lit. mp 121-122 °C)[28]

2,5-Bis(4-bromophenyl)-3,4-diphenylcyclopentadienone 105

Potassium hydroxide (0.6 g, 0.011 mol) was dissolved in ethanol (3 mL). Benzil (2.86 g, 0.021 mol) was combined with **103** (5.00 g, 0.014 mol). and dissolved in hot ethanol (150 mL).

A reflux condenser was attached and the potassium hydroxide in ethanol was added slowly. The solution was refluxed for 15 min, then cooled in ice. The precipitate was filtered and rinsed with cold ethanol (10-15 mL) to yield purple crystals (6.04 g, 89.5%): mp 232.9 - 233.4°C (lit. mp 302.5-303.0 °C)[28]

3,6-Bis(4-bromophenyl)-3,4-diphenylphthalic anhydride 108

Maleic anhydride (1.33 g, 0.014 mol), **105** (5.00 g, 0.010 mol) and bromobenzene (9 mL) were combined. This mixture was refluxed at 180 °C overnight. The mixture was then cooled to room temperature. Bromine (1 mL) in bromobenzene (4 mL) was added. The mixture was again refluxed at 180°C for 3 h. The mixture was cooled in ice. The precipitate was filtered. The remaining solution was added dropwise to petroleum ether (200 mL). The solution was cooled in ice, and the precipitate was filtered. The combined solids were recrystallized from toluene to yield a tan solid (3.40 g, 55.5%): mp 287.2 - 288.1°C

5,6-diphenyl-11,12-dioxo-11,12-dihydroindeno[2.1.a]fluorene 110

Benzene (100mL) was used to dissolve 3,6-Bis(4-phenyl)-3,4-diphenylphthalic anhydride (7.91 g, 0.018 mol), aluminum (III) chloride (11.86 g, 0.089 mol) was added and the mixture was heated at 90°C for 2 h. The mixture was then cooled to about 70°C, poured into dilute hydrochloric acid (300 mL) and stirred overnight. The solid was filtered and recrystallized from acetic acid to yield an orange solid (0.25 g, 8.3%): mp 415°C; mass spectrum, m/z (relative intensity) 434 (M+, 100)

5,6-diphenyl-11,12-dihydroindeno[2.1.a]fluorene 111

Potassium hydroxide (7.8 g, 0.137 mol), **110** (3.0 g, 0.007 mol), diethylene glycol (180 mL) and hydrazine hydrate (7.5 mL) were combined. The mixture was heated to 140°C overnight. The solution was poured into 0.5M hydrochloric acid (300 mL) and stirred for 30 min.

The precipitate was filtered, dried and recrystallized from toluene to yield an orange solid (0.25 g, 9.0%): mass spectrum, m/z (relative intensity) 406 (M+, 100); ^{1}H NMR δ 4.0 (s, 4H, CH_2), 7.2 (m, 18H, Ar-H)

2,10-dibromo-5,6-diphenyl-11,12-dioxo-11,12-dihydroindeno[2.1.a]fluorene 112

Benzene (25 mL) was added to **108** (2.0 g, 0.003 mol). After complete dissolution, aluminum (III) chloride (3.0 g, 0.048 mol) was added. The solution was heated to 90°C for 2 h. The solution was then poured into ice water and magnetically stirred overnight. Recrystallization of the precipitate from 1,2-dichloroethane yielded an orange solid (0.86 g, 44.3%).

2,10-dibromo-5,6-diphenyl-11,12-dihydroindeno[2.1.a]fluorene 113

Potassium hydroxide (2.6 g, 0.046 mol), **112** (0.9 g, 0.002 mol), diethylene glycol (60 mL) and hydrazine hydrate (2.5 mL) were combined. The mixture was heated to 160°C until completely dissolved, then to 180 – 190°C overnight. The solution was poured into 0.5M hydrochloric acid (100 mL) and stirred for 30 min. The precipitate was filtered, dried and recrystallized from toluene (0.21 g, 24.6%).

1,4-diiodo-2,5-dimethylbenzene 115

Acetic acid (500 mL) was mixed with 2M sulfuric acid (100 mL), periodic acid (22.4 g, 0.98 mol), p-xylene **114** (26.08 g, 0.246) and iodine (50.15 g, 0.198 mol). The solution was heated at 70°C for 3 h then cooled to 0°C for 1 h. The precipitate was filtered and recrystallized from 2:5 chloroform:methanol: mp 96.3 – 96.8°C (lit. mp 103-104 °C)[29]; ^{1}H NMR δ 2.35 (s, 6H, CH_3), 7.65 (s, 2H, Ar-H)

1,4-diphenyl-2,5-dimethylbenzene 118

Magnesium (4.85 g, 0.200 mol) was stirred in diethyl ether (20 mL). A solution (10 mL) of bromobenzene **116** (31.72 g, 0.202 mol) in diethyl ether (80 mL) was added. The mixture was heated at a gentle reflux while the remaining bromobenzene in diethyl ether was added. The mixture was heated at a gentle reflux for an additional 2 h and cooled to room temperature. Nickel (II) acetylacetonate **117** (0.459 g, 0.002 mol) was added slowly. A solution of **115** (28.81 g, 0.080 mol) in diethyl ether (200 mL) was added slowly. The solution was heated at a gentle reflux overnight. The solution was poured into ice (about 1 kg) and stirred with 50% hydrochloric acid (200 mL). After all the ice melted, the aqueous and ether phases were separated. The aqueous phase was extracted with diethyl ether (3 x 200 mL). The ether phases were combined, washed with water and dried over magnesium sulfate. The liquid was removed leaving a solid. The solid was recrystallized from ethanol to yield a white solid: mp 159.9-160.2°C (lit. mp 182-184 °C)[30]; ^{1}H NMR δ 2.25 (s, 6H, CH_3), 7.3 (m, 12H, Ar-H)

RESULTS AND DISCUSSION

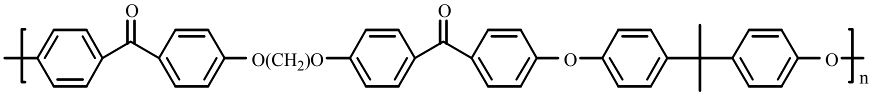
PEEK Polymer Molecular Weight Determinations

The samples were prepared at a concentration of approximately 1mg/mL (**Table 6**) using degassed nMP with 0.5% lithium bromide as solvent. The samples were filtered using a 0.2µ nylon syringe filter prior to injection into the GPC.

Gel permeation chromatography (GPC) is a method of determining the number average molecular weight (Mn) and the weight average molecular weight (Mw) of a polymer. The number average molecular weight (Mn) is the sum of all the molecular weights of the sample divided by the total number of molecules. The weight average molecular weight (Mw) is the ratio of a particular weight of a molecule to the total weight of the sample. Both of these are important in determining the polydispersity of the polymer. The polydispersity is a measure of the distribution of sizes of molecules in the sample.

GPC is a method of separation. Separation occurs through a series of columns that are packed with porous material. The largest molecules will elute first because they will travel the shortest route. The small molecules will elute last because they will move through the pores traveling the longest path. This is very simplistic view of what is occurring in the columns. The process is more complex, but has not been completely determined as of yet.[30]

The results of the analysis are reported in **Table 6** and **Table 7**. The GPC traces can be seen in **Figures 22-30**.



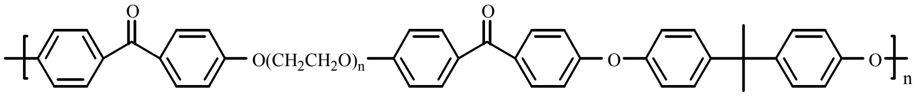
19, n = 2
20 ,n = 3
21, n = 4
22, n = 5
23, n = 6

Table 6

GPC Results for Poly(ether ether ketone)s with Oxyalkylene Linkages

Compound	Number of Carbons in bridge	Concentration (mg/mL)	Mn	Polydispersity
19	2	10.5	39,200	2.964
20	3	9.5	38,600	1.915
21	4	9.9	38,800	2.731
22	5	10.0	47,500	2.053
23	6	9.8	18,500	2.330

There is a general increase in the molecular weights as the oxyalkylene link increases in length. The polydispersity of the polymers are all greater than one. This means that the there is a larger distribution of sizes in the sample. A polydispersity of one would indicate that all of the molecules are the same size. As the value increases, there is a greater variety of sizes in the sample.



36, n = 2
37, n = 3
38, n = 4
39, n = 5

Table 7

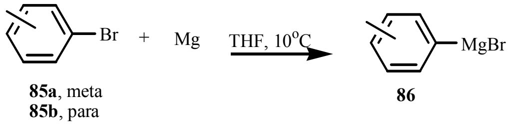
GPC Results for Poly(ether ether ketone)s with Oxyethylene Linkages

Compound	Number of Carbons in bridge	Concentration (mg/mL)	Mn	Polydispersity
36	2	10.5	25,800	1.872
37	3	9.8	36,400	4.214
38	4	10.0	55,800	2.143
39	5	9.7	55,900	2.240

Again, there is an increase in the molecular weight as the oxyethylene link increases in length.

Polybenzoxazoles

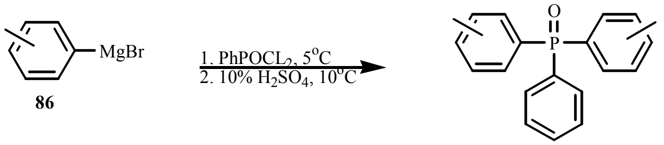
Bis(3-methylphenyl)phenylphosphine oxide **87** and bis(4-methylphenyl) phenylphosphine oxide **88** were prepared by forming a Grignard from the appropriate bromotoluene **85a** or **85b**. After complete dissolution of the magnesium,



85a, meta
85b, para

86

phenylphosphonic dichloride was added. A replacement of the chlorine with 3-methylphenyl and 4-methylphenyl occurred to form bis(3-methylphenyl)phenylphosphine oxide **87** and bis(4-methylphenyl)phenylphosphine oxide **88**.

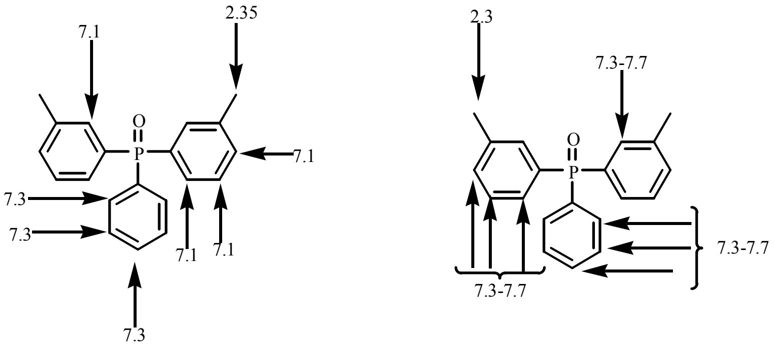


86

87, meta
88, para

Recrystallization in heptane (**88**) or hexane (**87**) produced **87** and **88** in high yields (97% and 85%, respectively).

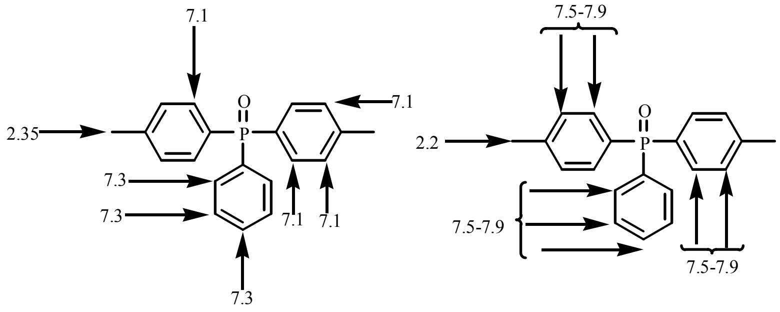
Experimental proton NMR values (**Figures 2** and **3**) correlate with the calculated values. The individual NMR spectra can be seen in **Figures 31** and **33**.



87
Calculated ^{1}H NMR Shifts

87
Experimental ^{1}H NMR Shifts

Figure 2

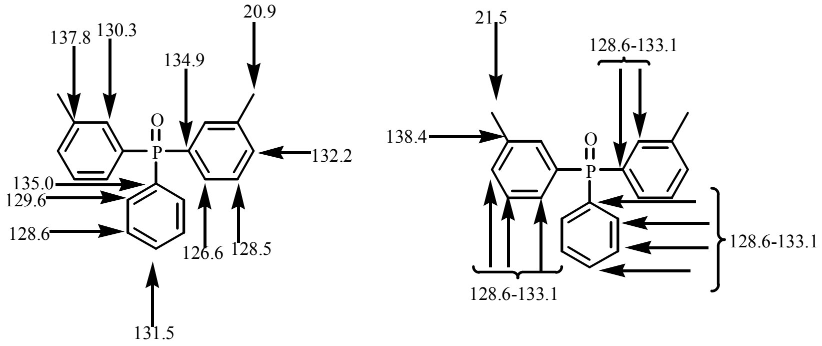


88
Calculated ^{1}H NMR Shifts

88
Eperimental ^{1}H NMR Shifts

Figure 3

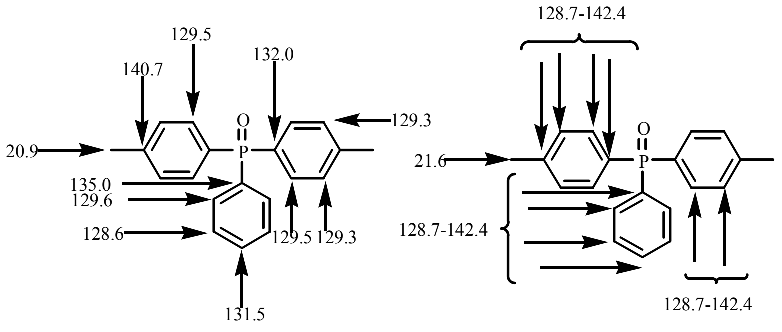
There is also good correlation of the experimental ^{13}C NMR shifts to the calculated values (**Figures 4** and **5**). The NMR spectra can be seen in **Figures 32** and **34**.



