Polymerization of PEEK AB Monomers with Oxyalkylene Linkages via NAS and Friedel-Crafts Reactions

Shannon Theresa Hennelly
Wright State University

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POLYMERIZATION OF PEEK AB MONOMERS WITH OXYALKYLENE LINKAGES
VIA NAS AND FRIEDEL-CRAFTS REACTIONS

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

By

SHANNON HENNELLY
B.S., Loras College, 2013

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Wright State University
WRIGHT STATE UNIVERSITY
GRADUATE SCHOOL

December 8, 2015


______________________________
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.

_________________________________
Daniel Ketcha, Ph.D.

_________________________________
William A. Feld, Ph.D.

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


The synthesis of the NAS monomer, 4-fluoro-4’-(2-(4-benzyloxyphenoxy)-ethoxy)benzophenone, was envisioned as a two-step process. Thus, the synthesis of 4-fluoro-4’-(2-(4-benzyloxyphenoxy)ethoxy)benzophenone was accomplished by the reaction of 4-fluoro-4’-hydroxybenzophenone and 1-(benzyloxy)-4-(2-bromoethoxy)benzene. Hydrogenation of 4-fluoro-4’-(2-(4-benzyloxyphenoxy)-ethoxy)benzophenone with 10% Pd/C was used to successfully remove the benzylic ether protective group, however, the reaction also reduced the benzophenone carbonyl. The synthesis of the EAS monomer, 4-(2-(4-phenoxyphenoxy)ethoxy)benzoic acid, was also a two-step process. The reaction of ethyl p-(2-hydroxyethoxy)benzoate and 4-phenoxyphenol gave ethyl 4-(2-(4-phenoxyphenoxy)ethoxy)benzoate in good yield. This ester could be easily hydrolyzed to 4-(2-(4-phenoxyphenoxy)ethoxybenzoic acid. The polymerization of the EAS monomer, 4-(2-(4-phenoxyphenoxy)ethoxybenzoic acid, was carried out using Eaton’s Reagent (methanesulfonic acid, phosphorous pentoxide). The polymer exhibits low solubility in common solvents, had an average inherent viscosity of 0.62 dL/g, exhibited DSC transitions from 100°-120° and showed a substantial weight loss in TGA around 400°.
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I would like to give a special thanks to my advisor, Dr. William Feld for giving me the opportunity to work in his group. His guidance and teaching inspired me to be a better student, researcher and teacher. I would not be the chemist I am today without all that he taught me and for that I am truly grateful.

I would also like to acknowledge the faculty, staff, and my fellow graduate students of the Wright State Chemistry Department for all I have learned from them and experienced with them as a student.
DEDICATION

I would like to dedicate this work to my parents, John and Sue, who have always believed in me and pushed me to be my best. My grandma, Rosemary Stanton, who shared her love of teaching with me and my friends who have supported me through this journey and made it more enjoyable.
INTRODUCTION

Poly(ether ether ketone)s (PEEK) are highly thermally-stable, semicrystalline polymers that retain their physical properties like mechanical strength, chemical/solvent resistance and lack of conductivity over a wide range of conditions like temperature and humidity. They also have high molding temperatures.$^1$-$^8$, $^{13}$-$^{18}$

PEEK containing oxyalkylene linkages have been synthesized from AA/BB monomer combinations by nucleophilic aromatic substitution (NAS) and from AB monomers by electrophilic aromatic substitution (EAS).$^9$-$^{12}$, $^{19}$ Because AB monomers present some synthetic advantages, a comparison of the two methods as applied to alkylene containing AB monomers was undertaken.

The objectives of this research were: (1) to synthesize 4-fluoro-4’-(2-(4-hydroxyphenoxo)ethoxy)benzophenone 1 and 4-(2-(4-phenoxyphe-noxy)ethoxy)benzoic acid 2; (2) to polymerize them via NAS and Friedel-Crafts reactions, respectively and; (3) to characterize the polymers 3 and determine structure-property relationships as related to the reaction conditions.
Poly(arylene ether)s (PAEs)

Poly(arylene ether)s, PAEs, are a class of thermoplastics that have been studied extensively due to their physical properties such as good thermal stability, high glass transition temperature, high mechanical performance and low dielectric constant. A typical structure of a poly(arylene ether) 4 contains aryl groups covalently connected by ether bonds in the polymer backbone.\(^1\)

\[
\begin{array}{c}
\text{O} \quad \text{X} \quad \text{O} \\
\text{Y}
\end{array}
\]

\[4 \quad \text{X} = \text{SO}_2, \text{C}=\text{O}; \text{Y} = \text{C(CH}_3)_2\]

The excellent physical and mechanical properties of these materials make them useful for a variety of industrial applications such as coatings, adhesives, composites and toughening agents. As thin-films and coating materials however they are difficult to use because of their poor solubility. PAEs have been extensively studied in order to improve or maintain their properties while altering the functionality. Many subclasses of PAEs have emerged such as poly(arylene ether ketone)s (PAEK) and poly(arylene ether sulfone)s (PAES) which are both synthesized by nucleophilic aromatic substitution or Friedel-Crafts processes.\(^1\)

**Nucleophilic Aromatic Substitution Reactions**

In 1951, Bunnett and Zahler\(^2\) demonstrated that alkali metal phenolates 5 react with certain “activated” aromatic halides 6 in appropriate solvents to produce the
corresponding aryl ethers 7. The most influential factor in these reactions is the nature and position of the activating group in the aryl halide. It must be electron withdrawing and be positioned either ortho or para to the halogen being removed.

\[
\text{M}^+ + \text{aryl} \rightarrow \text{product}
\]

\[M = \text{Na, K}; \text{X} = \text{ortho, para halogen}; W = -\text{NO}_2, -\text{SO}_2\text{R}\]

In 1967, Johnson et al.\textsuperscript{3} synthesized a poly(ether sulfone) 11 employing the synthetic strategy mentioned above. In this reaction, the sodium salt of bisphenol-A 9 was reacted with bis(p-chlorophenyl)sulfone 10 using a chlorobenzene/DMSO solvent mixture at 160° under nitrogen. It was observed that the solutions became colored, often orange or yellow, but sometimes deep green, upon the addition of the sulfone. This occurs presumably because of a Meisenheimer type σ-complex or maybe due to a charge transfer complex composed of the reactants and solvent.

In 1972, Vinogradova, Korshak, Salazkin and Kulkov\textsuperscript{4} synthesized aromatic polyethers 15 by reacting bisphenolates of suitable structure 12 with 4,4’-dichloro (or difluoro)diphenyl sulfone 13 or 4,4’-difluorbzophenone 14 in DMSO at elevated temperatures.
In 1981, Attwood et al.\textsuperscript{5} devised a synthetic method of making a poly(ether ketone) that industry uses today. In this method, bis(4-fluorophenyl) ketone 16 was reacted with the bispotassium salt of bis(4-hydroxyphenyl) ketone 17 in diphenyl sulfone at 335° for 2-3 h. Yields of polymer 18 were greater than 98% and an inherent viscosity of greater than 1.0 dL/g was reported.

In 1988, Hergenrother, Jensen and Havens\textsuperscript{6} utilized the same synthetic strategy as did Attwood et al.\textsuperscript{4} for making a series of poly(ether ketone)s except they used a different solvent system. Halogenated bisphenyl ketones 19 and sulfones 20 were reacted with
dihydroxyaryl compounds 21 in a dimethylacetamide/K$_2$CO$_3$ solution at just 155°. This lower temperature helped to eliminate decomposition of the polymer 18. Inherent viscosities as high as 1.9 dL/g were reported for some of these polymers 22.

\[
\begin{align*}
\text{X} - \text{Y} - \text{X} & \quad + \quad \text{HO-Ar-OH} \\
19 \quad \text{X}=\text{Cl/F}, \text{Y}=\text{CO} & \quad 21 \quad \text{Ar} = \text{varied aromatic groups} \\
20 \quad \text{X}=\text{Cl/F}, \text{Y}=\text{SO}_2 & \\
\end{align*}
\]

\[
\begin{array}{c}
\text{K}_2\text{CO}_3 \\
\text{DMAc}
\end{array}
\]

\[
\begin{array}{c}
\text{Y} = \text{CO, SO}_2; \text{Ar} = \text{varied aromatic groups} \\
22
\end{array}
\]

Research has been carried out to generate new dihalide monomers and react them with various bisphenols to obtain different poly(ether ether ketone)s. For example, in 1991, Cormier, Lucotte, and Delfort synthesized poly(arylene ether sulfone)s 24 and poly(arylene ether ketone)s 25 from two new bis(fluorobenzoyl) dibenzofuran monomers 23 and various bisphenols 21.

\[
\begin{align*}
\text{F} - \text{R} - \text{F} & \quad + \quad \text{HO-Ar-OH} \\
23a \quad \text{R} = \text{CO} & \quad 21 \quad \text{Ar} = \text{varied aromatic groups} \\
23b \quad \text{R} = \text{SO}_2 & \\
\end{align*}
\]

\[
\begin{array}{c}
\text{R} = \text{CO} \\
24 \quad 25 \quad \text{R} = \text{SO}_2
\end{array}
\]
Singh and Hay prepared amorphous poly(ether ketone)s 27 by reacting novel fluoro monomers containing the o-dibenzoylbenzene unit 26 with bisphenols 21. The polymers had high molecular weights, and were very soluble in common organic solvents. They formed flexible, colorless and transparent films.

