The Synthesis of
1,4-bis(2-(4-(4-fluorobenzoyl)phenoxyethoxy)Benzene and
poly(aralkyl ether)s Derived from
1,4-bis(2-tosyloxyethoxy)Benzene

Juraj Drzic
Wright State University

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THE SYNTHESIS OF
1,4-BIS(2-(4-(4-FLUOROBENZOYL)PHENOXYETHOXY)BENZENE
AND POLY(ARALKYL ETHER)S DERIVED FROM
1,4-BIS(2-TOSYLOXYETHOXY)BENZENE

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

By

JURAJ DRZIC
B.S., University of Zagreb, Faculty of Chemical Engineering and Technology, 2012

2014
Wright State University
WRIGHT STATE UNIVERSITY

GRADUATE SCHOOL

May 29, 2014

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Juraj Drzic ENTITLED The Synthesis of 1,4-Bis(2-(4-(4-fluorobenzoyl)phenoxyethoxy)benzene and Poly(aralkyl ether)s Derived from 1,4-Bis(2-tosyloxyethoxy)benzene BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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

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

Committee on Final Examination

_________________________________
Eric Fossum, Ph.D.

_________________________________
Vladimir Katovic, Ph.D.

_________________________________
William A. Feld, Ph.D.

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

Drzic, Juraj M.S., Department of Chemistry, Wright State University, 2013. The Synthesis of 1,4-Bis(2-(4-(4-fluorobenzoyl)phenoxyethoxy)benzene and Poly(aralkyl ether)s Derived from 1,4-Bis(2-tosyloxyethoxy)benzene.

The reaction of 1,4-bis(2-tosyloxyethoxy)benzene or 1,4-bis(bromoethoxy)-benzene with 4-fluoro-4’-hydroxybenzophenone was carried out under a variety of conditions. Changes were made in solvent, reaction time, work-up and base. All attempts to generate a bis(fluorobenzophenone) monomer were unsuccessful. In some cases the presence of the half-product could be determined. In other cases, an elimination product was indicated. The ditosylate, 1,4-bis(2-tosyloxyethoxy)benzene was reacted with bisphenol-A, bisphenol-AF, bis(4-hydroxyphenyl)diphenylmethane and 9,9-bis(4-hydroxyphenyl)fluorene in a dioxane - water solution in the presence of sodium hydroxide to produce four polymers. The polymers were characterized by thermal analysis (TGA) to reveal 5% weight loss temperatures of 338°, 350°, 365° and 377°, respectively. The increase in thermal stability, as judged by the 5% weight loss values, appears to be related to the aromatic content. The polymers exhibited reasonable solubility in a variety of solvents.
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DEDICATION

To my advisor Dr. William A. Feld for his guidance and many useful advices during my stay in the USA; to my friends and colleagues at Wright State University and friends from all over the world, for their support and tireless company and good times, to my parents who helped me to get where I am now.
INTRODUCTION

Poly(arylene ether)s (PAE) and poly(ether ether ketone)s (PEEK) are important classes of high performance thermoplastics and offer a combination of excellent chemical, physical and mechanical properties. They find application as coatings, adhesives and structural resins for aerospace vehicles and related systems.

Bis(fluorobenzophenone) monomers 1, containing different center groups, like poly(oxyalkylene) groups (some containing tertiary amine functions) can be used to synthesize PEEKs with various bisphenol comonomers. Inserting a hydroquinone unit as a center group as illustrated in 2 by using 1,4-bis(2-tosyloxyethoxy)benzene is expected to increase the rigidity and $T_g$ of the polymer.

The objective of this research was to investigate the use of 1,4-bis(2-tosyloxy-ethoxy)benzene in 1) the synthesis of a new bis(fluorobenzoyl) monomer containing a hydroquinone/oxyalkylene hybrid subunit and 2) the synthesis of a series of polyethers employing bisphenol-A and related “kinked” bisphenols followed by characterization.
HISTORICAL

Poly(ether ether ketone)s (PEEK) possess good properties which make them useful as engineering thermoplastics. They have good resistance to strong chemicals and semicrystalline PEEKs have good thermal stability with melting points up to 400°. They are however, hard to process because of their high melt transitions. On the other hand, amorphous PEEKs have better processability due to their lower glass transitions and higher solubility but these properties also lower their possible applications.\(^1\)

The most common way of synthesizing PEEKs is a nucleophilic substitution of activated aromatic dihalides with bisphenolates. Many bisphenolates are commercially available and activated aromatic dihalides have been prepared by Friedel-Crafts acylation as well as several other reaction sequences.

Nucleophilic aromatic substitutions

Aryl ethers 5, synthesized by Bunnett and Zahler in 1951,\(^2\) show that it is possible to react alkali metal phenolates 3 with aromatic halides 4 possessing electron-withdrawing groups either \textit{ortho} or \textit{para} to the halogen which is being displaced.

\begin{center}
\begin{tabular}{c c c}
\textbf{3} & \textbf{4} & \textbf{5} \\
\end{tabular}
\end{center}

In 1967, using similar methods, Johnson et al.\(^3\) synthesized a poly(ether sulfone) 8 by the reaction of the sodium salt of bisphenol-A 6 and bis(p-chlorophenyl) sulfone 7 in a chlorobenzene/DMSO solvent mixture at 160°C under a nitrogen atmosphere.
In 1972, Vinogradova et al. synthesized aromatic polyethers using bisphenolates in a reaction with 4,4-difluorobenzophenone in DMSO at elevated temperatures.

The synthetic method for making PEEK, which is used commercially today, was developed in 1981 by Attwood et al. The bispotassium salt of bis(4-hydroxyphenyl)ketone was reacted with 10 in diphenyl sulfone at 335° for 2-3 hours.
The same method was utilized by Hergenrother et al. in 1988 to make a series of poly(ether ketone)s. Instead of diphenyl sulfone, a dimethylacetamide (DMAC)/$K_2CO_3$ solution was used as a solvent system for the reaction of 10 with dihydroxyaryl compounds 14. Some of these polymers were reported to have viscosities as high as 1.9.