87
Calculated ^{13}C NMR Shifts

87
Experimental ^{13}C NMR Shifts

Figure 4

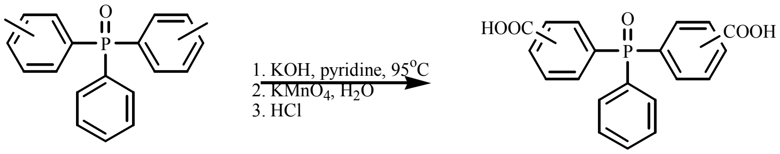


88
Calculated ^{13}C NMR Shifts

88
Eperimental ^{13}C NMR Shifts

Figure 5

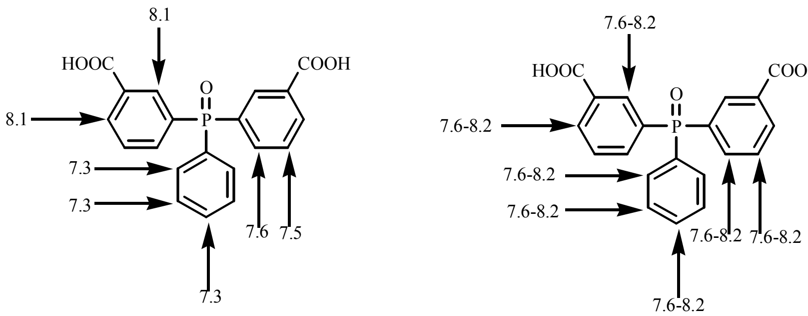
An oxidation of **87** and **88** was accomplished in basic solution using potassium permanganate as the oxidizing agent. The by-product manganese dioxide was removed by filtration. Partial purification was accomplished by extraction of the product solution with methylene chloride. The carboxylic acid solutions were then acidified with hydrochloric acid to pH2. Precipitation of **89** and **90** allowed collection by filtration. Both **89** and **90** were collected in good yield (85% and 78%, respectively). Fifty grams of each were prepared.



87, meta
88, para

89, meta
90, para

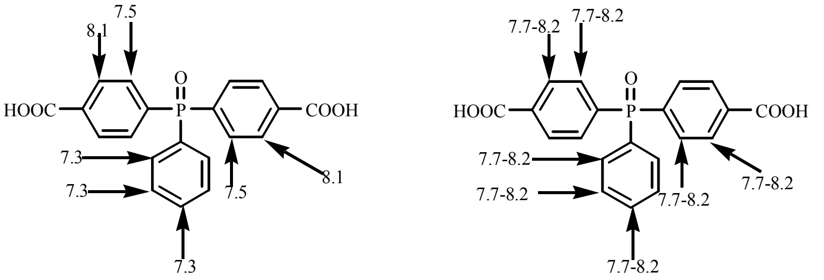
The proton NMR calculated values can be seen below (**Figures 6** and **7**). The NMR spectra can be seen in **Figures 35** and **37**. For both **89** and **90**, there was a multiplet between 7.7 and 8.2.



89
Calculated ^{1}H NMR Shifts

89
Experimental ^{1}H NMR Shifts

Figure 6

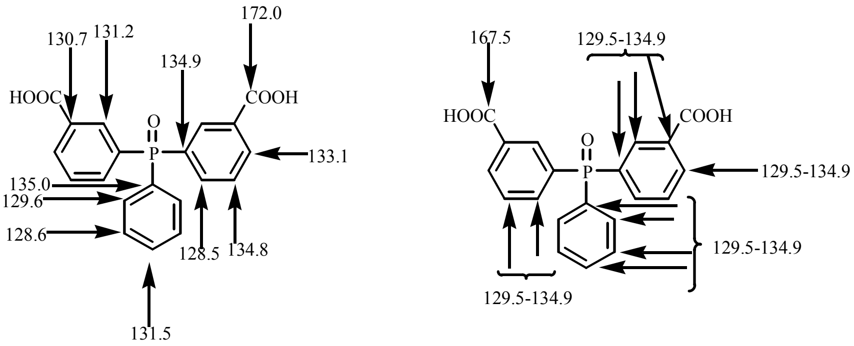


90
Calculated ^{1}H NMR Shifts

90
Eperimental ^{1}H NMR Shifts

Figure 7

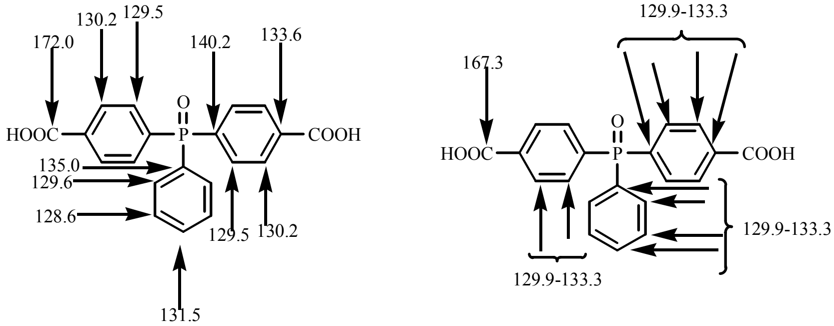
The experimentally determined carbon NMR values correlate to the calculated values (**Figures 8** and **9**). The NMR spectra can be seen in **Figures 36** and **38**.



89
Calculated ^{13}C NMR Shifts

89
Experimental ^{13}C NMR Shifts

Figure 8



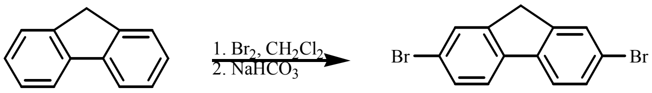
90
Calculated ^{13}C NMR Shifts

90
Experimental ^{13}C NMR Shifts

Figure 9

Poly(phenylene vinylene)

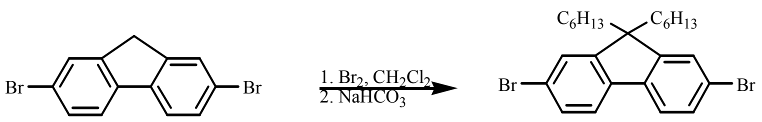
Fluorene **91** was brominated in methylene chloride using bromine and a catalytic amount of iodine to yield 2,7-dibromofluorene **92** in 96% yield.



91 **92**

Several derivatives of 2,7-dibromofluorene **92** were synthesized. These include 9,9-dihexyl-2,7-dibromofluorene **93** and 9,9-dibutyl-2,7-dibromofluorene **96**.

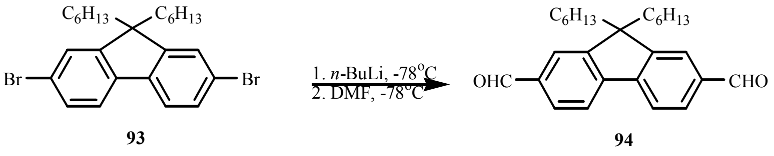
Preparation of 2,7-dibromo-9,9-dihexylfluorene **93** was accomplished by the reaction of **92** in basic DMSO and potassium iodide with n-hexyl bromide. Water was added to quench the reaction. Purification was achieved by extraction of the reaction



92 **93**

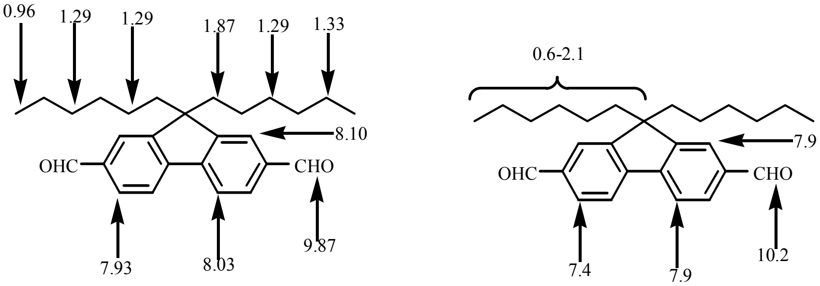
mixture with chloroform. Recrystallization of the residue with hexane afforded **93** at 82% yield.

The synthesis of 9,9-dihexylfluorene-2,7-dicarboxyaldehyde **94** was accomplished by the reaction of **93** with n-butyl lithium followed by



N,N-dimethylformamide (DMF). Water was added to quench the reaction. The dialdehyde **94** was extracted into diethyl ether and purified by column chromatography using 20% ethyl acetate in hexane as the eluant. The dialdehyde was collected in 82% yield.

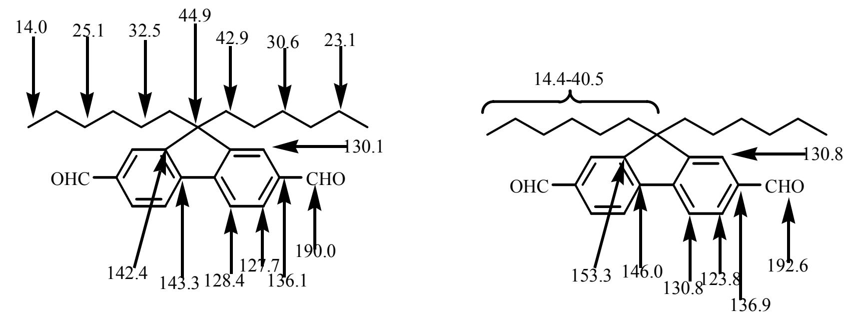
Proton and carbon NMR experimental and calculated values can be seen in **Figures 10** and **11**. The NMR spectra can be seen in **Figures 39** and **40**.



94
Calculated ^{1}H NMR Shifts

94
Experimental ^{1}H NMR Shifts

Figure 10



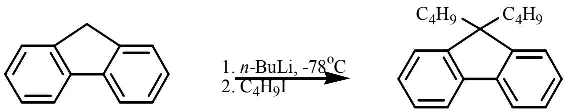
94
Calculated ^{13}C NMR Shifts

94
Experimental ^{13}C NMR Shifts

Figure 11

Infrared characterization (**Figure 52**) of **94** shows the typical aliphatic C-H stretch at 2928 cm^{-1}, aromatic C-H at 3055 cm^{-1}, the aldehyde carbonyl at 1694 cm^{-1} and the aldehyde CH at 2729 cm^{-1}.

Another derivative of **92** that was prepared was 2,7-bis(bromomethyl)-9,9-dibutylfluorene **96**.

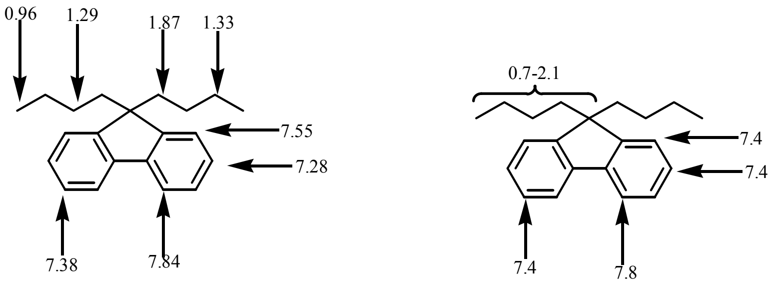


91

95

Initially, fluorene **91** was reacted with n-butyl iodide using n-butyl lithium in diethyl ether to form 9,9-dibutylfluorene **95**. Water was added to quench the reaction. The ether phase was collected and dried. The resulting residue was used without further purification.

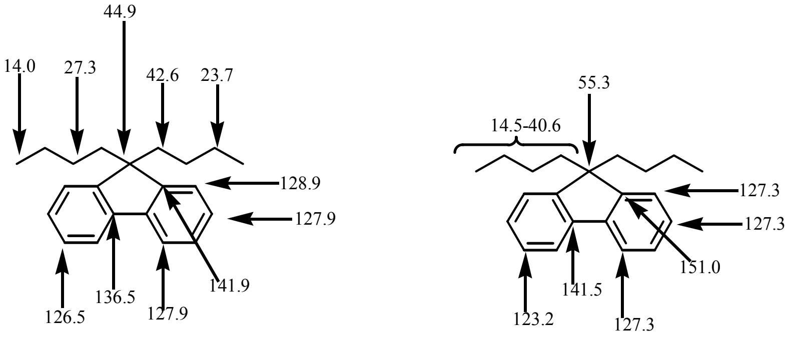
Proton and carbon NMR experimental and calculated values are shown below (**Figures 12** and **13**). The NMR spectra can be seen in **Figures 41** and **42**.



95
Calculated ^{1}H NMR Shifts

95
Experimental ^{1}H NMR Shifts

Figure 12



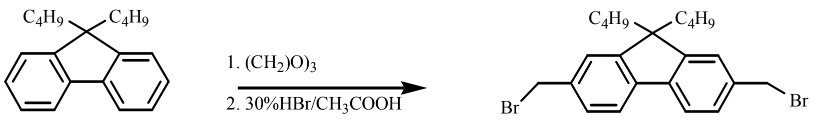
95
Calculated ^{13}C NMR Shifts

95
Experimental ^{13}C NMR Shifts

Figure 13

Infrared characterization (**Figure 53**) of **95** shows the typical aromatic C-H stretch at 3064 and 3014 cm^{-1} and the aliphatic C-H stretch at 2859 cm^{-1}.

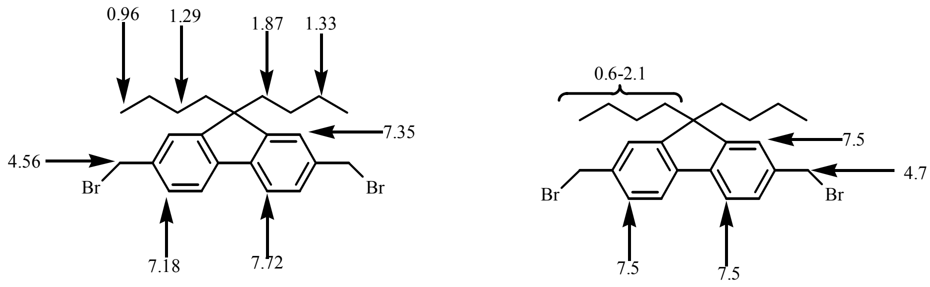
Paraformaldehyde was combined with **95** and cooled to 0^{o}C. To this reaction mixture, 30% hydrogen bromide in acetic acid was added. The formaldehyde and



95 **96**

bromine added to form 2,7-bis(bromomethyl)-9,9-dibutylfluorene **96** at 41% yield.