In 1992, B. Patel synthesized poly(ether ether ketone)s that contained alkylenedioxy units where the length of the alkylene chain, n, was varied from 1 to 5. The
reaction of 4-fluoro-4'-hydroxybenzophenone 28 with the appropriate dibromoalkanes 29-33 in the presence of potassium hydroxide in ethanol yielded the bis(fluorobenzophenone) monomers 34-38 by an SN2 reaction.

The condensation polymerization of the bis(fluorobenzophenone) monomers 34-38 was carried out in N-methyl-2-pyrrolidinone (NMP) with toluene as the drying agent using potassium carbonate as a base with bisphenol-A 21 to yield the corresponding poly(ether ether ketone)s 39-43. The polymers formed flexible, colorless and transparent films. The T_g s ranged from 91-136° and were inversely proportional to the length of the oxyalkylene chain. The polymers showed good thermal stability with only 5% weight loss at 450° in air and nitrogen.

In 1992, M. Patel\textsuperscript{10} synthesized poly(ether ether ketone)s in which ethylene glycol oligomers of varying lengths were incorporated. The reaction of 4-fluoro-4'-hydroxybenzophenone 28 with various ethylene glycol ditosylates 44-48 in the presence of potassium hydroxide in ethanol yielded the bis(fluorobenzophenone) monomers 49-53 by an SN2 reaction. The condensation polymerization of the bis(fluorobenzophenone) monomers 49-53 was carried out in N-methyl-2-pyrrolidinone and toluene using
potassium carbonate as a base with bisphenol-A 21 to yield the corresponding poly(ether ether ketone)s 54-58. The Tg's ranged from 74-115° and were

\[
\text{F} - \begin{array}{c|c|c}
\begin{array}{c|c|c}
\text{O} & \begin{array}{c|c|c}
\text{49-53} & \text{n = 1 - 5} & \\
\text{O} & \begin{array}{c|c|c}
\text{28} & \text{EtOH} & \\
\text{KOH} & \text{44-48} & \text{n = 1 - 5}
\end{array}
\end{array}
\end{array}
\end{array}
\]

observed to be inversely proportional to the length of the oxyalkylene units incorporated.

The polymers exhibited good thermal stability with only a 5% weight loss at 450° in air and nitrogen. They also have high solubility in chlorinated solvents and form flexible, transparent and colorless films.

In 2004, McGinty\textsuperscript{11} synthesized two different poly(ether ether ketone)s containing a tertiary amine subunit. The reaction of 4-fluoro-4'-hydroxybenzophenone 28 with the ditosylate 59 in the presence of potassium hydroxide in ethanol yielded the bis(fluorobenzophenone) monomer 60 by an SN2 reaction. The condensation polymerization of the bis(fluorobenzophenone) monomer 66 was carried out in N-methyl-2-pyrrolidinone using potassium carbonate as a base and toluene as dehydrating agent with the appropriate bisphenol. Bisphenol-A 21 as well as bisphenol-AF 61 were
used to yield the corresponding poly(ether ether ketone)s 62 and 63. The polymers had a 5% weight loss of 300° in air and 400° in nitrogen which shows good thermal stability. They also had inherent viscosities ranging from 0.11-0.32 dL/g and were very soluble in chlorinated solvents. The polymers made thin, flexible and colorless films.

In 2014, Drzic\textsuperscript{12} attempted to synthesize the difluoro monomer 67 that could be used in NAS polymerizations. First, the ditosylate 66 was synthesized from p-toluenesulfonyl chloride 64 and 1,4-bis(2-hydroxyethoxy)benzene 65 in tetrahydrofuran (THF). The reaction of 4-fluoro-4’-hydroxybenzophenone 28 with the ditosylate 66 in the presence of potassium hydroxide in ethanol did not yield the desired bis(fluorobenzophenone) monomer 67 by nucleophilic substitution. It was postulated that the reaction may have failed due to steric effects and/or possible π-π stacking effects. The proton NMR indicates that the half product is being formed but no indication of a
characteristic singlet in the aromatic region that would indicate the presence of the symmetrical para-substituted ring in 67 was found.

Electrophilic Aromatic Substitution

In 1962, Bonner\textsuperscript{13} was the first to synthesize an aromatic poly(ether ketone) by an acylation method. A Friedel-Crafts condensation polymerization between phenyl ether 68 and isophthaloyl chloride 69 using nitrobenzene as a solvent and aluminum chloride as a catalyst was employed. The polymer 70 had an inherent viscosity of 0.18 dL/g.

In 1964, Goodman et al.\textsuperscript{14} completed the synthesis of a similar polymer but used methylene chloride as solvent. An AB monomer, p-phenoxybenzoyl chloride 72a, was
used that eliminated the need for an accurate monomer balance to be maintained.

Polymer 73b had an inherent viscosity of 0.5 dL/g.

In 1968, Ikawara et al.\textsuperscript{15} reported similar polymerizations with phenoxybenzoic acids 71a and 71b as the AB monomers and polyphosphoric acid (PPA) as the solvent to produce polymers 73a and 73b. This solvent system may promote polymer solubility by protonation of the carbonyl group.

In 1973, Eaton, Carlson, and Lee\textsuperscript{16} investigated which solvents that could replace polyphosphoric acid in the preceding polymerization. Polyphosphoric acid is generally a good solvent to use for acylation of aromatic and olefinic systems. It is also good for dehydrations and the Beckmann and Schmidt rearrangements but the nature of the acid is a problem. Polyphosphoric acid is extremely viscous and can be nearly impossible to stir at temperatures below 60-90°. In addition, organics have low solubility in it. To address these issues, Eaton et al.\textsuperscript{16} reported the use of a 1:10 (wt/wt) solution of phosphorus pentoxide in methanesulfonic acid (P\textsubscript{2}O\textsubscript{5}/MSA, PPMA). This solvent system has the ability to dissolve more organics and the viscosity is much lower.
In 1984, Ueda and Kano\textsuperscript{17} used PPMA to perform condensation polymerizations with various dicarboxylic acids \textsuperscript{74} and aromatic hydrocarbons \textsuperscript{75} to obtain polymers \textsuperscript{76} as shown below. In 1987, Ueda and Sato\textsuperscript{18} used PPMA to conduct a self condensation polymerization of both para-phenoxynbenzoic acid \textsuperscript{71a} and meta-phenoxynbenzoic acid \textsuperscript{71b}. The reaction was performed at 100° for 24 hrs to yield poly(ether ketone)s \textsuperscript{73a, b} with inherent viscosities of about 1.0 dL/g. The para-substituted benzoic acid gave low molecular weight polymers that was thought to be due to the lower electrophilicity of the acid due to the deactivating group at the para position.

In 1991, Kirk\textsuperscript{19} synthesized poly(ether ether ketone)s containing oxyalkylene linkages from an AB monomer. First, the appropriate bromophenoxy alkanes \textsuperscript{77}-\textsuperscript{79} were reacted with the hydroxybenzoates \textsuperscript{80} and \textsuperscript{81} in the presence of potassium hydroxide in ethanol to yield the corresponding ethyl esters \textsuperscript{82}-\textsuperscript{87}. These ethyl esters were converted to their corresponding acids/monomers \textsuperscript{86}-\textsuperscript{91}, in the presence of excess potassium hydroxide in ethanol. The polymerization of \textsuperscript{86}-\textsuperscript{91} was carried out in phosphorus pentoxide/methanesulphonic acid (PPMA) to yield the corresponding poly(ether ether ketone)s \textsuperscript{92}-\textsuperscript{97}. Polymers \textsuperscript{92}-\textsuperscript{97} were not soluble in any common solvents but viscosities could be determined using methanesulphonic acid and ranged from 0.01-2.18 dL/g. Thermal analysis was only completed on polymers \textsuperscript{92} and \textsuperscript{93}. Polymer \textsuperscript{92} had a 7\% weight loss in air at 400-450° while polymer \textsuperscript{93} underwent continuous weight loss starting at 300°. A thin, white translucent film was generated from polymer \textsuperscript{92}. 

\begin{center}
\begin{align*}
&\text{HO\textsuperscript{-}R\textsuperscript{-}O} + \text{H}_5\text{C}_6\text{R-C}_6\text{H}_5 \xrightarrow{\text{PPMA}} \text{R-C}_6\text{H}_5\text{-C}_6\text{H}_5\text{-O-R}
\end{align*}
\end{center}
Williamson Synthesis Employing Tosylates