In last two decades, attention has been focused on obtaining poly(ether ether ketone)s from different dihalide monomers like the difluorodibenzofuran monomer 16 which can be reacted with various bisphenols 14. In 1991, a similar idea was utilized and poly(arylene ether ketone)s 17 were synthesized by Cormier et al.
High-molecular-weight polymers 20 were prepared by Singh and Hay\(^7\) by reacting the novel fluoro monomer 18 with bisphenol-A 19. The polymers had good solubility in common organic solvents and they formed flexible, colorless and transparent films.

\[
\begin{align*}
&\text{18} \\
&\text{19} \\
\end{align*}
\]

\[
\begin{align*}
\text{K}_2\text{CO}_3 \rightarrow \text{DMAC} \\
\text{20}
\end{align*}
\]

In 1992, B. Patel\(^8\) reported the synthesis of poly(ether ether ketone)s 24a-e containing alkane chains of different length. Bis(fluorobenzophenone) monomers 23a-e used in polymerizations were synthesized by a nucleophilic substitution reaction of 4-fluoro-4'-hydroxybenzophenone 22 with various dibromoalkanes 21a-e. These monomers were used in a condensation polymerization with 19 in NMP/toluene using potassium carbonate as the base. The polymers could be cast into flexible, colorless and transparent films and their T\(_g\)s were inversely proportional to the length of the alkene chain in the monomer unit. The thermal stability of these polymers was good with a 5% weight loss at 450\(^\circ\) in both air and nitrogen.
A similar synthetic sequence was reported the same year by M. Patel. Poly(ether ether ketone)s with multiple oxyalkylene units 27a-d were synthesized.

Bis(fluorobenzophenone) monomers 26a-d were synthesized from 22 with different
ethylene glycol ditosylates 25a-d in ethanol by nucleophilic substitution in the presence of potassium hydroxide. The condensation polymerization of the described monomers was carried out in NMP/toluene using potassium carbonate as a base with 19. These polymers had good thermal stability with 5% loss in weight at 450°C in both air and nitrogen. Flexible transparent films were obtained.

In 2004, McGinty synthesized two different poly(ether ether ketone)s in a similar way as for the previous two examples. The new polymers contained a tertiary amine subunit. The ditosylate 28 with tertiary amine subunit was reacted with 22 in the presence of potassium hydroxide in ethanol to synthesize the bis(fluorobenzophenone) monomer 29.

Polymerization of 29 was carried out in NMP using potassium carbonate as a base and toluene as dehydrating agent with an appropriate bisphenol. Bisphenol-AF 30 as well as the bisphenol-A 19 were used in the polymerization to yield the corresponding poly(ether ether ketone)s 31a - b.
Another example of preparing poly(ether ether ketone)s with bis(fluorobenzoyl) monomer 34 was reported by Dancevic in 2005. Preparation of 34 was accomplished by reacting the dialdehyde 32 with a Grignard reaction prepared with the \( p \)-bromofluorobenzene in THF. The second step of preparing 34 involved the Jones oxidation of the intermediate diol 33 obtained in the first step.
Polymerization of 34 was carried out with various bis(hydroxyl compounds) 35a-e in NMP using potassium carbonate as base and toluene as dehydrating agent yielding polymers 36a-e shown below.

\[
\text{HO-R-OH + } \text{35a-e} \xrightarrow{\text{K}_2\text{CO}_3, \text{NMP}, \text{toluene}} \text{36a-e}
\]

Tosylate Group Substitutions by Phenols

In 1950 patent, Reeder and Wallsgrove\textsuperscript{11} reported production of linear polymers by reacting different diphenols with various disulphonic esters. The solvent system used for the reactions was a mixture of dioxane and water with sodium hydroxide as base. One example is the reaction of ethylene di(p-toluenesulfonate) 37 and hydroquinone 38. The product, polyether 39, was white powder melting in a temperature range of 240° to 270°.
Alternately, the reaction of 1,4-bis(2-tosyloxyethoxy)benzene 40 with 38 yields a product with the same repeating unit as 39.

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{SO}_2 & \quad \text{SO}_2 \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{Ph} & \quad \text{Ph} \\
40 & + \\
\text{HO} & \quad \text{HO} \\
38 & \\
\text{NaOH} & \quad \text{Dioxane/H}_2\text{O} & \quad \text{HO} \quad \text{Ph}
\end{align*}
\]

39

In 1966, Jones and Mather\(^\text{12}\) prepared a series of fiber forming polyesters. The reaction of methyl p-hydroxybenzoate 41 with the ditosylate 40 yields 1,4-bis(2-(4-methoxycarbonylphenoxy)ethoxy)benzene 42 which was used in the preparation of polyesters.

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{SO}_2 & \quad \text{SO}_2 \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{Ph} & \quad \text{Ph} \\
40 & + \\
\text{HO} & \quad \text{C} \quad \text{O} \quad \text{CH}_3 \\
41 & \\
\text{K}_2\text{CO}_3, \quad \text{Acetone, H}_2\text{O} & \quad \text{HO} \quad \text{Ph} \quad \text{C} \quad \text{O} \quad \text{CH}_3
42
\end{align*}
\]

In 2003, Ono et al.\(^\text{14}\) reported the synthesis of materials used for the electrochemical synthesis of polymers with crosslinked structures. The reaction of

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{SO}_2 & \quad \text{SO}_2 \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{Ph} & \quad \text{Ph} \\
40 & + \\
\text{N} & \\
44
\end{align*}
\]

\[
\begin{align*}
\text{pyrrole, DMSO} & \quad \text{KOH} \\
\text{N} & \quad \text{Ph} \quad \text{O} \quad \text{N} \\
45
\end{align*}
\]
ditosylate 40 with the pyrrole 44 yields 1,4-bis(2-(N-pyrrolyl)ethoxy)benzene 45. It was electrochemically polymerized to produce uniform thin films that could be doped to produce conductive films.

The successful nucleophilic substitution of the tosyl functions in 40 suggests that reactions analogous to those reported by Patel, Patel and McGinty could be extended to 40. Thus, the main objective of the current research was the study of the reaction of 40 with 4-fluoro-4’-hydroxybenzophenone 22 to provide monomers similar to 23a-e, 26a-d and 29 that could be used in polymerization reactions with diphenols under typical PEEK synthesis conditions.
Experimental

Instrumentation and Chemicals

Melting points were obtained with a DigiMelt MPA-160 or Electrothermal MP Apparatus. 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\(_3\), DMSO-d\(_6\), and Acetone-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 a N\(_2\) atmosphere. Infrared (IR) spectra were recorded as thin films (KBr) with a Nicolet 6700 FT-IR spectrometer. Chemicals were purchased from Aldrich and used as received.