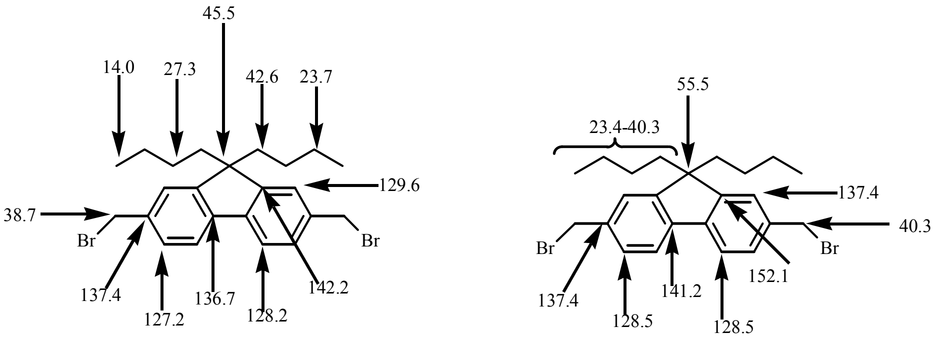
Proton and carbon NMR experimental and calculated values are shown below (**Figures 14** and **15**). The NMR spectra can be seen in **Figures 43** and **44**.



96
Calculated ^{1}H NMR Shifts

96
Experimental ^{1}H NMR Shifts

Figure 14



96
Calculated ^{13}C NMR Shifts

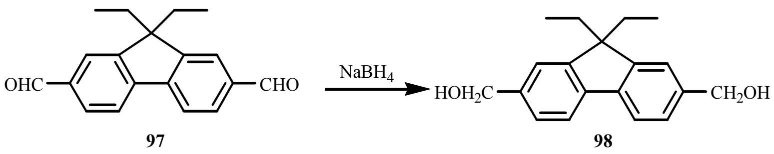
96
Experimental ^{13}C NMR Shifts

Figure 15

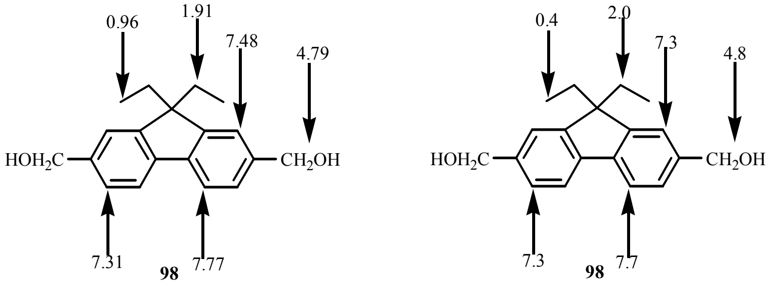
Infrared characterization (**Figure 54**) of **96** shows the aliphatic C-H stretch at 2930 and 2955 cm^{-1} and the aromatic C-H stretch at 3030 cm^{-1}

A sample of 9,9-diethyl-2,7-dicarboxaldehyde **97** was acquired from WPAFB. Compound **97** was used as a model to determine the ease of reduction of **94**. Compound

97 was reduced using sodium borohydride to form 2,7-bis(hydroxymethyl)-9,9-diethylfluorene **98** in 97% yield.



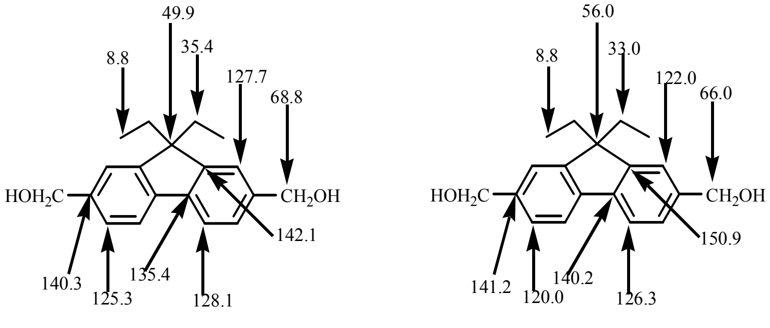
Proton and carbon NMR experimental and calculated values are shown below (**Figures 16** and **17**). The NMR spectra can be seen in **Figures 45** and **46**.



Calculated ^1H NMR Shifts

Experimental ^1H NMR Shifts

Figure 16



98

Calculated ^{13}C NMR Shifts

98

Experimental ^{13}C NMR Shifts

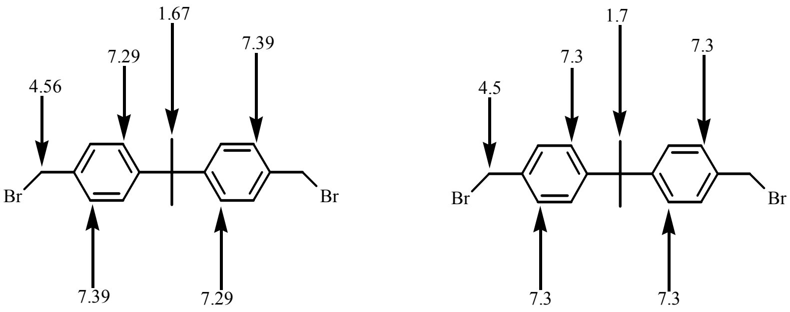
Figure 17

Infrared characterization (**Figure 55**) shows the hydroxyl peak at 3324 cm^{-1}, the aromatic C-H stretch at 3023 cm^{-1} and the aliphatic C-H stretches at 2961, 2927 and 2873 cm^{-1}.

Compound **100** was formed from the reaction of 2,2-diphenylpropane **99** with paraformaldehyde and hydrogen bromide. The product **100** was collected in approximately 81% yield after purification by chromatography and recrystallization.

99 **100**

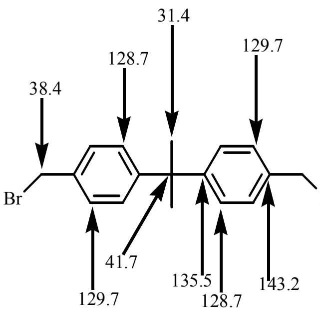
Experimental and calculated proton and carbon NMR values are shown below (**Figures 18** and **19)**. Proton and Carbon NMR spectra can be seen in **Figures 47** and **48**.



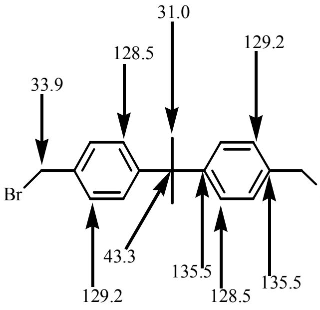
100
Calculated ^{1}H NMR Shifts

100
Experimental ^{1}H NMR Shifts

Figure 18



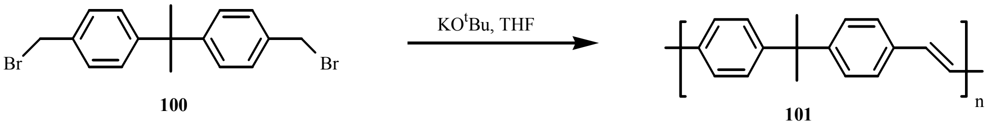
100
Calculated ^{13}C NMR Shifts



100
Experimental ^{13}C NMR Shifts

Figure 19

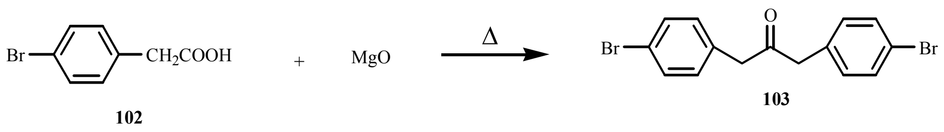
A polymerization of 2,2-bis[4-(bromomethyl)phenyl]propane **100** was performed.



Potassium *t*-butoxide was used as the base and tetrahydrofuran as solvent. There was no formation of a polymer. These results show the mechanism in **Scheme 1** is likely to be correct because the conjugation of the monomer is important. If the conjugation was not important, the polymerization of 2,2-bis[4-(bromomethyl)phenyl]propane **100** would have formed a polymeric product.

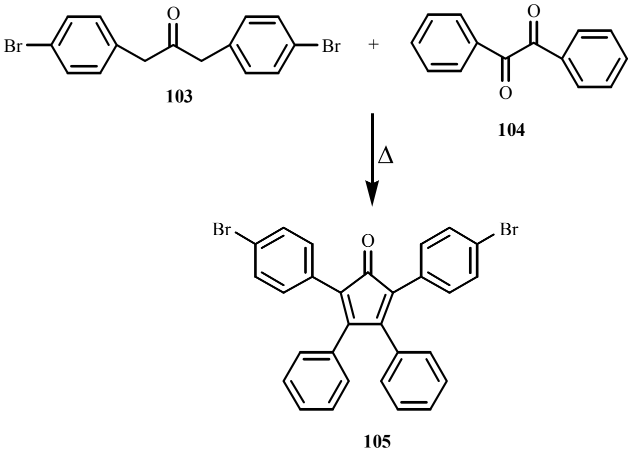
Nonlinear Optical Materials

The first step in the synthesis of the indenofluorene nonlinear materials involved the reaction of magnesium oxide with 4-bromophenyl acetic acid **102** to produce 1,3-bis(4-bromophenyl)-2-propanone **103**.

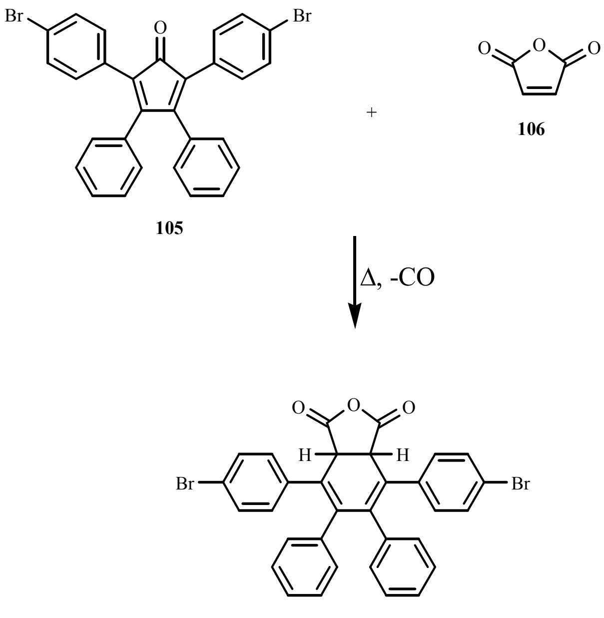


The yield of this reaction is always low but was slightly improved to 32% when the two reagents were ground together with a mortar and pestle. This yield is consistent with the literature[27]. This increase in yield is attributed to the increased surface area exposed for reaction.

Benzil **104** and 1,3-bis(4-bromophenyl)-2-propanone **103** were combined[31]. To this mixture, potassium hydroxide dissolved in ethanol was added slowly. The resulting precipitate, 2,5-bis(4-bromophenyl)-3,4-diphenylcyclopentadienone **105** was collected at 90% yield.

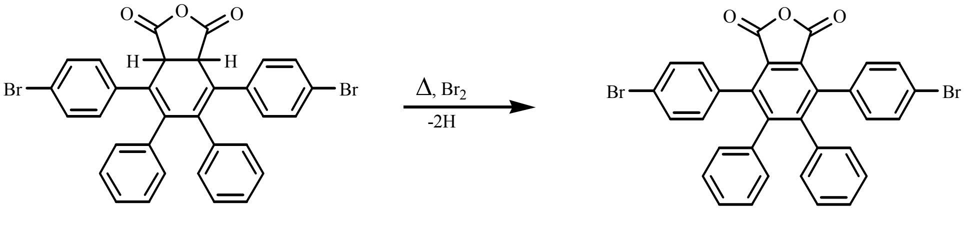


Maleic anhydride **106** was added to 2,5-bis(4-bromophenyl)-3,4-diphenylcyclopentadienone **105** in bromobenzene. Upon heating, the maleic anhydride added to the cyclopentadienone ring producing a six membered diene ring **107** while eliminating carbon monoxide.



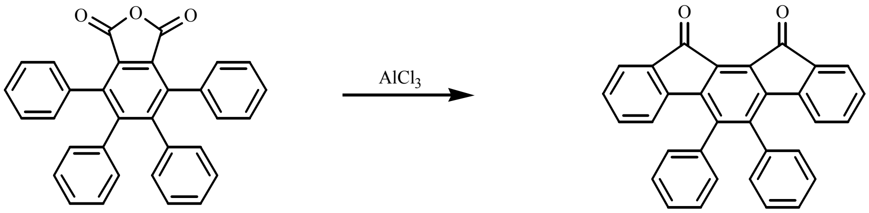
105 **106** **107**

Upon further heating and the addition of bromine, the six membered ring **107** aromatized after elimination of two hydrogens producing 3,6-bis(4-bromophenyl)-3,4-diphenylphthalic anhydride **108**.



107 **108**

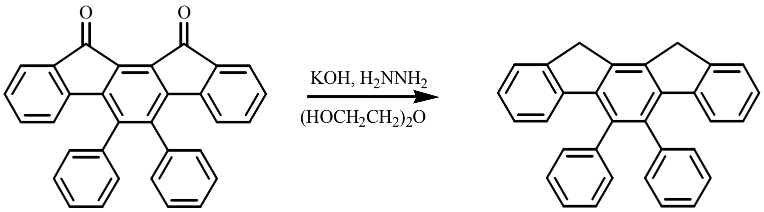
Two related compounds were prepared in the nonbrominated form, namely 5,6-diphenyl-11,12-dioxo-11,12-dihydroindeno[2.1-a]fluorene **110** and 5,6-diphenyl-11,12-dihydroindeno[2.1-a]fluorene **111**.