In a 1987 patent, Satomura et al.\textsuperscript{20} reported the preparation of ethers through the Williamson synthesis. Instead of reacting phenol derivatives with alkyl halides they used tosylates as the electrophilic substrate. The authors cited the lack of commercial availability of alkyl halides and the greater availability of alcohols from which tosylates are derived as the motivation for the research. They found that p-toluenesulfonyl chloride was the preferred sulfonyl halide due to its stability and responsiveness in an inorganic base-polar solvent combination. They also found that polar solvents that were water soluble, such as N-methylpyrrolidinone (NMP), worked best and made workup easier. They were able to produce a wide variety of ethers using various alcohols and phenols. An example of this was the synthesis of 1-phenoxy-2-(p-ethylphenoxy)ethane \textsuperscript{102}. In a “one-pot” synthesis, 2-phenoxyethanol \textsuperscript{98} was converted to the corresponding tosylate

\[
\text{Ph-O-Br} + \text{Ph-CH=CH} \rightarrow \text{(n)}
\]

\begin{align*}
\text{77-79} \quad n = 1-3 & \quad \text{80 p-(OH)} & \quad \text{82-84 para, } n = 1-3 \\
\text{81 m-(OH)} & \quad \text{85-87 meta, } n = 1-3 \\
\end{align*}

\[
\text{KOH} \rightarrow \text{Ph-O} \quad \text{n}
\]

\begin{align*}
\text{86-88} \quad \text{para, } n = 1-3 & \quad \text{89-91 meta, } n = 1-3 \\
\end{align*}

\[
\left[\text{Ph} \quad \left(\right) \quad \text{Ph}\right]
\]

\begin{align*}
\text{92-94} \quad \text{para, } n = 1-3 & \quad \text{95-97 meta, } n = 1-3 \\
\end{align*}
which was reacted in situ with p-ethylphenol 101, initially at room temperature, later at 85-95°. The product, 1-phenoxy-2-(p-ethylphenoxy)ethane 102, was obtained by precipitation into a water/methanol mixture giving a 96% yield.

The successful Williamson synthesis via tosylates suggests that similar reactions could be used to generate AB monomers.

Thus, the objectives of this research were: (1) to synthesize 4-fluoro-4’-(2-(4-hydroxyphenoxy)ethoxy)benzophenone 1 and 4-(2-(4-phenoxyphenoxy)ethoxy)benzoic acid 2; (2) to polymerize them via NAS and Friedel-Crafts reactions, respectively and; (3) to characterize the polymers and determine structure-property relationships as related to the reaction conditions.
Experimental

Instrumentation and Chemicals.

Melting points were obtained with a DigiMelt MPA-160 instrument. Nuclear magnetic resonance (NMR) $^1$H and $^{13}$C spectra were obtained using a Bruker Avance 300 MHz NMR Spectrometer. Solvents for NMR were CDCl$_3$ and DMSO-d$_6$. Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) spectra were obtained with a TA TGA Q 500 and a TA DSC Q 200 both employing air or N$_2$ atmospheres. Infrared (IR) spectra were recorded as thin films (NaCl) with a Nicolet 6700 FT-IR spectrometer. Elemental analyses were obtained through Midwest Microlab, LLC, Indianapolis, IN. Chemicals were purchased from Aldrich and used as received.

General Procedure for the Synthesis of 4-Fluoro-4’-(Ω-phenoxyalkoxy)benzophenones

In a 100 mL, round-bottomed flask, KOH (0.77 g, 13.8 mmol) was dissolved in ethanol (35 mL) and 4-fluoro-4’-hydroxybenzophenone (3.0473 g, 13.8 mmol) was added. After the phenol had reacted/dissolved, the appropriate bromoethoxy benzene (12.5 mmol) was added to the reaction mixture and the solution was heated at 90° for 20 h. The reaction mixture was cooled, poured into water (75 mL) and stirred. The precipitate was collected, washed with water and ethanol and recrystallized from toluene.
4-Fluoro-4’-(2-phenoxyethoxy)benzophenone 103

A white solid (1.69 g, 5.1 mmol, 66%) was obtained: mp 127.0-127.5°; IR (NaCl, cm⁻¹) 1642 (C=O); ¹H NMR (CDCl₃) δ 4.41 (m, 4H, CH₂), 6.97-7.06 (m, 5H, Ar-H), 7.17 (t, 2H, Ar-H), 7.33 (t, 2H, Ar-H), 7.80-7.84 (m, 4H, Ar-H); ¹³C NMR (CDCl₃, ppm) 66.27 (OCH₂), 66.81 (OCH₂), 114.32 (Ar, CH), 114.72 (Ar, CH), 115.35 (d, Ar, CH, J = 22.5 Hz), 129.59 (Ar, CH), 130.39 (Ar, CH), 132.30 (d, Ar, CH, J = 9 Hz), 132.39 (Ar, CH), 134.40 (d, Ar, C, J = 3 Hz), 158.51 (Ar, OC), 162.34 (Ar, OC), 165.10 (d, Ar, C-F J = 251 Hz), 194.05 (C=O). Anal. Calcd for C₂₁H₁₇FO₃: C, 74.99; H, 5.09; Found: C, 74.58; H, 5.08.

4-Fluoro-4’-(3-phenoxypropoxy)benzophenone 104

A white solid (1.82 g, 5.1 mmol, 77%) was obtained: mp 104.0-105.0°; IR (NaCl, cm⁻¹) 1642 (C=O); ¹H NMR (CDCl₃) δ 2.33 (m, 2H, CH₂), 4.20 (t, 2H, CH₂), 4.28 (t, 2H, CH₂), 6.93-7.03 (m, 5H, Ar-H), 7.17 (t, 2H, Ar-H), 7.31 (t, 2H, Ar-H), 7.79-7.84 (m, 4H, Ar-H); ¹³C NMR (CDCl₃, ppm) 29.22 (CH₂), 64.05 (OCH₂), 64.81 (OCH₂), 114.15 (Ar, CH), 114.52 (Ar, CH), 115.31 (d, Ar, CH, J = 21.75 Hz), 120.88 (Ar, CH), 129.50 (Ar, CH), 130.07 (Ar, CH), 132.27 (d, Ar, CH, J = 9 Hz), 132.40 (Ar, CH), 134.48 (d, Ar, CH, J = 3 Hz), 158.78 (Ar, OC), 162.62 (Ar, OC), 165.07 (d, Ar, C-F, J = 252 Hz), 194.07 (C=O). Anal. Calcd for C₂₂H₁₉FO₃: C, 75.41; H, 5.47; Found: C, 75.33; H, 5.39.
4-Fluoro-4'-(4-phenoxybutoxy)benzophenone 105

A white solid (2.56 g, 10.5 mmol, 76%) was obtained: mp 126.2-126.6°; IR (NaCl, cm\(^{-1}\) ) 1637 (C=O); \(^1\)H NMR (CDCl\(_3\) ) \(\delta\) 2.04 (m, 4H, CH\(_2\)), 4.07 (t, 2H, CH\(_2\)), 4.15 (t, 2H, CH\(_2\)), 6.91-7.00 (m, 5H, Ar-H), 7.17 (t, 2H, Ar-H), 7.31 (t, 2H, Ar-H), 7.80-7.84 (m, 4H, Ar-H); \(^13\)C NMR (CDCl\(_3\), ppm) 25.95 (CH\(_2\)), 67.22 (OCH\(_2\)), 67.82 (OCH\(_2\)), 114.10 (Ar, CH), 114.47 (Ar, CH), 115.31 (d, Ar, CH, J= 21.75 Hz), 120.70 (Ar, CH), 129.48 (Ar, CH), 129.93 (Ar, CH), 132.28 (d, Ar, CH, J= 9 Hz), 132.42 (Ar, CH), 134.49 (d, Ar, CH, J= 3 Hz), 158.91 (Ar, OC), 162.74 (Ar, OC), 165.05 (d, Ar, C-F, J= 251 Hz), 194.09 (C=O). Anal. Calcd for C\(_{23}\)H\(_{21}\)FO\(_3\): C, 75.81; H, 5.81; Found: C, 75.88; H, 5.79.

4-Fluoro-4'-(2-(4-benzzyloxyphenoxy)ethoxy)benzophenone 108

In a 50 mL, round-bottomed flask, 4-fluoro-4'-hydroxybenzophenone (0.83 g, 3.7 mmol) was dissolved in acetone (12 mL) and K\(_2\)CO\(_3\) (0.70 g, 5.1 mmol) and the 2-(4-benzzyloxyphenoxy)ethyl bromide (1.06 g, 3.4 mmol) were added to the reaction mixture and the solution was heated at 50° for 48 h. The reaction mixture was filtered and the solvent was removed under vacuo. The filtrate was dissolved in chloroform and washed with 20% NaOH solution. The organic solution was concentrated in vacuo to yield a white solid (0.87 g, 1.9 mmol, 65.5%): mp 170.9-171°; IR (NaCl, cm\(^{-1}\) ) 1637 (C=O); \(^1\)H
NMR (CDCl$_3$) δ 4.33 (m, 2H, CH$_2$), 4.40 (m, 2H, CH$_2$), 5.05 (s, 2H, CH$_2$), 6.89-6.96 (m, 4H, Ar-H), 7.03 (d, 2H, Ar-H), 7.17 (t, 2H, Ar-H), 7.34-7.43 (m, 6H, Ar-H), 7.79-7.84 (m, 4H, Ar-H); $^{13}$C NMR (CDCl$_3$, ppm) 66.86 (CH$_2$), 67.08 (CH$_2$), 70.69 (CH$_2$), 114.29 (Ar, CH), 115.34 (d, Ar, CH, J= 21.75 Hz), 115.80 (Ar, CH), 115.92 (Ar, CH), 127.45 (Ar, CH), 127.91 (Ar, CH), 128.56 (Ar, C), 130.38 (Ar, CH), 132.29 (d, Ar, CH, J= 9.75 Hz), 134.4 (d, Ar, CH, J= 3 Hz), 137.20 (Ar, C), 152.84 (Ar, C), 153.45 (Ar, C), 162.34 (Ar, C), 165.10 (d, Ar, C-F, J= 252 Hz), 194.07 (C=O). Anal. Caled for C$_{28}$H$_{23}$FO$_4$: C, 76.00; H, 5.24; Found: C, 76.12; H, 5.31.