1,4-bis(2-tosyloxyethoxy)benzene, 40

Into a 250 mL, round-bottomed flask equipped with a magnetic stirrer and an addition funnel containing a solution of 1,4-bis(2-hydroxyethoxy)benzene (6 g, 30 mmol) in THF(90 mL) was added an aqueous sodium hydroxide solution (7 g in 20 mL, 175 mmol) and the mixture was cooled to 0°. A solution of tosyl chloride (12.4 g, 65 mmol) in THF (35 mL) was added dropwise and the solution was stirred for 2 h at 0°. The reaction mixture was poured into water (200 mL), stirred overnight, filtered and dried to yield a white precipitate (14.5 g, 93%): mp 144° - 149°; \( ^1\)H NMR (CDCl\(_3\)) \( \delta \) 2.46 (s, 6H, CH\(_3\)), 4.10 (t, 4H, -CH\(_2\)-), 4.35 (t, 4H, -CH\(_2\)-), 6.71 (s, 4H, Ar hydroquinone), 7.34 (d, 2H, Ar tosyl), 7.83 (d, 2H, Ar tosyl).
**1,4-Bis(bromoethoxy)benzene, 48**

A solution of 1,4-bis(2-hydroxyethoxy)benzene (5.000 g, 0.0250 mol) and triphenylphosphine (15.801 g, 60 mmol) in acetonitrile (38 mL) was prepared in a 100 mL, round-bottomed flask equipped with an addition funnel and a magnetic stirrer. The solution was cooled with an ice bath and tetrabromomethane (20 g, 60 mmol) was slowly added with vigorous stirring. The reaction mixture was stirred at rt for 4 h and cold water (30 mL) was added to form a white precipitate. The precipitate was collected and washed with a methanol/water mixture (3/2, 3x15 mL). The product was recrystallized from methanol (10 mL) to yield 3.5 g of white crystals (43%): mp 112° -116°; $^1$H NMR (CDCl$_3$) δ 3.63 (t, 4H, CH$_2$), 4.26 (t, 4H, CH$_2$), 6.88 (s, 4H, aromatic).

**Fluorobenzophenone monomer, 49**

The synthesis of a bis(fluorobenzophenone) monomer from ditosylate 40 and 4-fluoro-4′-hydroxybenzophenone 22 was carried out using several combinations of solvent, reactant ratios and reaction times.

**Fluorobenzophenone monomer – 1st attempt**

In a 100 mL, round-bottomed flask equipped with a condenser, drying tube and a magnetic stirrer was placed a solution of KOH (88.7%) pellets (0.33 g, 6 mmol) in EtOH (18 mL), 4-fluoro-4′-hydroxybenzophenone 22 (1.3 g, 6 mmol) and 1,4-bis(2-tosyloxyethoxy)benzene 40 (1.0 g, 1.9 mol). The reaction mixture was refluxed for 18 h, cooled, and poured into water (180 mL). The mixture was stirred, filtered and dried to yield a white precipitate (1.102 g, 97%): mp 217° - 225°.
**Fluorobenzophenone monomer – 2\textsuperscript{nd} attempt**

In a 100 mL round-bottomed flask equipped with a condenser, drying tube and a magnetic stirrer was placed a solution of KOH (88.7%) pellets (1.340 g, 24 mmol) in EtOH (80 mL) and 4-fluoro-4’-hydroxybenzophenone 22 (5.202 g, 24 mmol) was added. Then reaction mixture was heated to 40° and 1,4-bis(2-tosyloxyethoxy)benzene 40 (3.800 g, 7.6 mmol) was added. The reaction mixture was refluxed for 20 h, cooled and poured into water (400 mL). The mixture was filtered and dried to collect a white-yellow precipitate (4.301 g, 95%).

**Fluorobenzophenone monomer – 3\textsuperscript{rd} attempt**

In a 50 mL, round-bottomed flask equipped with a condenser, drying tube and a magnetic stirrer was placed a solution of K\textsubscript{2}CO\textsubscript{3} (0.572 g, 4.1 mmol) in NMP (12 mL), 4-fluoro-4’-hydroxybenzophenone 22 (0.894 g, 4.1 mol) and 1,4-bis(2-tosyloxyethoxy)benzene 40 (1.000 g, 1.97 mmol). The reaction mixture was stirred at 90° for 6 h, cooled and poured into 200 mL of a saturated sodium bicarbonate solution. The mixture was stirred overnight, filtered and dried to yield a white-yellow precipitate (0.884 g, 75%).

**Fluorobenzophenone monomer – 4\textsuperscript{th} attempt**

In a 50 mL, round-bottomed flask equipped with a nitrogen inlet, a condenser and a nitrogen outlet, drying tube and a magnetic stirrer was placed K\textsubscript{2}CO\textsubscript{3} (0.925 g, 6.7 mmol) dissolved in an acetone/water mixture (6.5/3.5, 20 mL) followed by the addition of 4-fluoro-4’-hydroxybenzophenone 22 (1.405 g, 6.5 mmol) and 1,4-bis(2-tosyloxyethoxy)benzene 40 (1.500 g, 2.9 mol). The reaction mixture was refluxed for 66
h, cooled and poured into 50 mL of water. The precipitate was slurried with hot methanol (12 mL), filtered and dried to give a white precipitate (1.471 g, 85%).

**Fluorobenzophenone monomer – 5th attempt**

In a 50 mL, round-bottomed flask equipped with a nitrogen inlet, a condenser and a nitrogen outlet, drying tube and a magnetic stirrer was placed NaOH (0.523 g, 13.0 mmol) dissolved in a dioxane/water mixture (5/4, 18 mL) followed by the addition of 4-fluoro-4’-hydroxybenzophenone 22 (1.401 g, 6.5 mmol) and 1,4-bis(2-tosyloxyethoxy)benzene 40 (1.500 g, 2.9 mmol). The reaction mixture was refluxed overnight, cooled and the precipitate was washed with boiling water (80 mL) and boiling solution of HCL (1M, 80 mL). The white precipitate was collected (1.1004 g, 63%).

**Fluorobenzophenone monomer – 6th attempt**

In a 100 mL, round-bottomed flask equipped with a nitrogen inlet, a condenser and a nitrogen outlet, drying tube and a magnetic stirrer was placed a solution of K$_2$CO$_3$ (1.703 g, 12.4 mmol) in acetone/water mixture (6.5/3.5, 40 mL) followed by the addition of 4-fluoro-4’-hydroxybenzophenone 22 (2.602 g, 12.0 mmol) and 1,4-bis(2-tosyloxyethoxy)benzene 40 (1.500 g, 3.0 mmol). The reaction mixture was refluxed for 66 h, cooled and poured into water (50 mL). The precipitate was filtered and slurried with hot methanol (20 mL). Hot filtration gave a white precipitate (1.431 g, 80%).