109 **110**

Aluminum chloride was added to a solution of 3,6-bis(4-phenyl)3,4-diphenylphthalic anhydride **109** in benzene. Compound **109** undergoes a Friedel Crafts acylation reaction to give 5,6-diphenyl-11,12-dioxo-11,12-dihydroindeno[2.1-a]fluorene **110**.

To produce 5,6-diphenyl-11,12-dihydroindeno[2.1-a]fluorene **111**,



110 **111**

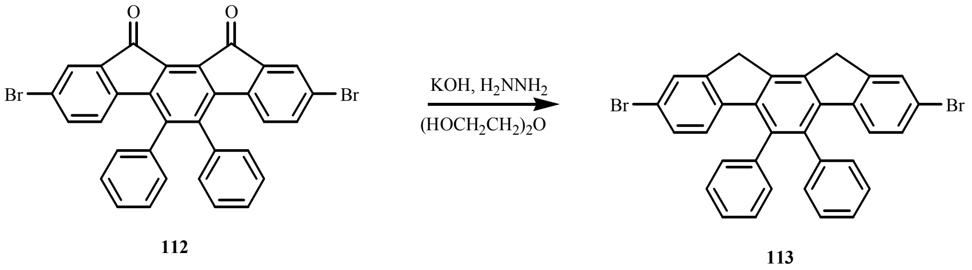
5,6-diphenyl-11,12-dioxo-11,12-dihydroindeno[2.1-a]fluorene **110** was subjected to a Wolff-Kishner reaction using the Huang-Minlon modification. The Wolff-Kishner reaction involves the heating of the ketone in hydrazine hydrate with a base. The Huang-Minlon modification, in which the reaction is carried out in refluxing diethylene glycol, is most commonly used today.[32]

The brominated forms of these compounds underwent the same reactions.

Aluminum chloride was added to a solution of 3,6-bis(4-bromophenyl)3,4-diphenylphthalic anhydride **108** in benzene. The 3,6-bis(4-bromophenyl)3,4-

diphenylphthalic anhydride **108** undergoes a Friedel Crafts acylation reaction to give 2,10-dibromo-5,6-diphenyl-11,12-dioxo-11,12-dihydroindeno[2.1-a]fluorene **112**.

To produce 2,10-dibromo-5,6-diphenyl-11,12-dihydroindeno[2.1-a]fluorene **113**,

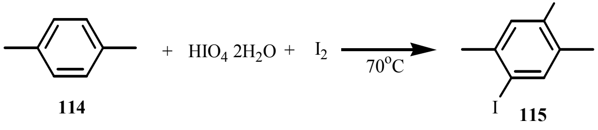


2,10-dibromo-5,6-diphenyl-11,12-dioxo-11,12-dihydroindeno[2.1-a]fluorene **112** was subjected to a Wolff-Kishner reaction using the Huang-Minlon modification.

An attempt at alkylating this compound **113** was made, but the results were inconclusive. Alkylation of the fluorene derivatives showed an increase in nonlinear optical character. It was theorized that the increase was due to less aggregation of the species. It was believed that alkylation of the indenofluorene derivatives would also follow this example.

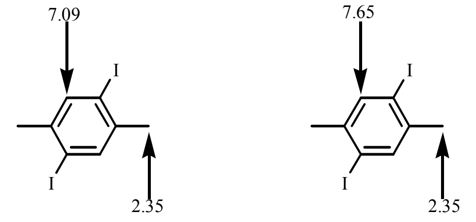
The yields of the Friedel-Crafts acylation reaction and the Wolff-Kishner reaction were consistently low for both the nonbrominated (8%, 9%, respectively) and brominated (44%, 25%) compounds.

An additional project involved the synthesis of the c-fused indenofluorene.



Periodic acid dihydrate and iodine were added to a solution of p-xylene **114** in 2.5% sulfuric acid in acetic acid. The p-xylene **114** was converted to 1,4-diiodo-2,5-dimethylbenzene **115** in 98% yield.

Proton NMR experimental and calculated shifts are shown below (**Figure 20**). The NMR spectrum can be seen in **Figure 50**.



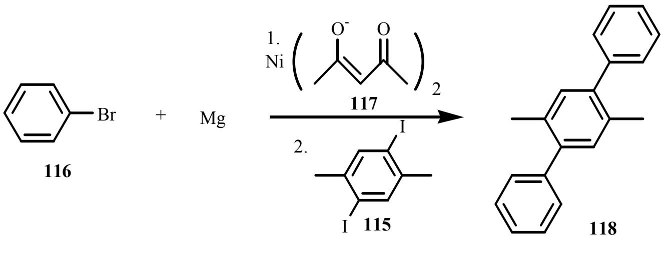
115
Calculated ^{1}H NMR Shifts

115
Experimental ^{1}H NMR Shifts

Figure 20

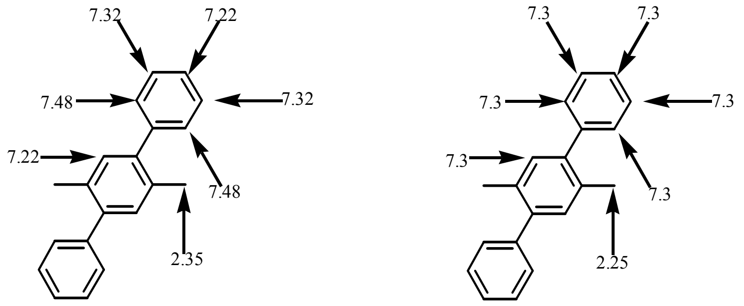
Conversion of 1,4-diiodo-2,5-dimethylbenzene **115** to 1,4-diphenyl-2,5-dimethylbenzene **119** was accomplished via a Grignard reaction using nickel (II) acetylacetonate **117** as a coupling catalyst.

Bromobenzene **116** and magnesium in ether were refluxed until the magnesium was completely dissolved. The catalyst **117** was added followed by a solution of 1,4-diiodo-2,5-dimethylbenzene **115** in diethyl ether. After about 16 hours of reflux, 1,4-diphenyl-2,5-dimethylbenzene **118** was collected as white needles. The reaction



produced the terphenyl **118** in 9.7% yield. This project was abandoned due to the consistently low yields of this reaction.

Proton NMR experimental and calculated values are shown below (**Figure 21**). The NMR spectrum can be seen in **Figure 51**.



118
Calculated ^{1}H NMR Shifts

118
Experimental ^{1}H NMR Shifts

Figure 21

Conclusions and Future Work

Polybenzoxazoles

Each of the following compounds were prepared in 50g quantities for polymerization to form polybenzoxazoles: bis(3-methylphenyl)phenylphosphine oxide, bis(4-methylphenyl)phenylphosphine oxide, bis(3-carboxyphenyl)phenylphosphine oxide and bis(4-carboxyphenyl)phenylphosphine oxide.

Poly(phenylene vinylene)

The compound 9,9-dihexylfluorene-2,7-dicarboxaldehyde **94** was prepared. In addition, 2,7-bis(bromomethyl)-9,9-dibutylfluorene **96** was prepared. These compounds will be used in future work to form isolated segments of conjugation in poly(phenylene vinylene) polymers.

Nonlinear Optical Materials

Each of the following compounds were prepared, but in yields that are not conducive to scaled up synthetic processes: 5,6-diphenyl-11,12-dioxo-11,12-dihydroindeno[2.1-a]fluorene **110**, 5,6-diphenyl-11,12-dihydroindeno[2.1-a]fluorene **111**, 2,10-dibromo-5,6-diphenyl-11,12-dioxo-11,12-dihydroindeno[2.1-a]fluorene **112** and 2,10-dibromo-5,6-diphenyl-dioxo-11,12-dihydroindeno[2.1-a]fluorene **113**. The c-fused system was never completed due to the consistently low yields (approximately 10%) in the formation of 1,4-diphenyl-2,5-dimethylbenzene **118**.