4-Fluoro-4’-(2-(4-hydroxyphenoxy)ethoxy)benzophenone 1

In a Parr hydrogenation flask was placed 4-fluoro-4’-(2-(4-benzyloxyphenoxy)ethoxy)benzophenone (0.49 g, 1.1 mmol), ethyl acetate (35 mL) and Pd/C. Hydrogenation was continued at 40 psi (H$_2$) and for 18 h. The reaction mixture was filtered, evaporated and the crude product was recrystallized from toluene to yield a white solid (0.27 g, 0.79 mmol, 52%); mp: 132.3-136°C; IR (NaCl, cm$^{-1}$) 3347 (OH), 1605 (C=O); $^1$H NMR (DMSO) δ 4.15-4.22 (m, 4H, CH$_2$), 6.66 (d, 2H, Ar-H), 6.77 (d, 2H, Ar-H), 6.89 (d, 2H, Ar-H), 7.10 (t, 2H, Ar-H), 7.24 (d, 2H, Ar-H) 7.35 (t, 2H, Ar-H); $^{13}$C NMR (DMSO, ppm) 66.42 (CH$_2$), 66.78 (CH$_2$), 114.09 (Ar, CH), 114.50 (Ar, CH), 114.79 (Ar, CH), 115.61 (d, Ar, CH, J= 22.5 Hz), 127.42 (Ar, CH), 127.96 (d, Ar, CH, J = 9 Hz), 132.16 (d, Ar, C, J= 4.5 Hz), 137.75 (Ar, C), 151.08 (Ar, C), 151.23 (Ar, C),
157.20 (Ar, C), 160.92 (d, Ar, C-F, J= 240 Hz), 193.23 (C=O). Anal. Calcd for C_{21}H_{17}FO_4: C, 71.58; H, 4.86. Found: C, 71.65; H, 4.92

2-[4-(Benzyloxy)phenoxy] ethanol^{21} 112

In a 500 mL, three-necked, round-bottomed flask, 4-(benzyloxy)phenol (20.02 g, 0.1 mol) was dissolved in ethanol (100 mL). The solution was heated at reflux and stirred. A solution of NaOH (8.00 g, 0.2 mol) in ethanol (100 mL) was added dropwise over 20-30 min and reflux was continued for 0.5 h. Then, 2-chloroethanol (16.10 g, 0.2 mol) was added slowly. The resulting mixture was refluxed for 15 h. The reaction mixture was cooled to room temperature and filtered and the crude product was recrystallized from ethanol to obtain a tan solid (19.40 g, 0.08 mol, 79%): mp 102.1-103° (lit.\textsuperscript{21} mp 100-102); IR (NaCl, cm\textsuperscript{-1}) 3419 (OH); \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \delta 3.95 (m, 2H, CH\textsubscript{2}), 4.05 (m, 2H, CH\textsubscript{2}), 5.04 (s, 2H, CH\textsubscript{2}), 6.92 (m, 4H, Ar-H), 7.35-7.47 (m, 5H, Ar-H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, ppm) 61.53 (CH\textsubscript{2}), 69.93 (CH\textsubscript{2}), 70.71 (CH\textsubscript{2}), 115.62 (Ar, CH), 115.94 (Ar, CH), 127.50 (Ar, CH), 127.93 (Ar, CH), 128.58 (Ar, CH), 137.26 (Ar, C), 153.02 (Ar, C), 153.32 (Ar, C). Anal. Calcd for C\textsubscript{15}H\textsubscript{16}O\textsubscript{3}: C, 73.75; H, 6.60. Found: C, 72.37; H, 6.48.

Ethyl p-(2-hydroxyethoxy)benzoate\textsuperscript{22} 113

In a 100 mL, round-bottomed flask, NaOH (2.40 g, 0.06 mol) was dissolved in ethanol and heated to 50°. Ethyl p-hydroxybenzoate (10.0 g, 0.06 mol) and 2-
chloroethanol (4.0 g, 0.05 mol) were added consecutively. The reaction mixture was
heated to reflux and stirred for 17 h. The mixture was cooled to room temperature and the
NaCl was filtered and the filtrate was concentrated in vacuo. The crude oil was dissolved
in methylene chloride and extracted with a 20% NaOH solution. The organic solution
was concentrated in vacuo to yield a clear oil (6.80 g, 0.03 mol, 60%): IR (NaCl, cm\(^{-1}\))
3463 (OH), 1697 (C=O); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.39 (t, 3H, CH\(_3\)), 4.00 (m, 2H, CH\(_2\)), 4.14
(m, 2H, CH\(_2\)), 4.36 (q, 2H, CH\(_2\)), 7.17 (t, 2H, Ar-H), 6.94 (d, 2H, Ar-H), 8.00 (d, 2H, Ar-
H); \(^13\)C NMR (CDCl\(_3\), ppm) 14.30 (CH\(_3\)), 60.72 (CH\(_2\)), 61.06 (CH\(_2\)), 69.39 (CH\(_2\)), 114.07
(Ar, CH), 123.11 (Ar, C), 131.53 (Ar, CH), 162.40 (Ar, C), 166.45 (Ar, CO). Anal. Calcd

Ethyl 4-(2-(4-phenoxyphenoxy)ethoxy)benzoate 111

In a 65 mL, round-bottomed flask equipped with a stirrer was placed acetone (15
mL), 4-phenoxyphenol (0.73 g, 3.6 mmol), K\(_2\)CO\(_3\) (0.74 g, 5.4 mmol) and ethyl 4-(2-
bromoethoxy)benzoate (1.00 g, 3.6 mmol) and the mixture was heated to 50° for 24 h.
The reaction mixture was than filtered and the solvent was removed under vacuo. The
filtrate was dissolved in chloroform and then washed with 20% NaOH solution. The
organic solution was concentrated in vacuo to yield a white solid which was
recrystallized from methanol (0.36 g, 0.95 mmol, 26.6%): mp 71-73;° IR (NaCl, cm\(^{-1}\))
1712 (C=O); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.40 (t, 3H, CH\(_3\)), 4.33-4.41 (m, 6H, CH\(_2\)), 6.95-7.09
(m, 8H, Ar-H), 7.32 (t, 2H, Ar-H), 8.03 (d, 2H, Ar-H); \(^13\)C NMR (CDCl\(_3\), ppm) 14.39
(CH\(_3\)), 60.69 (CH\(_2\)), 66.69 (CH\(_2\)), 66.94 (CH\(_2\)), 114.21 (Ar, CH), 115.85 (Ar, CH),

\[
\text{EtO}_2\text{C}\begin{array}{c}
\text{CH} \\
\text{CH} \\
\end{array}\text{O}\begin{array}{c}
\text{CH} \\
\text{CH} \\
\end{array}\text{O}\begin{array}{c}
\text{CH} \\
\text{CH} \\
\end{array}\text{O}\begin{array}{c}
\text{CH} \\
\text{CH} \\
\end{array}\text{O}
\]
117.76 (Ar, CH), 120.77 (Ar, CH), 122.59 (Ar, CH), 123.40 (Ar, C), 129.65 (Ar, C), 131.58 (Ar, CH), 150.73 (Ar, C), 154.78 (Ar, C), 158.34 (Ar, C), 162.30 (Ar, C), 166.31 (C=O). Anal. Calcd for C_{23}H_{22}O_5: C, 73.00; H, 5.86. Found: C, 72.54; H, 5.97.

**General Procedure for the Williamson Synthesis via Tosylates**

In a 100 mL, 3-necked, round-bottomed flask equipped with a stirrer was placed NMP (25 mL), the appropriate alcohol (50 mmol), and p-toluenesulfonyl chloride (9.54 g., 50 mmol). At room temperature, a 48% aqueous solution of sodium hydroxide (4.4 g., 110 mmol, 4.8 g H_2O) was added dropwise while keeping the internal temperature below 65° and the resulting mixture was allowed to stand for 20 min. Subsequently, the appropriate phenol (50 mmol) was slowly added and the resulting mixture was stirred for 2 h at 85-95°. The reaction mixture was allowed to cool and poured into a mixture of methanol/water (v/v%, 20/80) and the product was collected by filtration.