**Fluorobenzophenone monomer – 7th attempt**

In a 100 mL, round-bottomed flask equipped with a condenser, drying tube and a magnetic stirrer was placed a solution of KOH (1.680 g, 30.0 mmol) in EtOH (50 mL) followed by the addition of 4-fluoro-4’-hydroxybenzophenone 22 (3.240 g, 15.0 mmol) and 1,4-bis(2-tosyloxyethoxy)benzene 40 (1.501 g, 3.0 mmol). The reaction mixture was
refluxed for 66 h, cooled and poured into 400 mL of water. The precipitate was filtered and washed with hot methanol. The bright-yellow precipitate was collected by filtration (0.275 g, 15%).

**Fluorobenzophenone monomer – 8th attempt**

In a 50 mL, round-bottomed flask equipped with a condenser, drying tube and a magnetic stirrer was placed a solution of KOH (0.770 g, 13.8 mmol) in NMP (20 mL) followed by the addition of 4-fluoro-4’-hydroxybenzophenone 22 (3.000 g, 46 mmol) and 1,4-bis(2-bromoethoxy)benzene 48 (1.350 g, 13.8 mol). The reaction mixture was stirred for 5 h at 90°, cooled and poured into 100 mL of water and stirred overnight. The product was filtered and dried to yield a pink-white precipitate (2.523 g, 92%).

**Fluorobenzophenone monomer – 9th attempt**

In a 50 mL, round-bottomed flask equipped with a condenser, drying tube and a magnetic stirrer was placed a solution of 4-fluoro-4’-hydroxybenzophenone 22 (0.700 g, 3.2 mmol) and KI (0.220 g, 0.13 mmol) in acetonitrile (26 mL) followed by the addition of K₂CO₃ (1.000 g, 7.23 mmol) and 1,4-bis(2-bromoethoxy)benzene 48 (0.501 g, 1.5 mmol). The reaction mixture was refluxed overnight, cooled and filtered. The precipitate was collected in the form of a white powder (0.645 g, 72%).

**4-(2-hydroxyethoxy)-4’-fluorobenzophenone, 50**

In a 50 mL, round-bottomed flask equipped with a nitrogen inlet, condenser, a nitrogen outlet and magnetic stirrer was placed 4-fluoro-4’-hydroxybenzophenone 22 (5.000 g, 23.0 mol), 2-chloroethanol (4.650 g, 57.7 mmol), sodium iodide (0.700 g, 4.6 mmol) and potassium carbonate (6.400 g, 46.3 mmol) and N,N-dimethylformamide (20 mL). The reaction mixture was heated at 95° and stirred under a nitrogen atmosphere for
4 h at which time additional 2-chloroethanol (1.500 g, 18.6 mol) and sodium iodide (0.250 g, 1.6 mmol) were added to the mixture. After an additional 14 h at 95°, the reaction mixture was quenched into NaOH solution (200 mL) with vigorous stirring. The solid was filtered and a white precipitate was collected (5.485 g, 91%): \textsuperscript{1}H NMR (CDCl\textsubscript{3}, δ) 4.03 (t, 2H, CH\textsubscript{2}), 4.19 (t, 2H, CH\textsubscript{2}), 7.01 (d, 2H, Ar), 7.16 (t, 2H, Ar), 7.80 (m, 4H, Ar).

4-(2-bromoethoxy)-4′-fluorobenzophenone, 52

A solution of triphenylphosphine (2.270 g, 8.6 mmol) and 4-(2-hydroxyethoxy)-4′-fluorobenzophenone 50 (2.250 g, 8.6 mmol) in dry acetonitrile (30 mL) was prepared in a 100 mL, round-bottomed flask equipped with nitrogen inlet, nitrogen outlet, addition funnel and magnetic stirrer. Tetrabromomethane (2.860 g, 8.6 mmol) was added portionwise under vigorous stirring. The mixture was stirred at room temperature for 4 h. The solvent was removed under vacuum and the remaining solid was dissolved in methanol (15 mL) and cooled to re-precipitate. White-yellow crystals were collected (1.275 g, 45%): mp. 77° - 80° C; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, δ) 3.69 (t, 2H, CH\textsubscript{2}), 4.40 (t, 2H, CH\textsubscript{2}), 7.01 (d, 2H, Ar), 7.17 (t, 2H, Ar), 7.81 (m, 4H, Ar).

General 1,4-bis(2-tosyloxyethoxy)benzene/Bisphenol Polymerization Procedure

The polymerization was carried out in a 25 mL, three-necked round-bottomed flask equipped with a mechanical stirrer, a nitrogen inlet and a condenser with a nitrogen outlet. The calculated molar quantities of ditosylate 40 (1.000 g, 1.973 mmol) and the appropriate bisphenol (1.973 mmol) were dissolved with potassium hydroxide in a solution of dioxane and water (5:4 ratio). The reaction mixture was refluxed for 24 h.
After cooling, the mixture was filtered and the precipitate was washed with boiling water and boiling HCL (100 mL, 1 M).

**Polymer 1, 52a**

The bisphenol used in the polymerization was bisphenol A. A white powder was obtained in 76% yield: IR (KBr, cm\(^{-1}\)) 3421 (OH) 3042 (aromatic CH), 2963 (aliphatic CH), 1225, 1069 (C-O-C). Anal. Calcd. for C\(_{25}\)H\(_{28}\)O\(_5\): C, 73.51%; H, 6.91%. Found: C, 72.75%; H, 6.62%.

**Polymer 2, 52b**

The bisphenol used in the polymerization was bisphenol AF. A white powder was obtained in 63% yield: IR (KBr, cm\(^{-1}\)) 3447 (OH), 3051 (aromatic CH), 2920 (aliphatic CH), 1255, 1069 (C-O-C). Anal. Calcd. for C\(_{25}\)H\(_{22}\)F\(_6\)O\(_5\): C, 58.14%; H, 4.29%. Found: C, 58.87%; H, 4.44%.