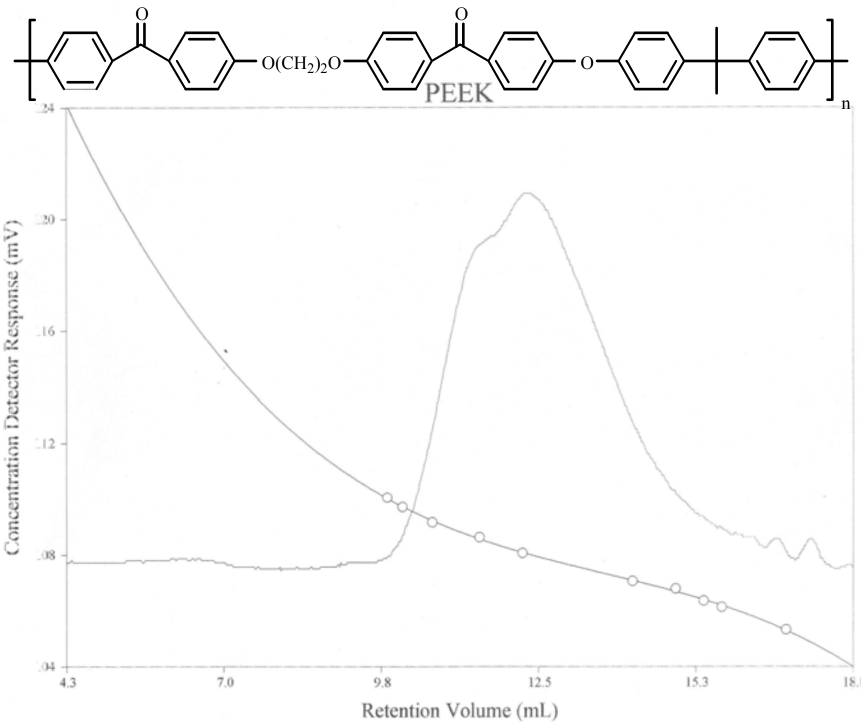


Figure 22 GPC Trace of **19**

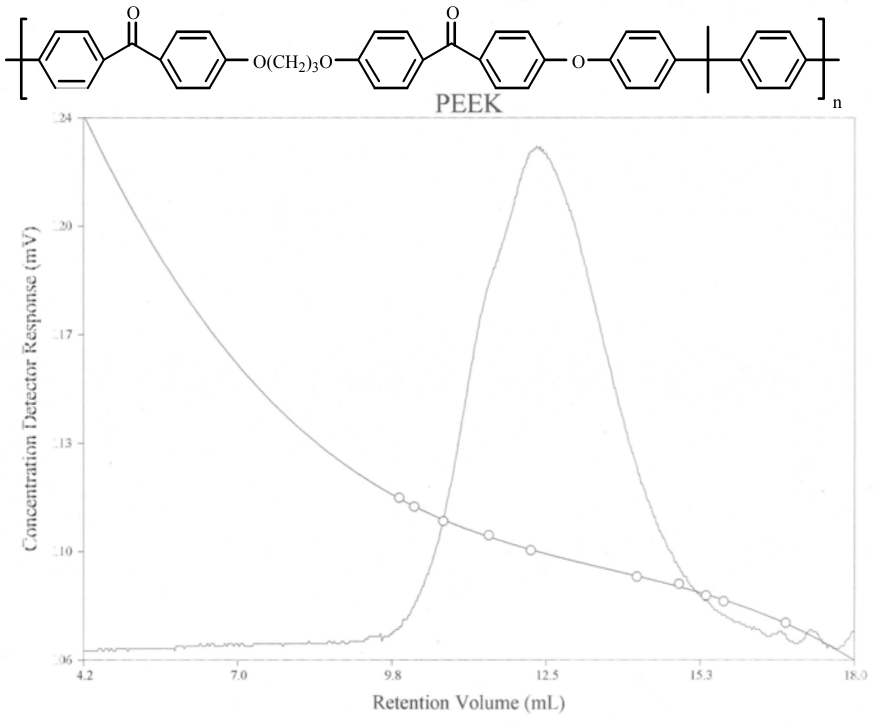


Figure 23 GPC Trace of **20**

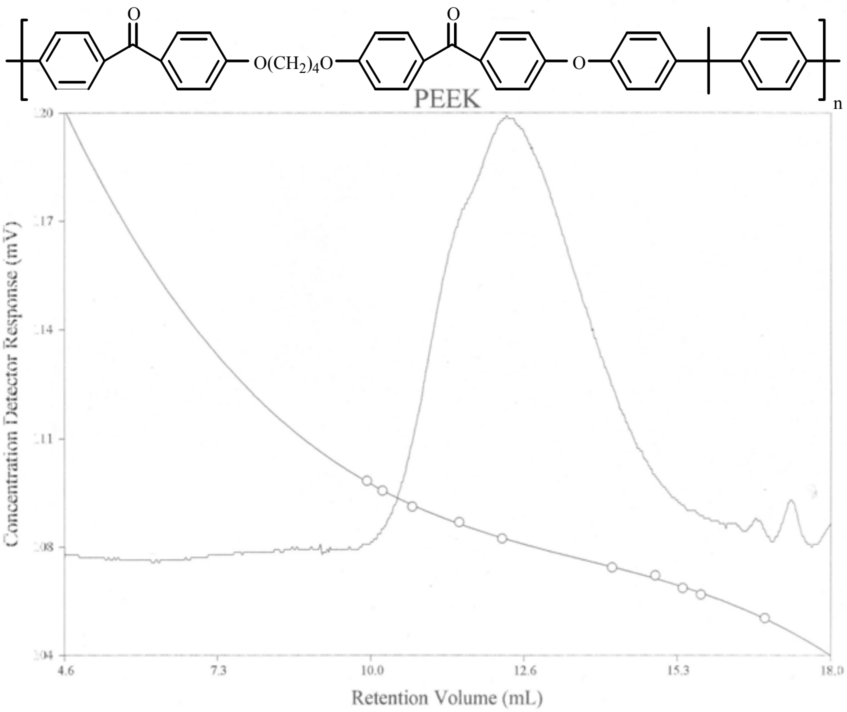


Figure 24 GPC Trace of **21**

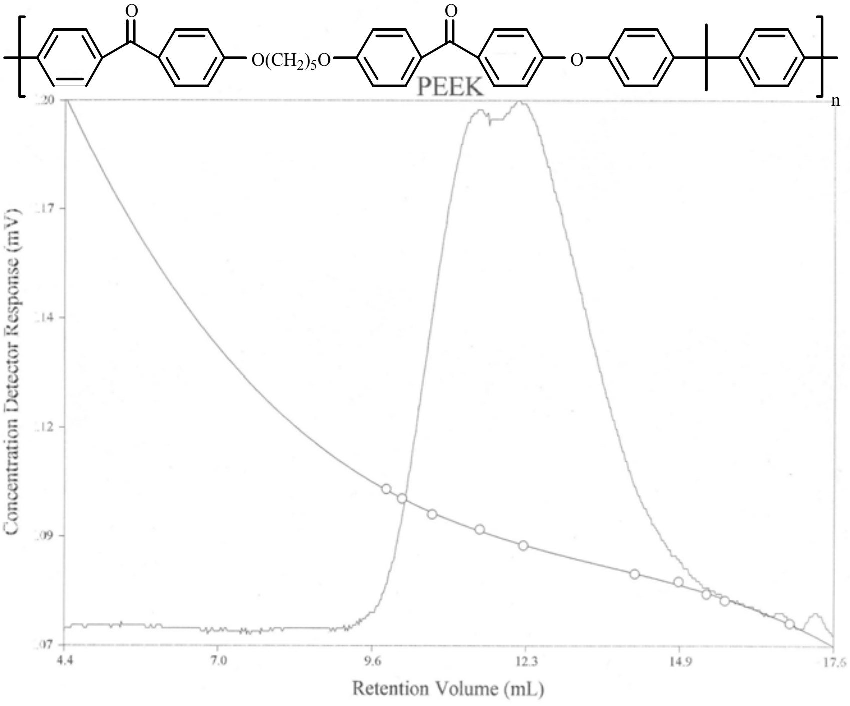


Figure 25 GPC Trace of **22**

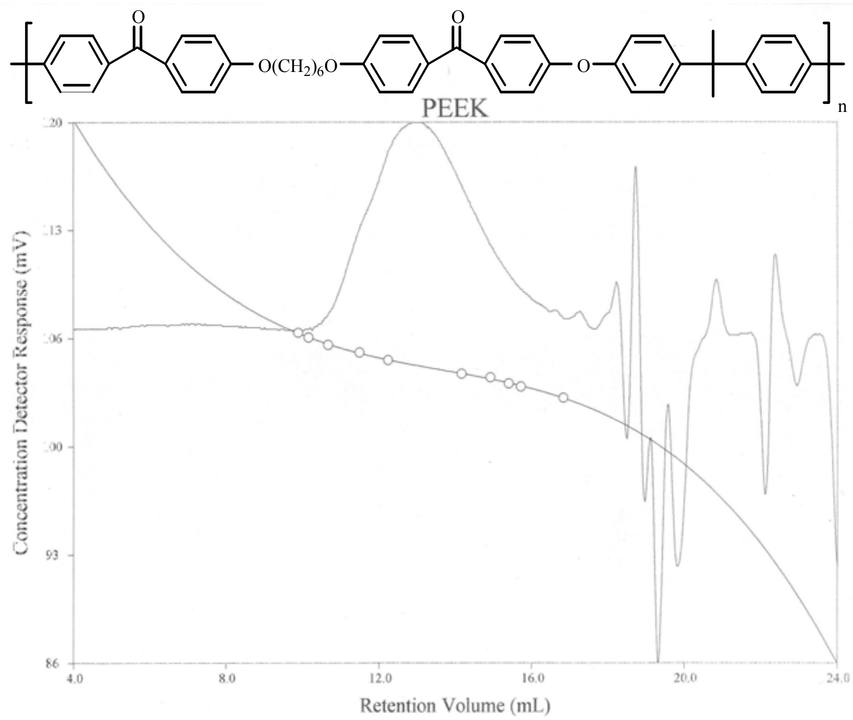


Figure 26 GPC Trace of **23**

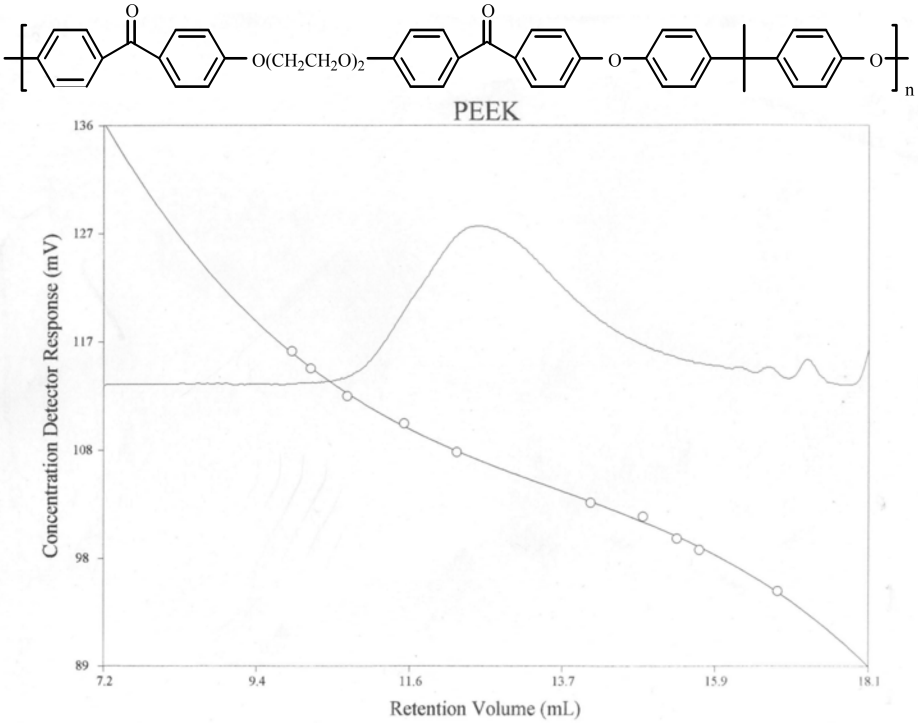


Figure 27 GPC Trace of **36**

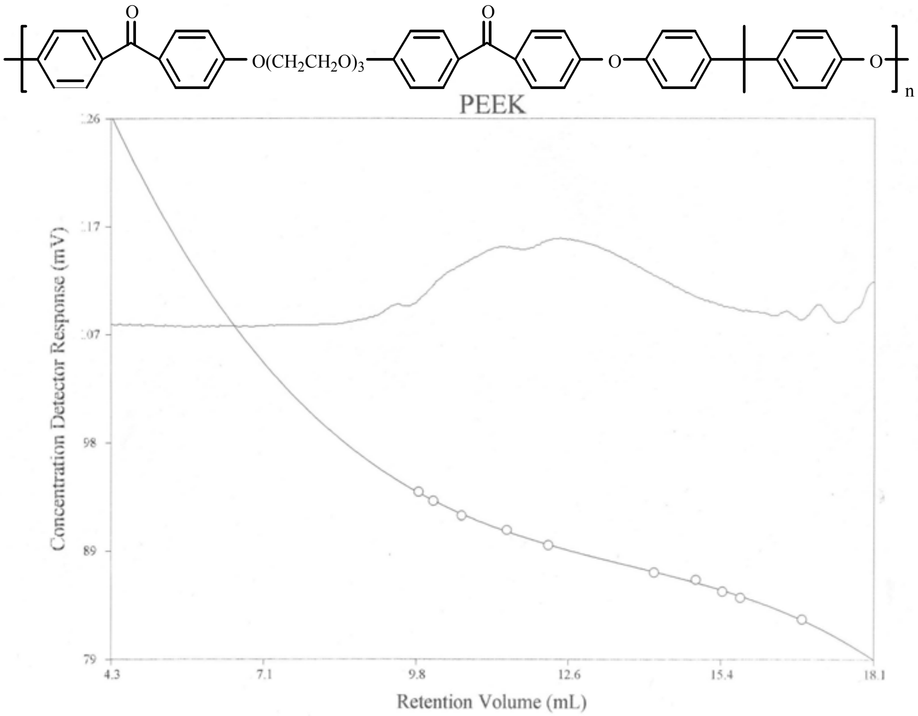


Figure 28 GPC Trace of **37**

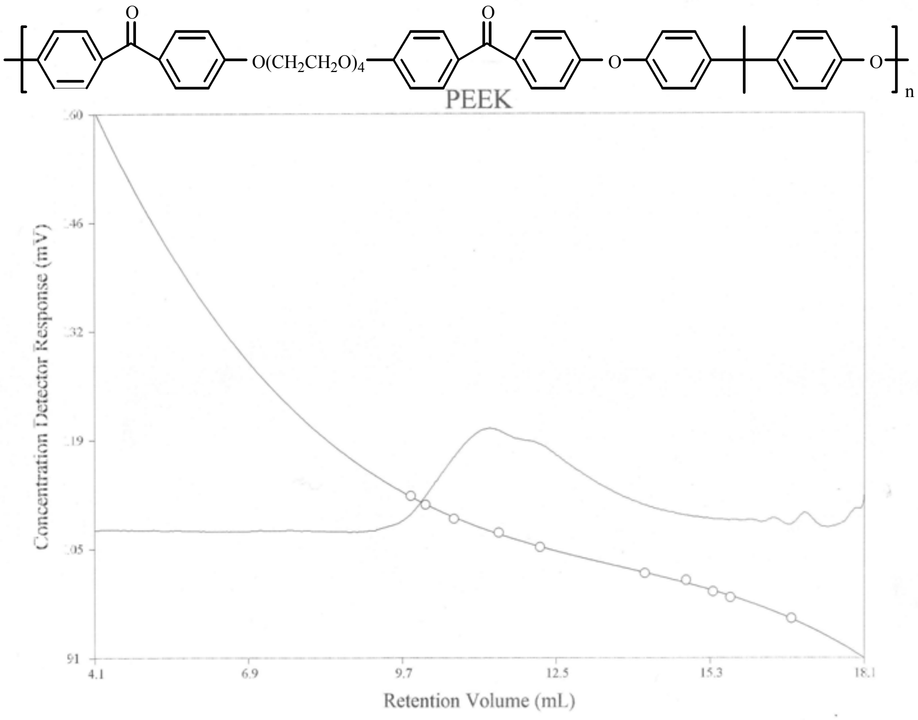


Figure 29 GPC Trace of **38**

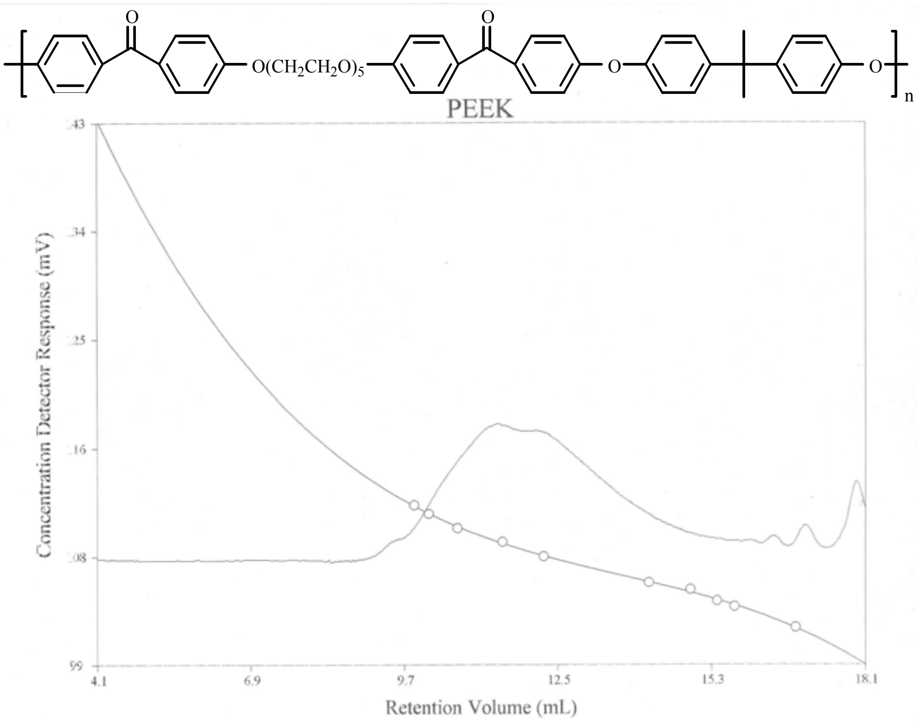


Figure 30 GPC Trace of **39**