![1-Phenoxy-2-(3-ethylphenoxy)ethane](image)

**1-Phenoxy-2-(3-ethylphenoxy)ethane**

A white solid (7.59 g, 30 mmol, 60%) was obtained: mp 74.4-76°; IR (NaCl, cm⁻¹) 3051 (ArCH), 2873 (CH aliphatic); ¹H NMR (CDCl₃) δ 2.36 (s, 3H, CH₃), 4.34 (s, 4H, CH₂), 6.78-6.83 (m, 3H, Ar-H), 6.97-7.02 (m, 3H, Ar-H), 7.20 (t, 1H, Ar-H), 7.33 (t, 2H, Ar-H); ¹³C NMR (CDCl₃, ppm) 21.55 (CH₃), 66.43 (CH₂), 66.51 (CH₂), 111.60 (Ar, CH), 114.76 (Ar, CH), 115.64 (Ar, CH), 121.10 (Ar, CH), 121.96 (Ar, CH), 129.26 (Ar, CH), 129.52 (Ar, CH), 139.57 (Ar, C), 158.71 (Ar, C). Anal. Calcd for C, 78.92; H, 7.06. Found: C, 78.77; H, 7.00.
4-Fluoro-4’-(2-phenoxyethoxy)benzophenone 103

A white solid (12.38 g, 36 mmol, 73.6%) was obtained: mp 124-126.6° (see p16).

![4-Fluoro-4’-(2-phenoxyethoxy)benzophenone](image)

Ethyl 4-(2-phenoxyethoxy)benzoate 119

A white solid (3.33 g, 12.2 mmol, 48.8%) was obtained: mp 76-77.8° (lit.19 mp 79-80°).

![Ethyl 4-(2-phenoxyethoxy)benzoate](image)

Ethyl 4-(2-(4-phenoxyphenoxy)ethoxy)benzoate 111

A white solid (1.79 g, 6.5 mmol, 34.2%) was obtained: mp 71.4-75° (see p20).

![Ethyl 4-(2-(4-phenoxyphenoxy)ethoxy)benzoate](image)

4-Fluoro-4’-(2-(4-benzylxyphenoxy)ethoxy)benzophenone 108

A tan solid (7.54 g, 17.0 mmol 100%) was obtained: mp 120-150° (see p17).

![4-Fluoro-4’-(2-(4-benzylxyphenoxy)ethoxy)benzophenone](image)

4-(2-(4-Phenoxyphenoxy)ethoxy)benzoic acid 2

In a 100 mL, round-bottomed flask equipped with a stirrer was placed ethanol (41 mL), KOH (1.05 g, 16 mmol) and ethyl 4-(2-(4-phenoxyphenoxy)ethoxy)benzoate (1.50
g, 4.1 mmol) and the mixture was heated at reflux for 17 h. The reaction mixture was cooled and poured into DI water (300 mL) and acidified to pH 2. The product was collected via vacuum filtration. A white solid (1.19 g, 3.4 mmol, 82.9%) was obtained: mp: 191-192.6°; IR (NaCl, cm\(^{-1}\)) 3397.12 (OH), 1674.95 (CO); \(^1\)H NMR (DMSO-\(d_6\)) \(\delta\) 4.31 (m, 4H, CH\(_2\)), 6.88-7.08 (m, 9H, Ar-H), 7.34 (t, 2H, Ar-H), 7.82 (d, 2H, Ar-H); \(^13\)C NMR (DMSO-\(d_6\), ppm) 66.60 (CH\(_2\)), 114.22 (Ar, CH), 115.78 (Ar, CH), 117.29 (Ar, CH), 120.65 (Ar, CH), 122.61 (Ar, CH), 123.66 (Ar, C), 129.86 (Ar, CH), 131.33 (Ar, CH), 148.61 (Ar, C), 154.55 (Ar, C), 157.85 (Ar, C), 161.71 (Ar, C), 167.14 (CO). Anal. Calcd for C\(_{21}\)H\(_{18}\)O\(_5\): Anal. Calcd for C, 71.99; H, 5.18. Found: C, 71.80; H, 5.27

**General EAS Polymerization Procedure**

To a 25 mL, three-necked, round-bottomed flask under nitrogen was added Eaton’s reagent (5 mL), 4-(2-(4-phenoxypheinoxoyethoxy)benzoic acid (0.75 g, 2.1 mmol) and the temperature was raised to 105° over 2.5 h and heating was continued for 17 h. The viscous solution was diluted with methanesulphonic acid (10 mL) and the polymer was precipitated into water (200 mL). The polymer was filtered and washed with distilled water to remove any residual acid. The polymer was re-precipitated twice by dissolving it into 10 mL MSA and pouring it into water (200 mL). The polymer was then filtered and vacuum dried at rt for 24 h.

![Chemical Structure](image-url)
Trial 1. Polymer 3a

This reaction mixture was heated for 3 h (until it became viscous) instead of 17 h. A pink powder was obtained in 93% yield.

Trial 2. Polymer 3b

This reaction mixture was heated for 10 h instead of 17 h. A pink stringlike solid was obtained in quantitative yield.

Trial 3. Polymer 3c

A red-brown powder was obtained in 95% yield.

Trial 4. Polymer 3d

This reaction mixture was heated for 24 h instead of 17 h. A light pink powder was obtained in quantitative yield.
RESULTS AND DISCUSSION

The objective of this research was to produce an alkylene based PEEK by nucleophilic aromatic substitution (NAS) or electrophilic aromatic substitution (EAS) polymerization methods. The synthesis of the two respective monomers began with the synthesis of model compounds.

Synthesis of Model Compounds

A series of model compounds, 4-fluoro-4′-(2-phenoxyethoxy)benzophenone 103, 4-fluoro-4′-(3-phenoxypropoxy)benzophenone 104, and 4-fluoro-4′-(4-phenoxybutoxy)-benzophenone 105 were produced by the reaction of 4-fluoro-4′-hydroxybenzophenone 28 and the appropriate bromoalkoxybenzene in ethanol with potassium hydroxide. The physical properties and spectral data of the three 4-fluoro-4′-(Ω-phenoxyalkoxy)-benzophenones are listed in Table 1. Yields of 103-105 were relatively high and their melting points showed an alternating melting point behavior associated with other alkylene containing systems.9,10

The IR spectra of 103-105 (Figures 7, 11, 14, respectively) all show ketone carbonyl absorptions in the 1635-1645 cm⁻¹ region typical of fluorosubstituted benzophenone derivatives.9,10
Table 1. IR, $^1$H NMR, and $^{13}$C NMR Spectral Data for 103, 109, and 110.

<table>
<thead>
<tr>
<th>Cmpd</th>
<th>Yield (NaCl)</th>
<th>MP (°C)</th>
<th>IR (cm$^{-1}$) (NaCl)</th>
<th>$^1$H NMR (δ)</th>
<th>$^{13}$C NMR (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>103</td>
<td>66%</td>
<td>127.0-127.5</td>
<td>1642 (C=O)</td>
<td>CDCl$_3$, 4.41 (m, 4H, CH$_2$), 6.97-7.06 (m, 5H, Ar CH), 7.17 (t, 2H, Ar CH), 7.33 (t, 2H, Ar CH), 7.80-7.84 (m, 4H, Ar CH)</td>
<td>CDCl$_3$, 66.27, 66.81, 114.32, 114.72, 115.35, 129.59, 130.39, 132.30, 132.39, 134.40, 158.51, 162.34, 165.11, 194.05</td>
</tr>
<tr>
<td>104</td>
<td>77%</td>
<td>104-105</td>
<td>1642 (C=O)</td>
<td>CDCl$_3$, 2.33 (m, 2H, CH$_2$), 4.20 (t, 2H, CH$_2$), 6.93-7.03 (m, 5H, Ar CH), 7.17 (t, 2H, Ar CH), 7.31 (t, 2H, Ar CH), 7.79-7.84 (m, 4H, Ar CH)</td>
<td>CDCl$_3$, 29.22, 64.05, 64.81, 114.15, 114.52, 115.31, 120.88, 129.50, 130.07, 132.27, 132.40, 134.48, 158.78, 162.62, 165.07, 194.07</td>
</tr>
<tr>
<td>105</td>
<td>76%</td>
<td>126.2-126.6</td>
<td>1637 (C=O)</td>
<td>CDCl$_3$, 2.04 (m, 4H, CH$_2$), 4.07 (t, 2H, CH$_2$), 4.15 (t, 2H, CH$_2$), 6.91-7.00 (m, 5H, Ar CH), 7.17 (t, 2H, Ar CH), 7.31 (t, 2H, Ar CH), 7.80-7.84 (m, 4H, Ar CH)</td>
<td>CDCl$_3$, 25.95, 67.22, 67.82, 114.10, 114.47, 115.31, 120.70, 129.48, 129.93, 132.28, 132.42, 134.49, 158.91, 162.74, 165.05, 194.09</td>
</tr>
</tbody>
</table>

The $^1$H NMR spectra for all model compounds, 103, 104 and 105 (Figure 8, 12 and 15, respectively) exhibit similar aromatic regions with multiplets at 7.0 δ, 7.2 δ, 7.3 δ and 7.8 δ. The multiplets can be assigned using a $^1$H COSY NMR experiment (Figure 10). The multiplet at 7.8 δ can be assigned to the protons (4) ortho to the carbonyl group,$^{24}$ the multiplet at 7.2 δ assigned to the protons (2) ortho to the fluorine, the multiplet at 7.3 δ assigned to protons (2) in the pendent phenyl and the remaining protons (5) assigned to the multiplet at 7.0 δ. Of these protons (2) are assigned to the protons meta to the carbonyl and the rest of the protons (3) are assigned to the outer ring.