**Polymer 3, 52c**

The bisphenol used in the polymerization was bis(4-hydroxyphenyl)-diphenylmethane. A white powder was obtained in 73% yield: IR (KBr, cm\(^{-1}\)) 3446 (OH), 3052 (aromatic CH), 2923 (aliphatic CH), 1225, 1069 (C-O-C). Anal. Calcd for C\(_{35}\)H\(_{32}\)O\(_5\): C, 78.92%; H, 6.06%. Found: C, 76.88%; H, 5.88%.

**Polymer 4, 52d**

The bisphenol used in the polymerization was 9,9-(4-hydroxyphenyl)fluorene. A white powder was obtained in 91% yield: IR (KBr, cm\(^{-1}\)) 3449 (OH), 3036 (aromatic CH), 2920 (aliphatic CH), 1223, 1068 (C-O-C). Anal. Calcd for C\(_{35}\)H\(_{30}\)O\(_5\): C, 79.22%; H, 5.70%. Found: C, 77.11%; H, 5.76%.
RESULTS AND DISCUSSION

1,4-bis (tosylethoxy) benzene, 40

The ditosylate that was used for monomer synthesis was prepared by tosylation of 1,4-bis(2-hydroxyethoxy)benzene 47 with p-toluenesulphonyl chloride 46 in THF. The ditosylate was characterized by $^1$H NMR spectroscopy.

The $^1$H NMR spectrum of 40 exhibited unique absorptions in the aromatic region specific for hydrogen in a tosyl group. Doublet absorptions at 7.35 δ and 7.83 δ are associated with the protons on the aromatic ring of the tosylate group. A large singlet absorption at 6.71 δ corresponds to the protons in the symmetrical para-substituted aromatic ring derived from the diol. In the aliphatic region, the $^1$H NMR confirmed the presence of alkyl chains. Triplet absorptions at 4.10 δ and 4.35 δ integrated to 4 protons each. A sharp singlet absorption located in the aliphatic region at 2.47 δ corresponds to the methyl substituents in the tosyl groups.
An alternative starting material for fluorobenzophenone monomer synthesis was synthesized by the conversion of an alcohol to an alkyl bromide by the Appel reaction. The reaction of 1,4-bis(2-hydroxyethoxy)benzene 47 with tetrabromomethane in acetonitrile in the presence of triphenylphosphine yielded 1,4-bis(bromoethoxy)benzene, 48.
Figure 2. $^1$H NMR spectrum of 1,4-bis(bromoethoxy)benzene 48.

The $^1$H NMR spectrum of the 1,4-bis(bromoethoxy)benzene, 48 (Figure 2) gave an overall integration of the aromatic region versus the aliphatic region being 4:8 as expected. The aromatic region showed a sharp absorption singlet at 6.88 $\delta$ associated with the hydrogens located on the symmetrical para-substituted aromatic ring, while the aliphatic region contained two triplets at 4.26 $\delta$ and 3.63 $\delta$ representing the protons in the alkyl chains.

**Fluorobenzophenone Monomer, 49**

The attempted synthesis of difluoro monomer 49 that could later be used in polymerizations was carried out, essentially in accordance to the previous work carried out with similar molecules by Patel, Patel and McGinty, as previously noted.
The product is expected to be a symmetrical molecule with a para-substituted aromatic ring in the middle of the structure. This should, in the $^1$H NMR spectrum of 49, give rise to a singlet absorption in the aromatic region similar to that observed in Figure 1 and 2 for the ditosylate 40 and the dibromo compound 48. The integration of aromatic and aliphatic regions should give a ratio of 20:8. A pair of absorption triplets in the aliphatic region representing aliphatic chains located on both sides of the middle ring should also be present. The aromatic region should also contain absorption peaks for the other 16 protons located in the fluorobenzophenone end groups (Figure 3). Theoretically, protons assigned a should have HH ortho coupling and HF ortho coupling and give a multiplicity of three (assuming the J values are identical). Proton absorptions assigned as b would be present as a pair of doublets. The protons assigned c and d would give absorption doublets as expected.

**Figure 3.** Fluorobenzophenone monomer end group with marked proton sets.

In the attempt to synthesize the fluorobenzophenone monomer 49, different solvent systems were used with different reactant ratios or the reaction was run for a
longer amount of time. Table 1 shows a series of reaction conditions including the reaction conditions described previously.

**Table 1. Reaction conditions used in the synthesis of bis(fluorobenzophenone) 49.**

<table>
<thead>
<tr>
<th>Attempt #</th>
<th>Solvent</th>
<th>Base</th>
<th>Rxn time</th>
<th>Reactants ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>EtOH</td>
<td>KOH</td>
<td>24h</td>
<td>1:2</td>
</tr>
<tr>
<td>2.</td>
<td>EtOH</td>
<td>KOH</td>
<td>24h</td>
<td>1:2</td>
</tr>
<tr>
<td>3.</td>
<td>NMP</td>
<td>K$_2$CO$_3$</td>
<td>6h</td>
<td>1:2</td>
</tr>
<tr>
<td>4.</td>
<td>H$_2$O/Acetone</td>
<td>K$_2$CO$_3$</td>
<td>66h</td>
<td>1:2</td>
</tr>
<tr>
<td>5.</td>
<td>H$_2$O/Dioxane</td>
<td>NaOH</td>
<td>24h</td>
<td>1:2</td>
</tr>
<tr>
<td>6.</td>
<td>H$_2$O/Acetone</td>
<td>K$_2$CO$_3$</td>
<td>66h</td>
<td>1:4</td>
</tr>
<tr>
<td>7.</td>
<td>EtOH</td>
<td>KOH</td>
<td>66h</td>
<td>1:5</td>
</tr>
<tr>
<td>8.</td>
<td>NMP</td>
<td>KOH</td>
<td>5h</td>
<td>1:2</td>
</tr>
<tr>
<td>9.</td>
<td>CH$_3$CN</td>
<td>K$_2$CO$_3$</td>
<td>12h</td>
<td>1:2</td>
</tr>
</tbody>
</table>

**Fluorobenzophenone monomer - 1st attempt**

The first attempt at monomer synthesis was performed by imitating previous methods and was done in EtOH in the presence of KOH as base for 17h.