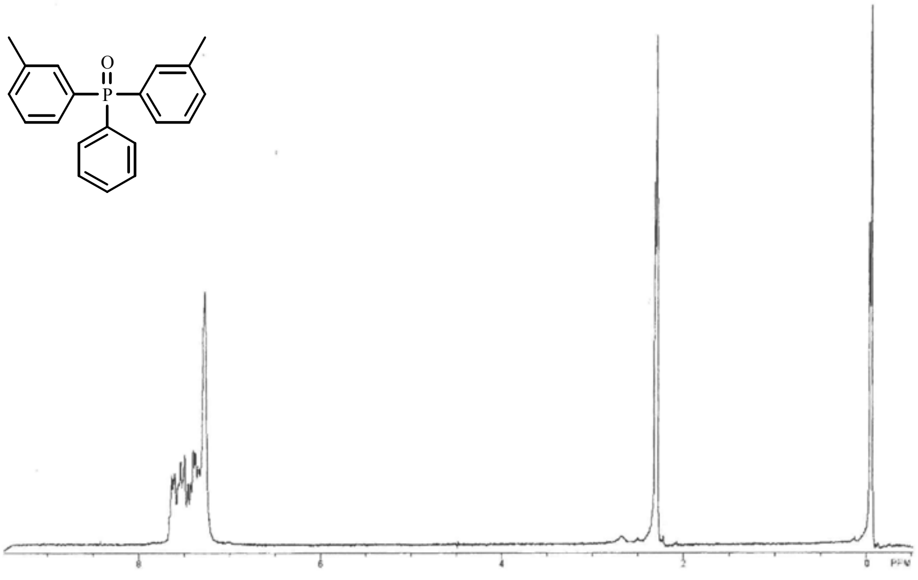


Figure 31 Proton NMR of **87**

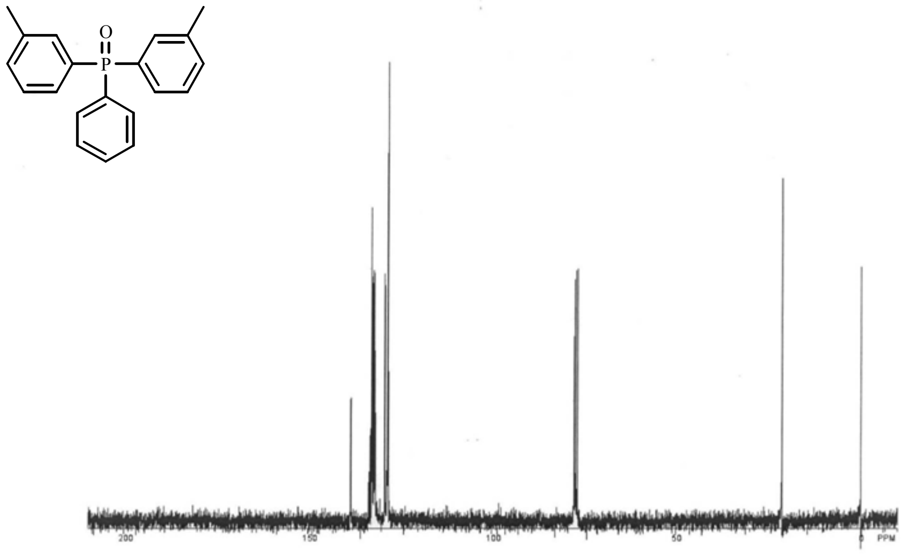


Figure 32 Carbon NMR of **87**

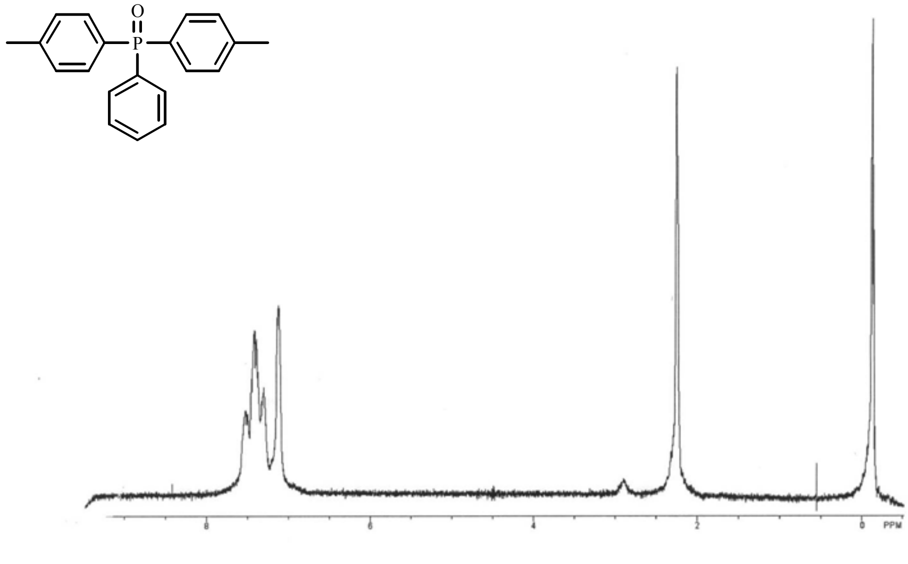


Figure 33 Proton NMR of **88**

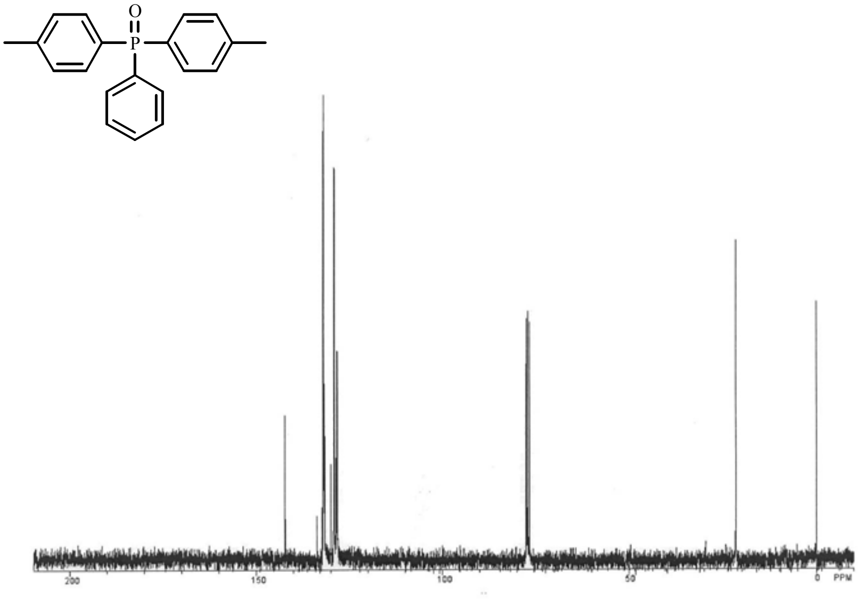


Figure 34 Carbon NMR of **88**

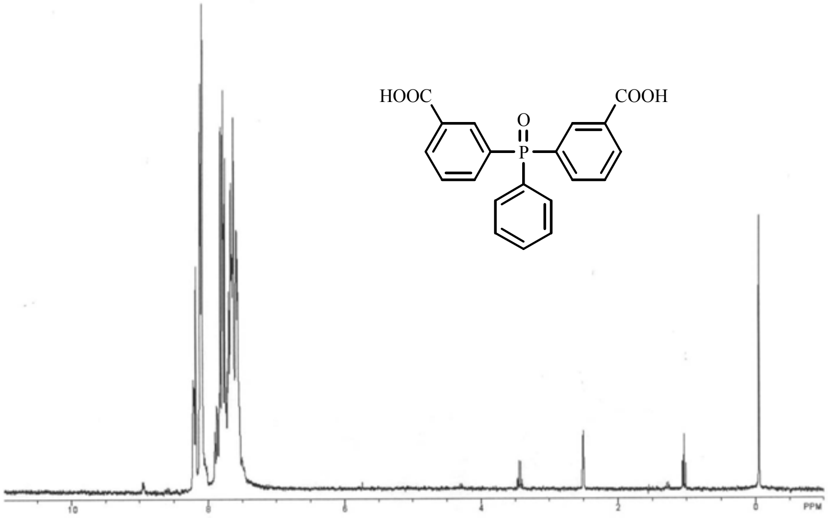


Figure 35 Proton NMR of **89**

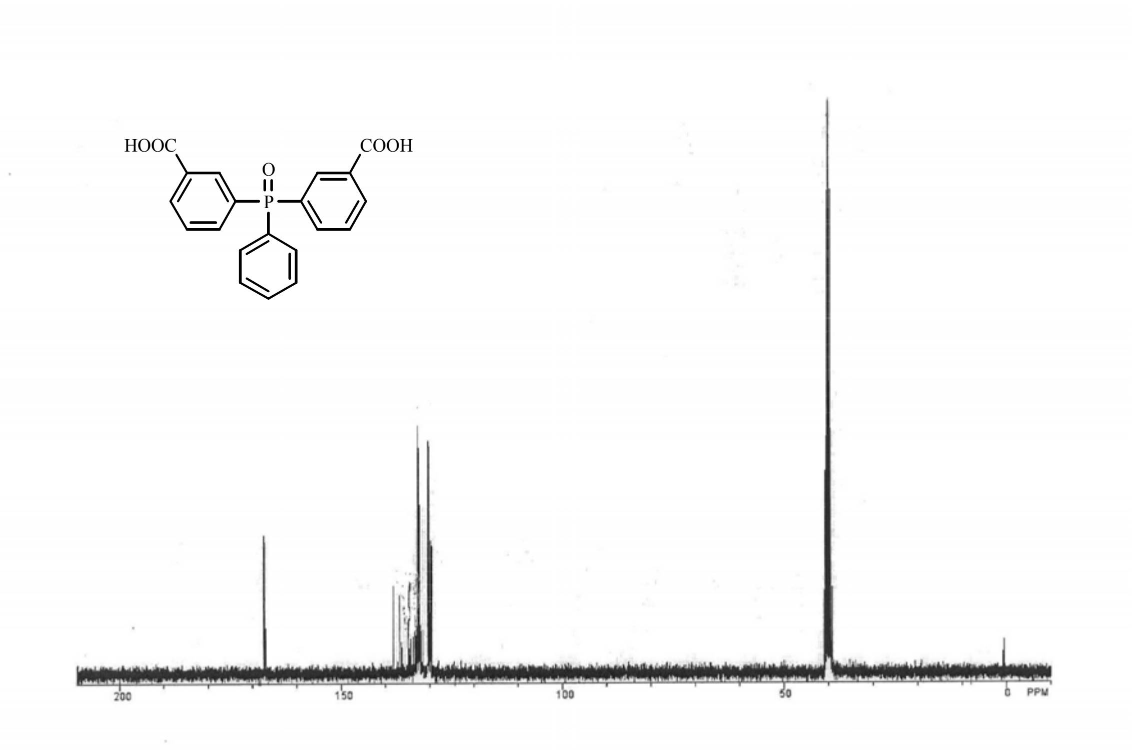


Figure 36 Carbon NMR of **89**

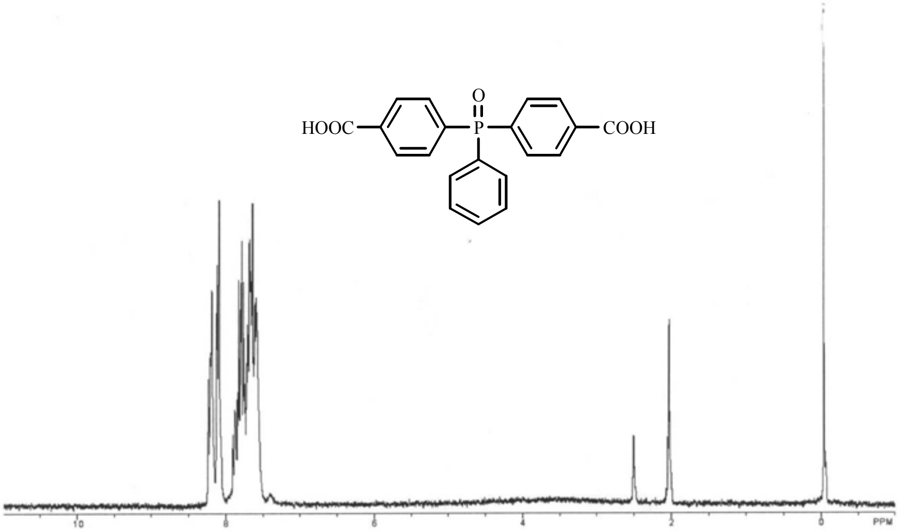


Figure 37 Proton NMR of **90**

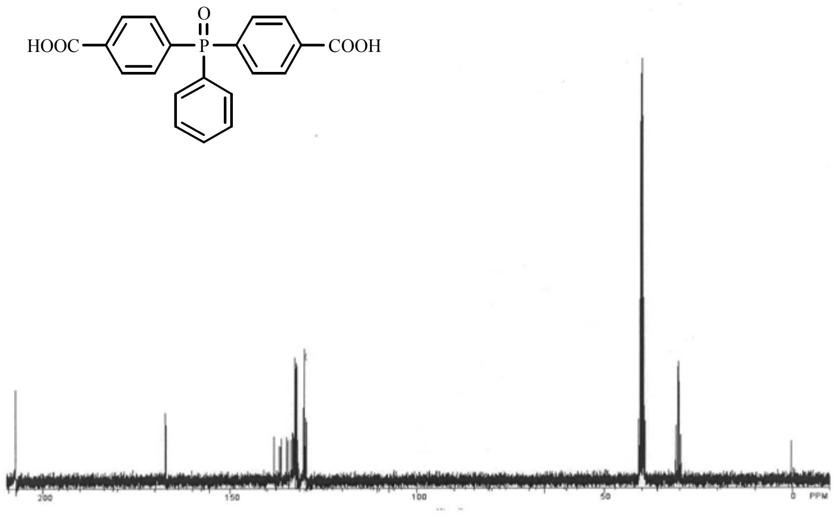


Figure 38 Carbon NMR of **90**

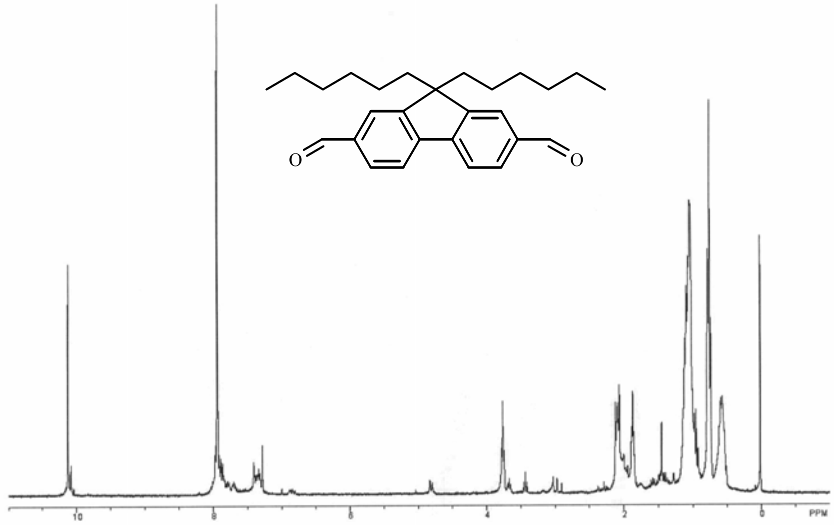