Significant differences in the $^1$H NMR of these compounds appear in the 0-4.5 δ region (Figure 1).
Figure 1. Partial $^1$H NMR spectra of 103 (top), 104 (middle) and 105 (bottom).

The aliphatic regions (0-5 $\delta$) in the $^1$H NMR spectra of compounds 103-105 are unique due to the oxyalkylene chain in each compound. The $^1$H NMR spectrum of 103 (Figure 1) exhibited two non-equivalent, non-first-order multiplets at 4.42 $\delta$ and 4.38 $\delta$ due to the asymmetric oxyalkylene chain. The $^1$H NMR spectrum of 104 (Figure 1) exhibited two clear triplets at 4.20 $\delta$ and 4.28 $\delta$ due to the two methylenes next to the oxygens and a quintet at 2.33 $\delta$ due to the middle CH$_2$ in the asymmetric oxyalkylene chain. The $^1$H NMR spectrum of 105 (Figure 1) exhibited two distorted triplets at 4.07 $\delta$ and 4.15 $\delta$ due to the two methylenes next to the oxygens and an unresolved multiplet at 2.04 $\delta$ due to the two center methylenes in the asymmetric oxyalkylene chain.

The $^{13}$C NMR spectra of 103-105 (Figures 9, 13, 16, respectively) all exhibit absorptions characteristic of a carbonyl carbon (194.05, 194.07 and 194.09 ppm, respectively), an aromatic carbon with an attached fluorine (doublets at 163.72, 163.85 and 163.89 ppm, respectively), two aromatic carbons attached to oxygen (162.35/158.52, 162.63/158.78 and 162.74/158.91 ppm, respectively), two aliphatic carbons attached to
oxygen (66.27/66.81, 64.05/64.81 and 67.22/67.82 ppm, respectively) and the remaining carbons of the aliphatic chain (nil, 29.22 and 25.95, respectively).

Synthesis of 4-Fluoro-4’-(2-(4-benzyloxyphenoxy)ethoxy)benzophenone

The precursor to monomer 1, 4-fluoro-4’-(2-(4-hydroxyphenoxy)ethoxy)-benzophenone 108, was produced via an SN2 reaction. The starting material 4-fluoro-4’-hydroxybenzophenone 28 is commercially available and 1-(benzyloxy)-4-(2-bromoethoxy)benzene 107 was produced by the reaction of 4-benzyloxy phenol 106 and 1,2-dibromoethane 30 in acetonitrile in the presence of potassium carbonate by a known procedure in 37% yield.25

Compound 107 was then used to produce 4-fluoro-4’-(2-(4-benzyloxyphenoxy)-ethoxy)benzophenone 108, in a 65% yield, using the same reaction conditions as stated for the model compounds.

The IR spectrum of 108 (Figure 17) shows an absorption at 1637 cm$^{-1}$ for the ketone carbonyl.
The $^1$H NMR spectral assignments for 108 are shown in Figure 2 and 18. The presence of the benzylic protective group is clearly indicated by the methylene absorption at 5.05 δ. The remaining assignments are in accord with those made for the model compounds.

The $^{13}$C NMR spectrum of 108 (Figure 19) exhibited three aliphatic peaks, nine aromatic peaks with three of them being doublets at 115.34 ppm, 132.29 ppm and 134.4 ppm with $J$-values of 21 Hz, 9 Hz, and 3 Hz respectively, six quaternary peaks with one being a doublet at 165.1 ppm ($J = 252$ Hz) due to the ipso fluorine splitting and a peak at 194.07 ppm due to the carbonyl carbon.

**Synthesis of 4-fluoro-4'-(2-(4-hydroxyphenoxy)ethoxy)benzophenone 1**

One convenient method for removal of the benzyl protective group is a reaction of the substrate with hydrogen in the presence of a 10% Pd/C catalyst. Thus, the reaction of 108 with H$_2$ in the presence of a palladium catalyst (10% Pd/C) in ethyl acetate gave a product originally identified as 1a in 52% yield.

![Chemical structure](image)

The IR spectrum of what was believed to be compound 1a (Figure 20) shows a hydroxyl absorbance at 3347 cm$^{-1}$ and a very weak carbonyl absorption at 1650 cm$^{-1}$.
The original $^1\text{H}$ NMR spectral assignments for what was believed to be 1a are shown in Figure 2 and 21. The most obvious change is the lack of a peak at 5.05 $\delta$ due to

![NMR Spectra](image)

**Figure 2.** $^1\text{H}$ NMR spectrum of 108 (top, CDCl$_3$), 1b (middle, DMSO-d$_6$) and expanded $^1\text{H}$ NMR spectrum of 1b (bottom, DMSO-d$_6$).
the benzyl methylene. The remaining assignments are in accord with those made for 108 with the exception of the obvious upfield shift for the protons ortho to the carbonyl (only small absorption at ~7.8 δ) that was attributed to the change of solvent (CDCl₃ to DMSO) at the time. The initial proton assignments remained in place until a series of experiments²⁴ was carried out involving the oxidation of fluoro-substituted benzhydrols. It was apparent from those experiments, that the absorption at ~ 7.8 δ in the proton NMR corresponded to the protons ortho to the carbonyl. Therefore, the reduction was not only removing the benzyl protective function but also reducing the carbonyl with peaks at 5.65 δ and 5.9 δ indicating the presence of the benzhydrol CH-OH moiety and the compound originally identified as 1a was actually 1b (Figure 2).

The ¹³C NMR spectrum of 1b (Figure 22) (determined later because of low solubility in DMSO-d₆) shows two methylene peaks, an unidentified peak at 73.1 ppm, six aromatic CH peaks with three of them being doublets at 115.61 ppm, 127.9 ppm and 132.1 ppm with J-values of 22 Hz, 9 Hz and 4.5 Hz respectively due to the fluorine splitting, six quaternary carbon peaks with one of them being a doublet at 160.92 ppm (J = 240 Hz) due to the ipso fluorine and a small carbonyl carbon peak at 193.23 ppm. Compared to the ¹³C NMR spectrum of 108, there is a loss of one CH₂ peak and six aromatic peaks indicating that the benzyl group has been successfully cleaved. In retrospect, the peak at 73.1 ppm occurs due to the benzhydrol carbon.

**Synthesis of Ethyl 4-(2-(4-phenoxyphenoxy)ethoxy)benzoate**

Ethyl 4-(2-(4-phenoxyphenoxy)ethoxy)benzoate 111 was synthesized by the reaction of 4-phenoxyphenol 110 and ethyl 4-(2-bromoethoxy)benzoate 109 in acetone with potassium carbonate in 26.6% yield. Of the starting materials, 4-phenoxyphenol 110
is commercially available and ethyl 4-(2-bromoethoxy)benzoate 109 was produced by the reaction of ethyl p-hydroxybenzoate 80 and 1,2-dibromoethane 30 in KOH/ethanol by an known procedure in a yield of 31%.25

![Chemical reaction diagram]

The IR spectrum 111 (Figure 23) shows an absorbance at 1712 cm\(^{-1}\) due to the ester carbonyl.

The \(^1\)H NMR spectrum of compound 111 (Figure 24) exhibits a triplet at 1.4 \(\delta\) due to the protons (3) of the methyl of the ethyl group, a multiplet at 4.3 \(\delta\) due to the protons (6) of the three methylenes (ethylene linkage and ethyl group), multiplets at 7.0 \(\delta\) and 7.3 \(\delta\) due to the aromatic protons (10) with the exception of those ortho (2) to the ester carbonyl which give rise to a doublet at 8.0 \(\delta\).

The \(^{13}\)C NMR spectrum of 111 (Figure 25) shows four aliphatic peaks with one being at 14.39 ppm due to the methyl of the ethyl group, seven aromatic peaks, five quaternary carbon peaks and one ester carbonyl peak at 166.31 ppm.

**Synthesis of Intermediate Alcohols**

Because of low yields in the preparation of 107 and 108, an alternative approach to 108 was sought. A patent\(^{20}\) described Williamson reactions in which tosylates were used in place of expensive and environmentally problematic halo compounds. The
Williamson synthesis using tosylates requires an alcohol to first be converted to the corresponding tosylate (in situ) and then reacted with the appropriate phenol. The phenols, 4-phenoxyphenol and 4-fluoro-4' -hydroxybenzophenone, were commercially available. The two alcohols that were needed were 2-[4-(benzyloxy)phenoxy]ethanol$^{22}$ \textbf{112} and ethyl p-(2-hydroxyethoxy)benzoate$^{21}$ \textbf{113}.