After 17 h, the product was collected, dried and analyzed. Due to insolubility of the product in DMSO-d$_6$, only a $^1$H NMR spectrum could be obtained.
The $^1$H NMR spectrum gave inconclusive results (Figure 4). The aromatic region as well as aliphatic region did not contain any sign of symmetry, i.e. the appearance of a singlet between 6.6 and 6.8 δ as observed for the ditosylate 40 and the dibromo compound 48. Integration of aromatic versus aliphatic region (as well as could be done) gave a ratio of around 14:8. Although integration of the aliphatic region absorption peaks gives a total of 8 protons located in the alkyl chains of the molecule, a variety of multiplets can be found as opposed to the expected pair of triplet absorptions which should integrate to four protons each. This could mean that there is still starting material present and that the reaction was not complete. Next to the absorption peak at 2.5 δ, typical for the DMSO, there is a small absorption singlet that could be associated with the six protons of the methyl substituents in the tosyl groups since its location is the same as
the location of the sharp peak in the starting ditosylate 40. It is a clear sign of the presence of the starting material in the product.

**Fluorobenzophenone monomer – 2\textsuperscript{nd} attempt**

The synthesis was attempted additional two times with the same reaction conditions as the first attempt.

![Reaction scheme](image)

**Figure 5.** \(^1\)H NMR spectrum of the bis(fluorobenzophenone) monomer 49 – 2\textsuperscript{nd} attempt.

Again, the \(^1\)H NMR spectrum (Figure 5) showed inconclusive results. Integration of the aromatic versus aliphatic regions gave a ratio of 12:3 confirming that the method
used in synthesis of previous fluorobenzophenone monomers was not successful for the desired monomer or at least did not give a pure product. As before, the absence of a singlet between 6.6 and 6.8 δ in the spectrum indicates the absence of the symmetrical para-substituted aromatic ring. The product from one of the repeated attempts was stirred in hot toluene and filtered. The 1H NMR spectrum (Figure 6) of the filtered product showed absorption peaks characteristic of the starting material, ditosylate 40, with matching integration of aromatic versus aliphatic region being 12:14.

Figure 6. 1H NMR spectrum of ditosylate 40 (top, CDCl₃) and the 1H NMR spectrum of the product collected after recrystallization from toluene (bottom, DMSO-d₆).

**Fluorobenzophenone monomer – 3rd attempt**

With the first two attempts being unsuccessful possibly due to EtOH not completely dissolving the ditosylate when it was added to the reaction mixture, a third attempt was
performed using K$_2$CO$_3$ as the base in NMP for 6 hours.

\[
\begin{align*}
\text{TsO} & \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{OTs} \\
\text{H} & \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{H} \quad \text{F} \\
\text{F} & \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{F} \\
\end{align*}
\]

The $^1$H NMR spectrum (Figure 7) obtained for the product collected after completion of the reaction gave inconclusive data with an integration ratio of approximately 10:7 between the aromatic and aliphatic absorption regions. Furthermore, lack of the sharp strong absorption peak (6.6 - 6.8 δ) in the aromatic region representing the protons located in the middle of the new molecule showed that the product of the reaction is not the desired symmetrical monomer 49.

Figure 7. $^1$H NMR spectrum of the bis(fluorobenzophenone) monomer 49 – 3$^{rd}$ attempt.
Similarly to the first attempt, there is a resemblance to the $^1$H NMR spectrum of the starting material 40, indicated by a weak, yet still present absorption peak at 2.4 $\delta$. The integration of aliphatic region peaks also suggests some close similarity to the ditosylate 40 starting material. Other than the signal strength, there is very little difference in chemical shifts at 4.3 and 4.4 $\delta$ in the product from the third attempt of fluorobenzophenone monomer synthesis, compared to the proton absorptions of the ditosylate 40 (Figure 1). The other absorption peaks in the aliphatic region are similar to the expected absorption peaks for the expected bis(fluorobenzophenone) monomer. The peaks at 3.68 and 3.92 $\delta$ appear as two triplets integrated to a value close to two protons total. That value disagrees with the expected integration of total of eight protons for the aliphatic chains in the expected monomer.

**Fluorobenzophenone monomer – 4th attempt**

In the 4th attempt to synthesize the bis(fluorobenzophenone) monomer, a solvent mixture of water and acetone was used in the presence of $\text{K}_2\text{CO}_3$ as base over a period of 66h. The reaction was modeled on an example reported in 1966 by Jones and Mather. They reported the reaction of ditosylate 40 with methyl p-hydroxybenzoate in a solvent system of water and acetone. The similarity of the structures of methyl
p-hydroxybenzoate and 4-fluoro-4’-hydroxybenzophenone and the use of ditosylate 40 prompted the idea for the 4th attempt of bis(fluorobenzophenone) monomer synthesis.

The characterization of the product from the 4th attempt by $^1$H NMR (Figure 8), showed different results compared to the previous attempts. The integration of the aromatic and aliphatic regions gave a ratio close to 11:8. Once again there were similarities with the ditosylate spectrum, with a strong absorption singlet at 2.4 $\delta$ most likely representing the protons of the methyl groups substituted on the rings of the tosylate end groups. The integration of the rest of the aliphatic region of the spectrum was far from expected most likely due to the presence of different products along with starting material in the sample. The pair of symmetrical multiplets found close to 4.5 $\delta$ in the

![Figure 8](image.jpg)

**Figure 8.** $^1$H NMR spectrum of the bis(fluorobenzophenone) monomer 49 – 4th attempt.

previous attempts, presenting the protons from the alkyl chains of either new product or the ditosylate, was not symmetrical in the 4th attempt. Another difference from the previous spectra was a sharp absorption singlet in the aromatic region, although the
integration was inconclusive as to whether it can be associated with the symmetry of the molecule and there is a possibility it belonged to the starting material.

**Fluorobenzophenone monomer – 5th attempt**

Similar to the 4th attempt, the reaction model used for the 5th attempt was based on a patent by Reedr and Wallsgrove\textsuperscript{11} that involved a reaction of ditosylate 40. The reaction was performed in a solvent mixture of dioxane and water with sodium hydroxide as base.

![Reaction Scheme](image)

The integration of the aromatic and aliphatic region gave a ratio of 12:8 that is similar to the integration ratios for ditosylate 40. However the absorption singlet at 2.4 \( \delta \), specific for methyl groups of the ditosylate, was not present. The aromatic region showed a multiplet around 7.7 \( \delta \) that could represent the four protons residing ortho to the carbonyl of the fluorobenzophenone. The carbonyl function is a good electron-withdrawing group that makes it possible for those proton absorption peaks to be shifted downfield. On the other side of the benzophenone, fluorine, having an electron-donating effect, shifts the ortho proton signals more upfield, so the absorption triplet at 7.4 \( \delta \) most likely represents those protons. The observed absorption data could indicate the formation of the half-product. If only one of the tosylate leaving groups underwent substitution, the product would not be symmetrical and that would correspond well with the given spectra since the aromatic absorption singlet, which would indicate the middle
ring as a center of a symmetrical molecule, is not present. On the other hand, it is also possible that both starting materials were present. The absorption doublet at 7.3 δ, next to the residual CHCl₃ singlet, showed almost no difference from the one in the spectra of the starting material, ditosylate 40, potentially associated with the protons next to the methyl groups on ditosylate, 40.