Figure 39 Proton NMR of **94**

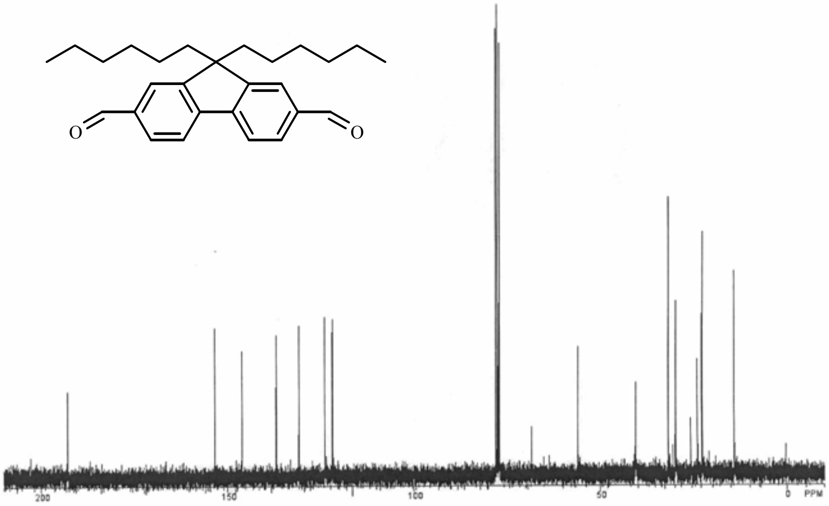


Figure 40 Carbon NMR of **94**

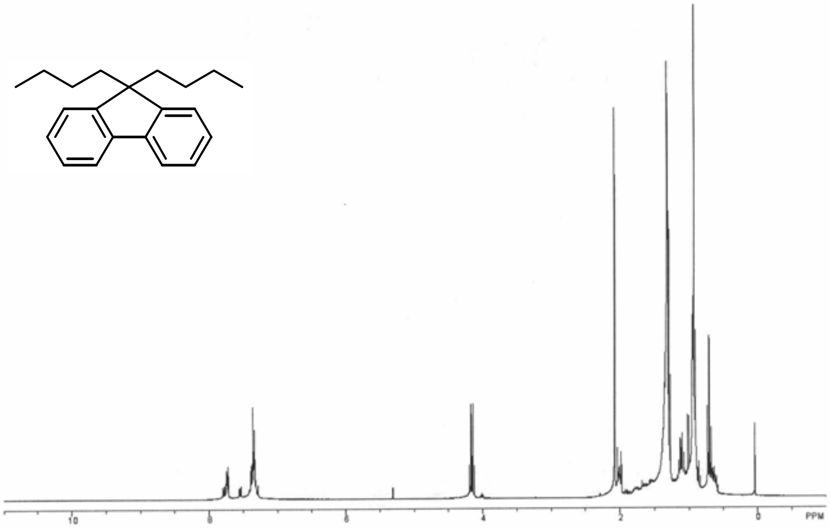


Figure 41 Proton NMR of **95**

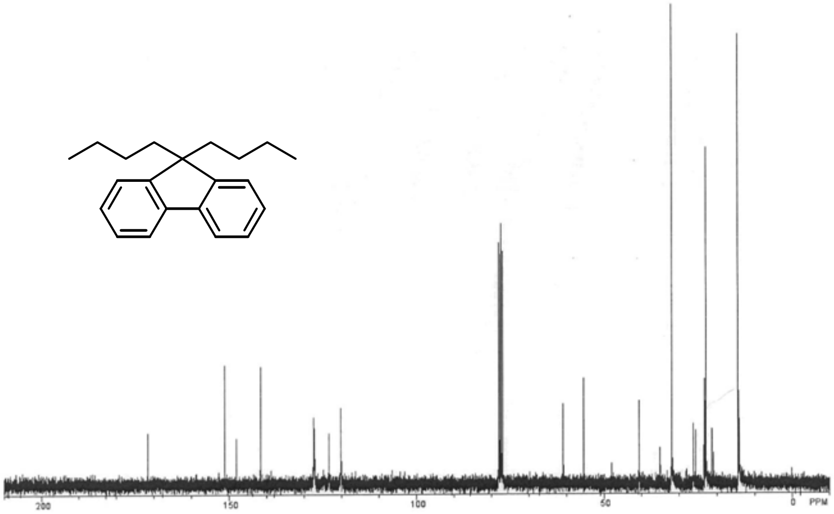


Figure 42 Carbon NMR of **95**

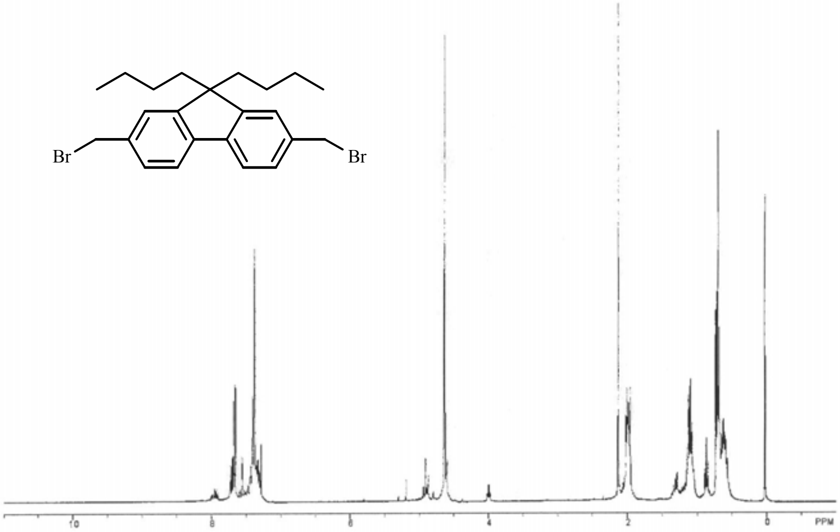


Figure 43 Proton NMR of **96**

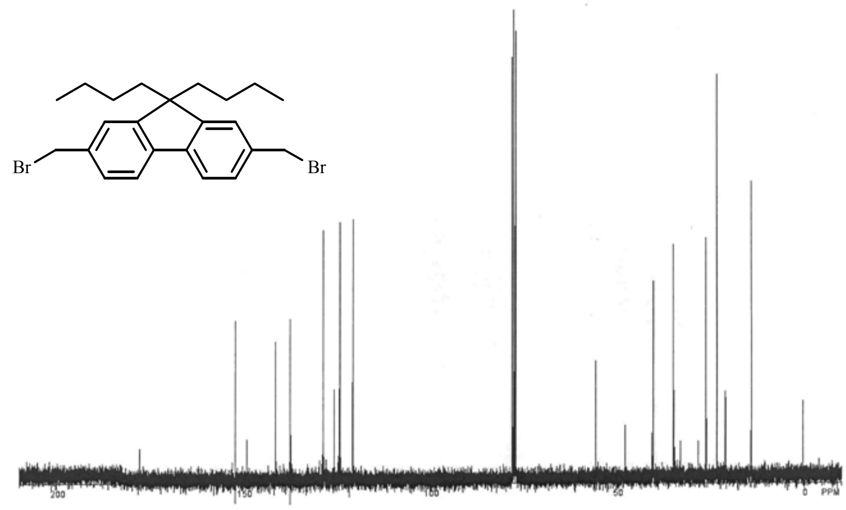


Figure 44 Carbon NMR of **96**

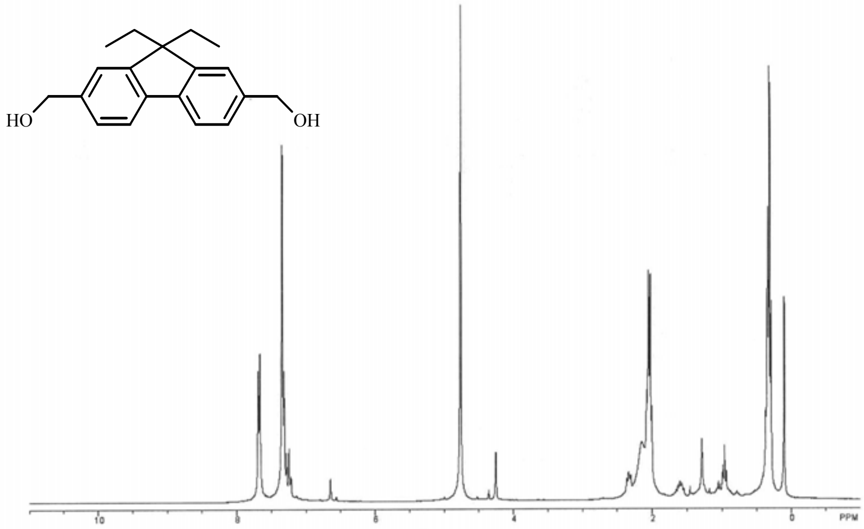


Figure 45 Proton NMR of **98**

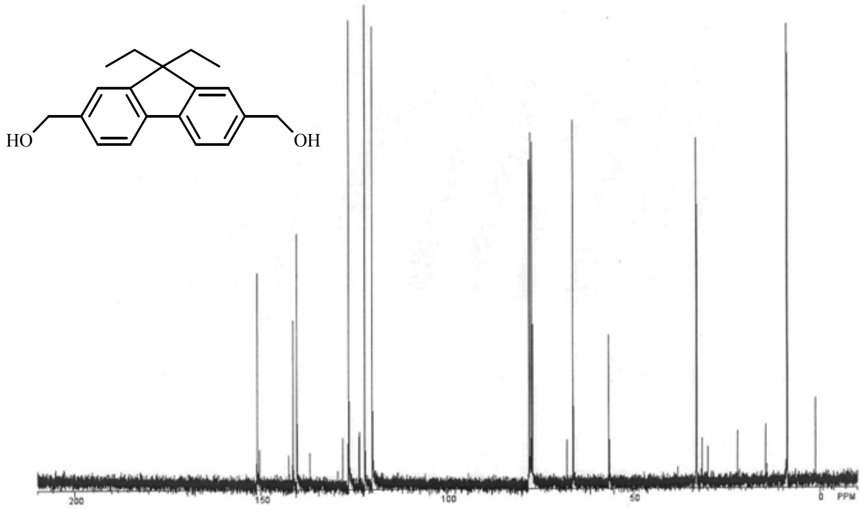


Figure 46 Carbon NMR of **98**

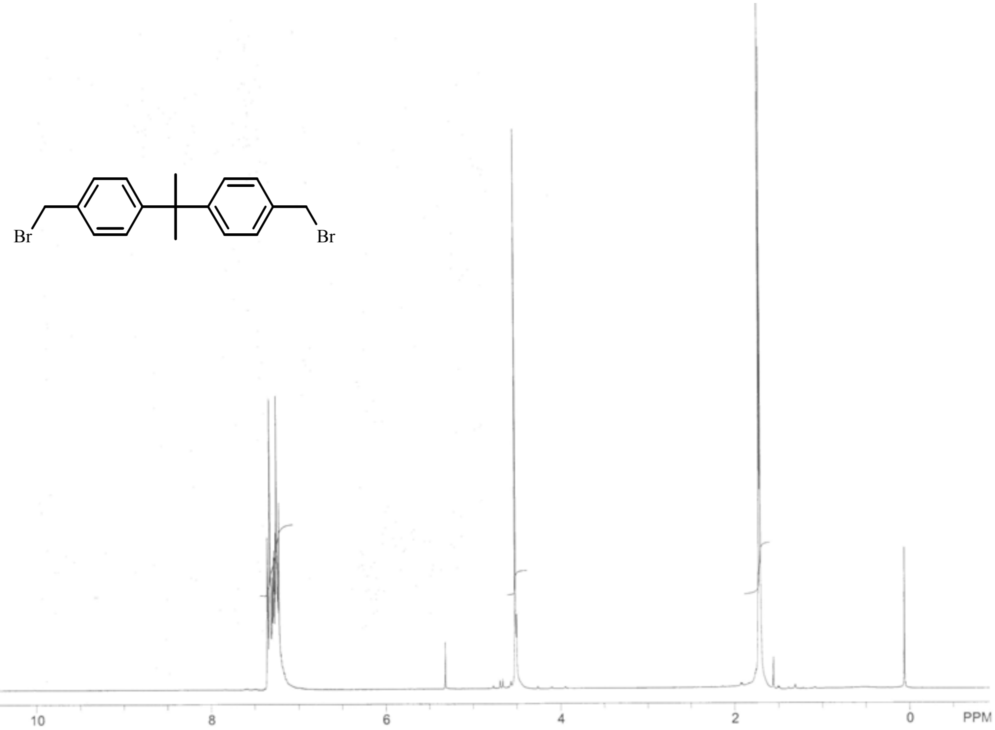


Figure 47 Proton NMR of **100**

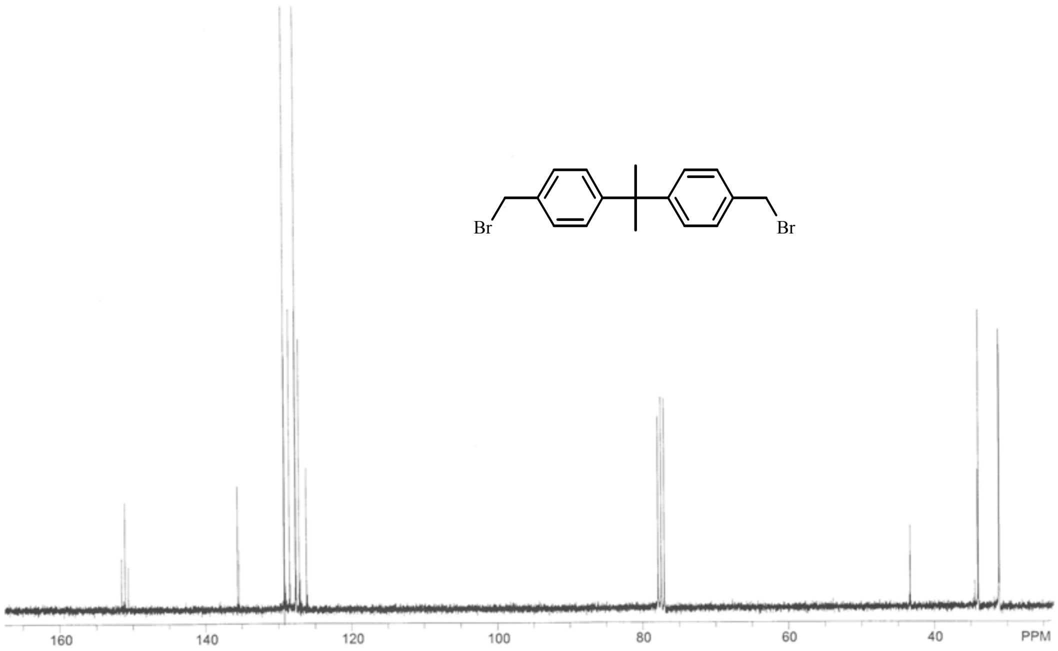