The synthesis of 2-[4-(benzyloxy)phenoxy]ethanol \textbf{112}, was carried out by the reaction of 4-(benzyloxy)phenol \textbf{106} and 2-chloroethanol in NaOH/ethanol by a known procedure in 79\% yield.$^{21}$
The IR spectrum of compound 112 (Figure 26) shows a broad absorbance at 3419 cm\(^{-1}\) due to the alcohol OH.

The \(^1\)H NMR spectrum of compound 112 (Figure 27) exhibits a triplet at 2.4 \(\delta\) due to the proton coupling of the OH with an adjacent methylene, multiplets at 3.9 \(\delta\) and 4.0 \(\delta\) due the protons of the hydroxyethoxy methylenes, a singlet at 5.0 \(\delta\) due to the protons of the benzylic methylene, a multiplet (distorted pair of doublets) at 6.9 \(\delta\) due to the protons of the para-substituted aromatic protons and a multiplet at 7.3 \(\delta\) due to the five aromatic protons of the benzyl group.

The \(^{13}\)C NMR spectrum of 112 (Figure 28) shows three aliphatic peaks at 61.53 ppm, 69.93 ppm and 70.7 ppm due to the three methylenes, five aromatic peaks and three quaternary carbon peaks, one at 137.26 ppm due to the aromatic quaternary carbon of the benzyl group and the other two at 153.02 ppm and 153.32 ppm due to the aromatic quaternary carbons attached to oxygen.

Ethyl p-(2-hydroxyethoxy)benzoate 113 was synthesized by the reaction of ethyl p-hydroxybenzoate 80 and 2-chloroethanol in NaOH/ethanol by a known procedure in 60% yield.\(^{22}\)

\[
\begin{align*}
\text{HO-} & \quad \text{CO}_2\text{Et} & + & \text{Cl} & \quad \text{OH} & \xrightarrow{\text{NaOH/Ethanol}} & \text{HO} & \quad \text{O} & \quad \text{CO}_2\text{Et} \\
80 & & & & & & & & 113
\end{align*}
\]

The IR spectrum of compound 113 (Figure 29) shows a broad absorbance at 3463 cm\(^{-1}\) due to the alcohol OH and a ester carbonyl absorption at 1697 cm\(^{-1}\).

The \(^1\)H NMR spectrum of compound 113 (Figure 30) shows a triplet at 1.4 \(\delta\) due to the protons (3) of the methyl of the ethyl group, two multiplets at 4.0 \(\delta\) and 4.1 \(\delta\) due to the protons (4) of the two methylenes of the hydroxyethoxy group, a quartet at 4.3 \(\delta\) due
to the protons (2) of the methylene of the ethyl group, a doublet at 7.1 δ due to aromatic protons (2) ortho to the hydroxyethoxy group, and a doublet at 7.9 δ due to the protons (2) ortho to the ester carbonyl.

The \(^{13}\text{C} \) NMR spectrum of 113 (Figure 31) shows four aliphatic peaks one at 14.30 ppm due to the methyl of the ethyl group, four aromatic peaks, two quaternary carbon peaks and one carbonyl peak at 166.45 ppm.

**Williamson Synthesis via Tosylates**

A series of model compounds, 1-phenoxy-2-(3-ethylphenoxy)ethane 118, 4-fluoro-4’-(2-phenoxyethoxy)benzophenone 103 and ethyl 4-(2-phenoxyethoxy)benzoate 119 were synthesized by a “one-pot” reaction. In the first part of the reaction, 1 mole of 2-phenoxyethanol 116 and 1 mole p-toluenesulfonyl chloride were stirred in NMP in the presence of 2.2 moles of sodium hydroxide; this yielded the tosylate intermediate. In the second step, 1 mole of the appropriate phenol 117, 28 or 80 was added to the reaction mixture.\(^{20}\)
Compound 118 was obtained in a 60% yield and was not purified further. The IR spectrum of compound 118 (Figure 32) shows an absorption at 3051 cm\(^{-1}\) due to the aromatic C-H stretches and at 2873 cm\(^{-1}\) due to the aliphatic C-H stretches.

The \(^1\)H NMR spectrum of compound 118 (Figure 33) shows a singlet at 2.3 \(\delta\) due to the protons (3) of the methyl group, a singlet at 4.3 \(\delta\) due to the protons (4) of the two methylenes, a multiplet at 6.8 \(\delta\) and a singlet at 7.2 \(\delta\) due to the protons (4) of the meta substituted ring and a multiplet at 6.9 \(\delta\) and a triplet at 7.3 \(\delta\) due to the protons (5) of the mono substituted ring.

The \(^13\)C NMR spectrum of 118 (Figure 34) shows three aliphatic peaks one at 21.55 ppm due to the methyl and one at 66.47 ppm due to the two methylenes, ten aromatic peaks and two quaternary carbon peaks one at 139.57 ppm due to the ipso methyl group and one at 158.71 ppm due to the two ipso oxygens.

Both 103 and 119 were previously known and were identified by melting point. Compound 103 was obtained in a 73% yield while compound 119 was obtained in a 48%
yield and neither was purified further. The synthesis of 103 and 119 clearly indicated that 4-fluoro-4’-(2-(4-benzyloxyphenoxy)ethoxy)benzophenone 108 and ethyl 4-(2-(4-phenoxyphephonyoxy)ethoxy)benzoate 111 could be synthesized by this procedure.

Thus, the EAS precursor, ethyl 4-(2-(4-phenoxyphephonyoxy)ethoxy)benzoate 111 was synthesized by a reaction of ethyl p-(2-hydroxyethoxy)benzoate 114 and p-toluenesulfonyl chloride in the presence of sodium hydroxide in NMP followed by the addition of 4-phenoxyphephonyol 110 in 34% yield.20

The NAS precursor, 4-fluoro-4’-(2-(4-benzyloxyphenoxy)ethoxy)benzophenone 108, was also synthesized by a reaction of 2-[4-(benzyloxy)phenoxy]ethanol 113 and p-toluenesulfonyl chloride in the presence of sodium hydroxide in NMP followed by the addition of 4-fluoro-4’-hydroxybenzophenone 28.20

The synthesis of 4-fluoro-4’-(2-(4-benzyloxyphenoxy)ethoxy)benzophenone 108 was successful but presented purification problems. The starting material, 2-[4-(benzyloxy)phenoxy]ethanol 113, was present in the final product (Figure 3) without a
non-chromatographic way to purify it. This can be seen in the $^1$H NMR of compound 108 by the two sets of triplets around 4-4.5 δ due to the protons (4) of the methylenes in compound 113, as well as the higher than expected integration in the aromatic region at 6.9 δ and 7.4 δ that correspond to the protons in the aromatic group in compound 113. Compound 121 was isolated in hopes of getting a pure intermediate and subsequently reacting it with the 4-fluoro-4’-hydroxybenzophenone 28 to yield compound 108. The intermediate 121 was also impure, as not all of the 2-[4-(benzyloxy)phenoxy]ethanol 113 was converted to the intermediate (Figure 3). This can be seen in the $^1$H NMR spectrum of compound 121 by the multiplets around 4-4.5 δ due to the methylenes in compound 113, as well as the higher than expected integration in the aromatic region around 6.9 δ and 7.4 δ that correspond to the aromatic group of compound 113.

**Figure 3.** $^1$H NMR spectrum of compound 113 (top), 121 (middle) and 108 (bottom).
Synthesis of 4-(2-(4-phenoxyphenoxy)ethoxy)benzoic acid

The monomer, 4-(2-(4-phenoxyphenoxy)ethoxy)benzoic acid 2, was synthesized by the hydrolysis of ethyl 4-(2-(4-phenoxyphenoxy)ethoxy)benzoate 111 in KOH/ethanol in 82% yield.

The IR spectrum of compound 2 (Figure 35) shows an absorbance at 3397 cm\(^{-1}\) due to an OH stretch and at 1674 cm\(^{-1}\) due to the carbonyl function.

The conversion of ethyl 4-(2-(4-phenoxyphenoxy)ethoxy)benzoate 111 to 4-(2-(4-phenoxyphenoxy)ethoxy)benzoic acid 2 is clearly indicated by the \(^1\)H NMR, Figure 4, and 36, in which the loss of the ethyl group is evident.

**Figure 4.** \(^1\)H NMR spectrum of compound 2(bottom) and compound 111 (top).
The $^{13}$C NMR of compound 2 (Figure 37) shows one aliphatic peak at 66.60 ppm due to the two methylenes, twelve aromatic peaks with five of them being quaternary carbons and one carbonyl carbon peak.