![Figure 9. ¹H NMR spectrum of the bis(fluorobenzophenone) monomer 49 – 5th attempt.](image)

**Fluorobenzophenone monomer – 6th attempt**

With the results of the 5th attempt being inconclusive and the ¹H NMR spectra of the other attempts suggesting that the half-product was forming, the reaction was repeated in a manner similar to the 4th attempt with the same solvent system and same base but with a different reactant ratio. Instead of a 1:2 ratio between the ditosylate and the 4-fluoro-4’-hydroxybenzophenone 22, a ratio of 1:4 was used in order to promote the formation of the complete molecule instead of a half-product.
The results were again inconclusive. The $^1$H NMR spectrum (Figure 10) showed the integration between aromatic and aliphatic absorption regions to be 11:7. The aromatic region did not contain an absorption peak that would indicate the presence of a symmetrical para-substituted aromatic structure. A multiplet at 7.7 $\delta$, a triplet at 7.39 $\delta$, a doublet 7.15 $\delta$ and a quartet at 6.9 $\delta$ showed very little difference from the previous two attempts. In the aliphatic region, a small absorption singlet at 2.4 $\delta$, once again suggested the presence of the methyl groups of the ditosylate.

Figure 10. $^1$H NMR spectrum of the bis(fluorobenzophenone) monomer 49 – 6th attempt.
**Fluorobenzophenone monomer – 7th attempt**

In the 7th attempt, the reaction was carried out in EtOH with KOH as base. The ratio of the reactants was increased to 5:1 (4-fluoro-4’-hydroxybenzophenone:ditosylate) and the reaction was refluxed for 66 hours.

![Chemical reaction diagram](image)

The $^1$H NMR spectrum of the product (Figure 11) showed results similar to the first two attempts. The aromatic region was integrated to a total of 12 protons, while aliphatic region integration gave a total of 13 protons. However, EtOH was not

**Figure 11.** $^1$H NMR spectrum of the bis(fluorobenzophenone) monomer 49 – 7th attempt.
completely removed from the product so the aliphatic region contained EtOH absorptions.

**Fluorobenzophenone monomer – 8\textsuperscript{th} attempt**

The 8\textsuperscript{th} attempt to synthesize the fluorobenzophenone monomer utilized a different starting material. Instead of 1,4-bis(2-tosylethoxy)benzene 40, which was used in the previous 7 attempts, 1,4-bis(bromoethoxy)benzene 48 was used. The reaction was carried out in NMP with KOH as a base for 5 hours.

![Chemical reaction diagram]

**Figure 12.** $^1$H NMR spectrum of the bis(fluorobenzophenone) monomer 49 – 8\textsuperscript{th} attempt
The $^1$H NMR spectrum of 49 (Figure 12) showed similar results as for the previous attempts. Integration of aromatic and aliphatic region gave a ratio of 10:3. The aliphatic region showed absorption peaks specific for alkyl chains with low intensity. The absorption peak at 7.0 δ in the aromatic region indicates the presence of the starting 1,4-bis(2-tosylethoxy)benzene, 40, due to its low intensity.

**Fluorobenzophenone monomer – 9th attempt**

The last attempt employed the same starting materials as used in the 8th attempt, 1,4-bis(bromoethoxy)benzene 48 and 4-fluoro-4’-hydroxybenzophenone 22. The reaction was carried out in CH$_3$CN in the presence of the K$_2$CO$_3$ and KI overnight.

![Reaction scheme and NMR spectrum](image)

**Figure 13.** $^1$H NMR spectrum of the bis(fluorobenzophenone) monomer 49 – 9th attempt.
The analysis of the $^1$H NMR spectrum for 49 is similar to results obtained for the 8th attempt. The aliphatic region showed an absorption multiplet at 4.4 $\delta$ corresponding to the protons in the alkyl chain. The aromatic region gave a relative integration of 23 protons that probably indicates the presence of starting material.

**Fluorobenzophenone Monomer Synthesis Conclusions**

The synthesis of a bis(fluorobenzophenone) monomer using 1,4-bis(tosylethoxy)benzene or 1,4-bis(bromoethoxy)benzene with 4-fluoro-4’-hydroxybenzophenone was unsuccessful. Changing the solvent system, reaction time and/or reactant ratio did not improve the outcome of the reaction. One possible explanation is that the tosylate or bromo groups undergo substitution only at one tosylate location of the starting molecule, creating a “half” product containing only one 4-fluorobenzooylphenoxy group. Although it is inconclusive, the $^1$H NMR data supports this theory. The $^1$H NMR spectrum aromatic region did not contain the specific peak, a singlet, which would indicate the presence of the symmetrical para-substituted ring of 49.

Another possibility is that the formation of the desired molecule is not possible due to steric effects in 40. Alternately, the original aromatic ring in the ditosylate 40 could be creating a sort of $\pi$- $\pi$ stacking effect with the rings of the fluorobenzophenone from the first substitution making the second substitution less likely (Figure 14).

![Figure 14. Possible $\pi$ - $\pi$ effect (a-parallel; b-parallel offset, c-T-shaped, d-Y-shaped)]
A Different Approach to the Bis(fluorobenzophenone) Monomer

In the attempt to find an alternate approach to synthesizing a bis(fluorobenzo-
phenone) monomer, the synthesis of an alternative hydroxyethoxy containing component, 4-(2-hydroxyethoxy)-4’-fluorobenzophenone was synthesized. Unlike the previous attempts of synthesis, the monomer could be created by synthesizing the end groups first and then assemble the monomer by reaction with hydroquinone.