Figure 48 Carbon NMR of **100**

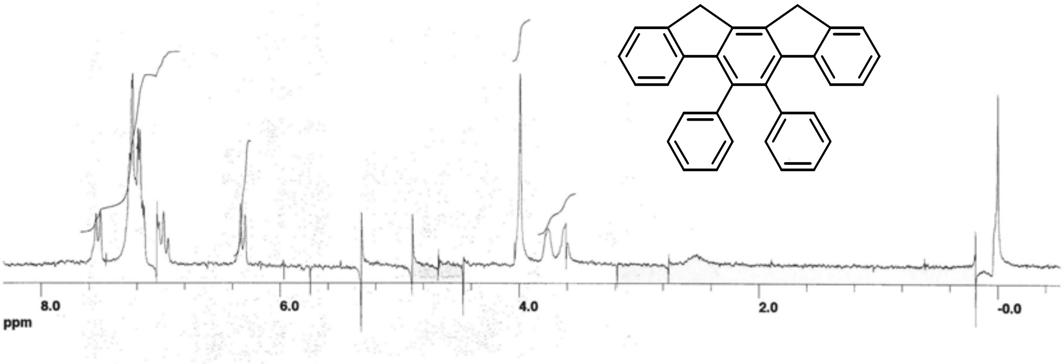


Figure 49 Proton NMR of **111**

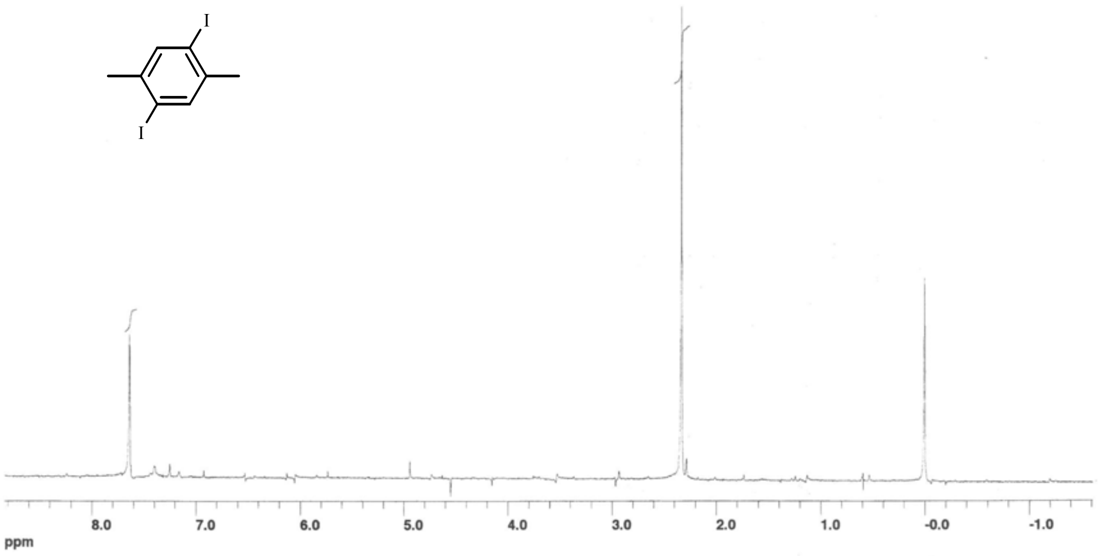


Figure 50 Proton NMR of **115**

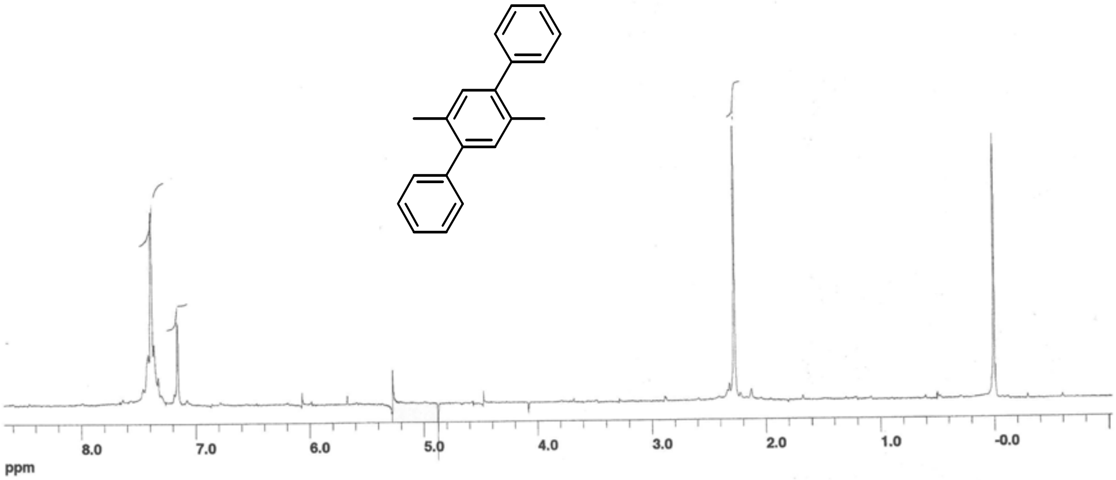


Figure 51 Proton NMR of **118**

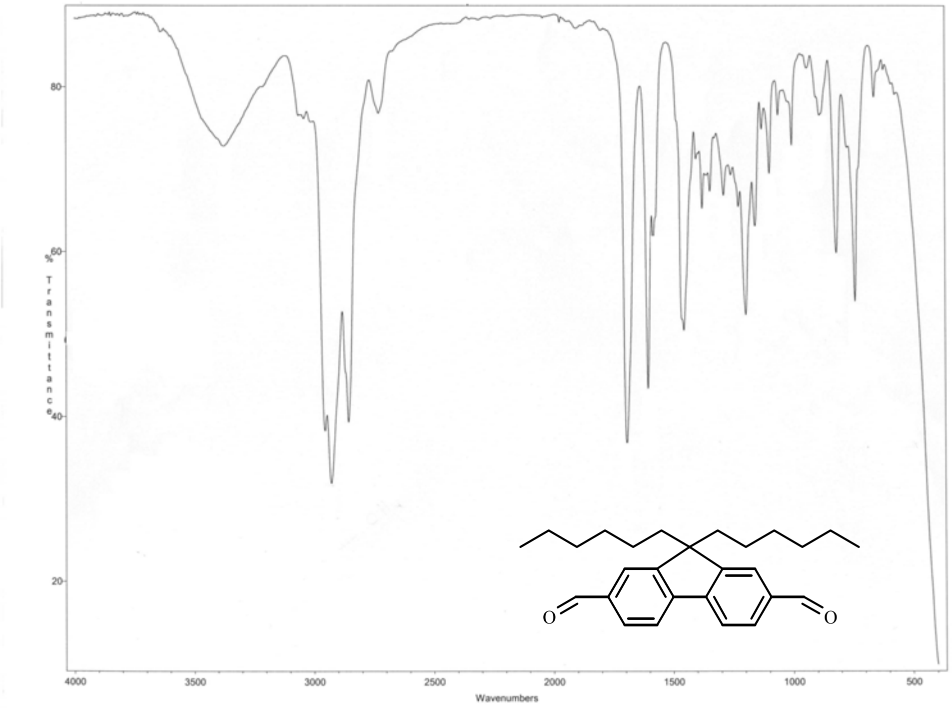


Figure 52 Infrared Spectrum of **94**

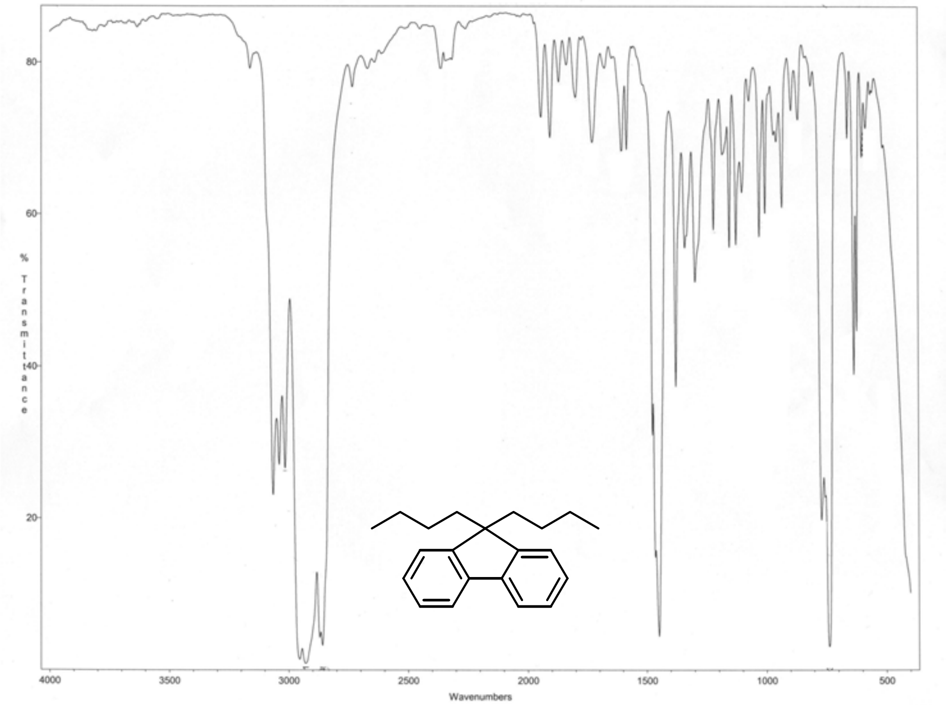


Figure 53 Infrared Spectrum of **95**

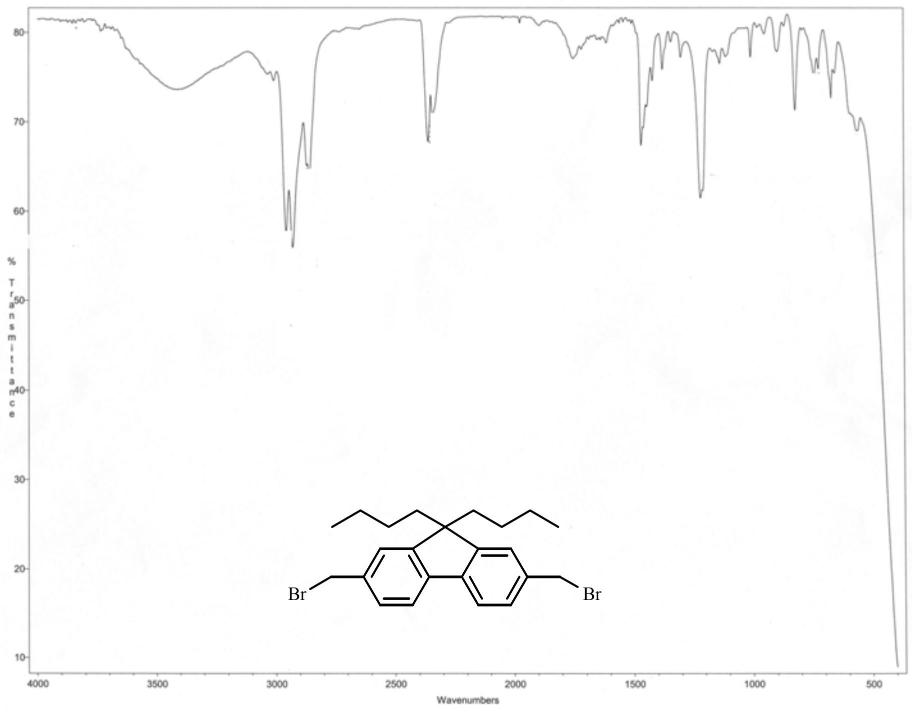


Figure 54 Infrared Spectrum of **96**

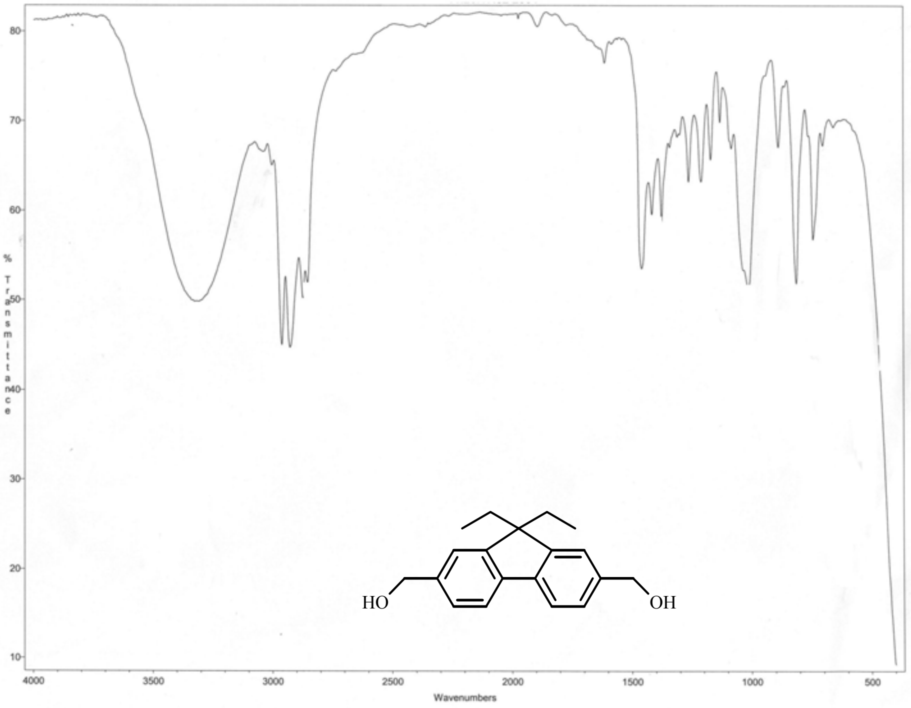


Figure 55 Infrared Spectrum of **98**

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