EAS Polymerization

The EAS polymers 3a-d were synthesized by the reaction of 4-(2-(4-phenoxyphenoxy)ethoxy)benzoic acid 2 with Eaton’s Reagent (methanesulfonic acid (MSA)/P$_2$O$_5$). The polymers were precipitated into water and reprecipitated from MSA into water. Physical and thermal properties of the polymers are shown in Table 2.

![Chemical structure of compounds 2 and 3](image)

Table 2. Physical and Thermal Properties of the Polymers 3a-d and 92.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Time (h)</th>
<th>% yield</th>
<th>$T_{5%}$ (°C)</th>
<th>$T_g$ (°C)</th>
<th>$\eta_{inh}^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>3</td>
<td>93</td>
<td>252</td>
<td>120</td>
<td>n/a</td>
</tr>
<tr>
<td>3b</td>
<td>10</td>
<td>100</td>
<td>207</td>
<td>116</td>
<td>0.63</td>
</tr>
<tr>
<td>3c</td>
<td>17</td>
<td>95</td>
<td>191</td>
<td>101</td>
<td>0.59</td>
</tr>
<tr>
<td>3d</td>
<td>24</td>
<td>~100</td>
<td>377</td>
<td>120</td>
<td>0.65</td>
</tr>
<tr>
<td>92</td>
<td>17</td>
<td>&gt;95</td>
<td>406</td>
<td>126</td>
<td>2.18</td>
</tr>
</tbody>
</table>

a) inherent viscosity measured in methansulfonic acid 0.25 g/dL at 20°

* See pp. 42-43 for explanation

It was obvious from initial TGA data of each polymer that additional drying was necessary. Subsequent TGA samples were first heated to 120° and then subjected to standard thermogravimetric analysis as shown in Figure 5. The curves clearly show that additional drying at temperatures above 120° would be helpful to get more realistic thermal stability estimates. Polymer 92, which was used for comparison because of its
Figure 5. TGA Data of polymers 3a-d and 92.

structure, exhibited a $T_{5\%}$ of about 400° was most similar to polymer 3d which has a $T_{5\%}$ of 377° (Figure 5). Because of the incomplete drying of polymers 3a–3d, a comparison of $T_g$ values seems tenuous.

Polymers 3a-d had $T_g$ values in the range of 100-120° with 3a and 3d having the highest at 120°. Polymer 3c and 3b had the lowest $T_g$’s at 99° and 117°, respectively. These can be compared to the $T_g$ of 126° for the model compound 92. Polymer 3 had the additional phenoxy group compared to 92 and it was expected that the $T_g$ may decrease due to an increase in flexibility of polymer 3. The decrease in $T_g$ may also be attributed to
the possibility of branching. Polymer, 92, exhibits a $T_m$ around 275° in accord with its semicrystalline nature. Polymers 3a-d do not exhibit any clear indication of a $T_m$.

![Figure 6. DSC Data of polymers 3a-d and 92.](image)

Polymers 3a-d were not soluble in common solvents such as hydrocarbons, halocarbons, DMSO or DMF. Viscosities were determined using methanesulfonic acid (Table 2) as had been previously used for polymer 92. The inherent viscosities of polymers 3a-d were much lower than that observed for polymer 92. Two possibilities exist for the difference; 1) the molecular weights produced were considerably lower and 2) branching occurred. The branching theory is in part indicated by the observation that one polymer, 3a, did not dissolve in MSA but swelled. It is difficult to attribute the swelling to crosslinking as the components for that behavior are not present. More likely, monomer 2 is behaving like an AB$_x$ ($x>2$) monomer, a classic branching monomer system. The most likely sites for branching are shown below and the behavior here may
be linked to the increased number of branching sites relative to the monomer used to produce polymer 92.

\[
\begin{align*}
92 & \quad \quad \quad \quad 3
\end{align*}
\]
Conclusions

The synthesis of the EAS monomer, 4-(2-(4-phenoxyphenoxy)ethoxy)benzoic acid 2 in good yield was successful. It can be polymerized using a Friedel-Crafts procedure employing Eaton’s Reagent. However, the polymers produced from several reactions show evidence of branching behavior.

The synthesis of the NAS monomer, 4-fluoro-4’-(2-(4-hydroxyphenoxy)ethoxy)benzophenone 1 was not successful in the sense that the procedure used for the removal of the benzyl protective group also resulted in the reduction of the carbonyl group. It was successful in that construction of the basic NAS monomer framework, i.e. the synthesis of 4-fluoro-4’-(2-(4-benzyloxyphenoxy)ethoxy)benzophenone, 108, can be accomplished.
Future Work

A more detailed study of the polymerization of monomer 2 should be conducted. Special emphasis should be given to the potential branching behavior of the monomer.

![Chemical structure of monomer 2](image)

Because the synthesis of the precursor 4-fluoro-4’-(2-(4-benzyloxyphenoxy)-ethoxy)benzophenone, 108, occurs in good yield, other methods for the removal of the benzyl protective group should be investigated, such as using HBr and acetic acid in TFA.27 Successful polymerization of monomer 1 would eliminate the possibility of branching behavior and the polymer produced could serve as a comparison standard to that produced by the EAS method. The successful preparation of 108 also suggests that other, longer alkyene chain derivatives 112 could be generated which could be polymerized without the possibility of branching.

![Chemical structure of monomer 1](image)

![Chemical structure of monomer 112](image)
Figure 7. The IR Spectrum (NaCl) of 103.

Figure 8. The 300 MHz ¹H NMR Spectrum (CDCl₃) of 103.
Figure 9. The 75 MHz $^{13}$C NMR Spectrum (CDCl$_3$) of 103.

Figure 10. COSY of aromatic $^1$H NMR region of 103.
Figure 11. The IR Spectrum (NaCl) of 104.

Figure 12. The 300 MHz $^1$H NMR Spectrum (CDCl$_3$) of 104.
Figure 13. The 75 MHz $^{13}$C NMR Spectrum (CDCl$_3$) of 104.

Figure 14. The IR Spectrum (NaCl) of 105.
Figure 15. The 300 MHz $^1$H NMR Spectrum (CDCl$_3$) of 105.

Figure 16. The 75 MHz $^{13}$C NMR Spectrum (CDCl$_3$) of 105.
Figure 17. The IR Spectrum (NaCl) of 108.

Figure 18. The 300 MHz $^1$H NMR Spectrum (CDCl$_3$) of 108.
Figure 19. The 75 MHz $^{13}$C NMR Spectrum (CDCl$_3$) of 108.

Figure 20. The IR Spectrum (NaCl) of 1b.
Figure 21. The 300 MHz $^1$H NMR Spectrum (DMSO-d$_6$) of 1b.

Figure 22. The 75 MHz $^{13}$C NMR Spectrum (DMSO-d$_6$) of 1b.
**Figure 23.** The IR Spectrum (NaCl) of 111.

**Figure 24.** The 300 MHz $^1$H NMR Spectrum (CDCl$_3$) of 111.
Figure 25. The 75 MHz $^{13}$C NMR Spectrum (CDCl$_3$) of 111.

Figure 26. The IR Spectrum (NaCl) of 112.
**Figure 27.** The 300 MHz $^1$H NMR Spectrum (CDCl$_3$) of 112.

**Figure 28.** The 75 MHz $^{13}$C NMR Spectrum (CDCl$_3$) of 112.
Figure 29. The IR Spectrum (NaCl) of 113.

Figure 30. The 300 MHz $^1$H NMR Spectrum (CDCl$_3$) of 113.
Figure 31. The 75 MHz $^{13}$C NMR Spectrum (CDCl$_3$) of 113.

Figure 32. The IR Spectrum (NaCl) of 118.
Figure 33. The 300 MHz $^1$H NMR Spectrum (CDCl$_3$) of 118.

Figure 34. The 75 MHz $^{13}$C NMR Spectrum (CDCl$_3$) of 118.
Figure 35. The IR Spectrum (NaCl) of 2.

Figure 36. The 300 MHz $^1$H NMR Spectrum (DMSO-d$_6$) of 2.
Figure 37. The 75 MHz $^{13}$C NMR Spectrum (DMSO-$d_6$) of 2.

Figure 38. TGA of EAS Polymer 3c
**Figure 39.** DSC EAS Polymer 1 3c

**Figure 40.** TGA EAS Polymer 2 3a
Figure 41. DSC EAS Polymer 2 3a

Figure 42. TGA EAS Polymer 3 3d
Figure 43. DSC EAS Polymer 3 3d

Figure 44. TGA EAS Polymer 4 3b
Figure 45. DSC EAS Polymer 4 3b
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24. A series of oxidations of known benzhydrol compounds by James Herbor of the Feld research group clearly established the correlation of absorptions at ~7.8 δ in the 'H NMR spectrum with protons ortho to the carbonyl and an absorption at ~5.6 δ with the benzhydrol HO-C-H.

25. The author would like to thank Brian Twarek of the Feld research group for the gift of this compound.

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VITAE

Shannon Hennelly was born on February 1, 1991. She graduated from Prairie Ridge High School in 2009. She attended Loras College where she earned her Bachelor of Science in Chemistry and Mathematics in 2013. She expects to receive her Master of Science Degree in Chemistry in December 2015.