4-(2-hydroxyethoxy)-4’-fluorobenzophenone, 50

The first part of the new approach was to synthesize 4-(2-hydroxyethoxy)-4’-
fluorobenzophenone, 50. The reaction of 4-hydroxy-4’-fluorobenzophenone 22 and 2-
chlorethanol, 51 was carried out in DMF in the presence of potassium carbonate and sodium iodide.

\[
\begin{align*}
\text{F} & \quad \text{O} \\
\text{H} & \quad \text{Cl} \\
\text{OH} & \quad \text{OH}
\end{align*}
\]

22 + ClCH₂CH₂OH → K₂CO₃, NaI → DMF → 
\[
\begin{align*}
\text{F} & \quad \text{O} \\
\text{H} & \quad \text{O} \\
\text{OH} & \quad \text{OH}
\end{align*}
\]

50

The \(^1\)H NMR spectrum (Figure 15) showed the expected absorptions. The integration of the aromatic and aliphatic region gave a proton ratio of 8:5. An absorption multiplet at 7.80 corresponds to the four protons located next to the carbonyl, while the other aromatic proton absorptions appear more upfield as a triplet at 7.16 δ and an absorption doublet at 7.01 δ. The aliphatic region exhibited a pair of triplet absorptions at
4.19 δ and 4.03 δ indicative of the protons in the alkyl chain, while a broad absorption peak at 2.01 δ is associated with the proton of the OH group.

**4-(2-bromoethoxy)-4’-fluorobenzophenone, 52**

The second step in the new approach for the synthesis of the bis(fluorobenzophenone) monomer is converting the 4-(2-hydroxyethoxy)-4’-fluorobenzophenone 50 to an alkyl halide which would be prone to attack by the deprotonated form of hydroquinone.

The conversion of 4-(2-hydroxyethoxy)-4’-fluorobenzophenone, 50 to 4-(2-bromoethoxy)-4’-fluorobenzophenone, 52 was carried out in acetonitrile in the presence of triphenylphosphine and tetrabromomethane at room temperature. The byproduct of the reaction is triphenylphoshine oxide and can be difficult to remove. The product was
dissolved in methanol at room temperature and cooled to temperatures below 0° and filtered in order to successfully remove the byproduct.

![Chemical structure diagram]

**Figure 16.** $^1$H NMR spectrum of the 4-(2-bromoethoxy)-4’-fluorobenzophenone 52.

The $^1$H NMR spectrum (Figure 16) exhibited similar absorptions as the previous 4-(2-hydroxyethoxy)-4’-fluorobenzophenone, 50. The aromatic region again showed an absorption multiplet at 7.81 δ associated with the four protons *ortho* to the carbonyl. A triplet absorption at 7.17 δ and a doublet absorption at 7.01 δ are associated with the remaining aromatic protons. A pair of triplet absorptions associated with the alkyl protons were found at 4.40 δ and 3.69 δ.

When compared (Figure 17) to the previous spectra of 4-(2-hydroxyethoxy)-4’-fluorobenzophenone, 50, the aliphatic absorption peaks are more separated due to the replacement of the OH by a bromine atom at the end of the chain.
Figure 17. $^1$H NMR Spectrum aliphatic regions of 4-(2-hydroxyethoxy)-4’-fluorobenzophenone 50 and 4-(2-bromoethoxy)-4’-fluorobenzophenone 52.

Polymerization of Ditosylate 40

The polymerization of the ditosylate, 40 with the appropriate bisphenol was carried out in dioxane/water solvent mixture using sodium hydroxide as a base to yield the corresponding poly(aralkyl ether)s 52a-d.
Polymerization of ditosylate 40 with bisphenol-A, bisphenol-AF, bis(4-hydroxyphenyl)diphenylmethane and 9,9-bis(4-hydroxyphenyl)fluorene yielded the polymers 52a-d as white powders. Thermal analysis (TGA, Figures 22 and 23) of polymers 52a-d gave 5% weight loss temperatures of 338°, 350°, 365° and 377°, respectively.

The IR spectra of polymers 52a-d (Figures 18-21) showed characteristic peaks for ether functions and terminal hydroxyl groups. The stretching absorptions of aryl alkyl ether linkages (C-O-C) were found at 1225 and 1069 cm\(^{-1}\) for the polymers 52a-c, while polymer 52d had peaks at 1223 and 1068 cm\(^{-1}\).

![Figure 18. IR spectrum (KBr) of polymer 52a.](image-url)
Figure 19. IR spectrum (KBr) of polymer 52b.

Figure 20. IR spectrum (KBr) of polymer 52c.
Figure 21. IR spectrum (KBr) of polymer 52d.

Figure 22. TGA of polymers 52a-d.
The solubility of the polymers 52a-d (Table 2) was investigated over a period of 24 hours by mixing 4 mg of the polymer with 1 mL of an appropriate solvent. All the polymers were at least partially soluble in most of the solvents.

**Table 2. Solubility of polymers 52a-d.**

<table>
<thead>
<tr>
<th>Solubility</th>
<th>52a</th>
<th>52b</th>
<th>52c</th>
<th>52d</th>
</tr>
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<tbody>
<tr>
<td>m-Cresol</td>
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<td>+</td>
<td>+</td>
</tr>
<tr>
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<td>±</td>
<td>-</td>
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<td>±</td>
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<tr>
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<td>+</td>
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<tr>
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<tr>
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<td>-</td>
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</tr>
<tr>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Acetone</td>
<td>±</td>
<td>-</td>
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</tbody>
</table>

(+ soluble; - not soluble; ± partially soluble)
Summary

Numerous attempts to synthesize a new bis(fluorobenzophenone) monomer, 1,4-bis (2-(4-(4-fluorobenzoyl)phenoxyethoxy)benzene 49, were unsuccessful in spite of the use of a variety of conditions. Monosubstitution and elimination reactions may be important side reactions.

The polymerization of 1,4-bis(2-tosyloxyethoxy)benzene 40 with a series of bisphenols gave a series of poly(aralkyl ether)s. Although the molecular weights were not determined, the polymers showed good thermal stability in a nitrogen atmosphere. It appears that having larger aromatic units in the bisphenol can improve the thermal stability and solubility of the polymers.

Future Work

The synthesis of a bis(fluorobenzophenone) monomer using 4-(2-bromoethoxy)-4’-fluorobenzophenone 52 and hydroquinone needs to be further investigated.

Creating bis(fluorobenzophenone) monomers using alternate bis(hydroxyethoxy)aromatics should be investigated. The steric influence of the central aromatic unit could be investigated.
REFERENCES


VITAE

Juraj Drzic was born in Zagreb, Croatia on March 27, 1990. He graduated with a Bachelor of Science Degree majoring in Chemical Engineering at Faculty of Chemical Engineering and Technology, University of Zagreb in 2012. Juraj expects to receive his Master of Science Degree in Chemistry in May, 2014.