2013

The Synthesis of Benzyloxy Substituted DP-PPVs

Ryan Oostendorp
Wright State University

Follow this and additional works at: https://corescholar.libraries.wright.edu/etd_all

Part of the Chemistry Commons

Repository Citation
https://corescholar.libraries.wright.edu/etd_all/795

This Thesis is brought to you for free and open access by the Theses and Dissertations at CORE Scholar. It has been accepted for inclusion in Browse all Theses and Dissertations by an authorized administrator of CORE Scholar. For more information, please contact corescholar@www.libraries.wright.edu, library-corescholar@wright.edu.
THE SYNTHESIS OF
BENZYLOXY SUBSTITUTED DP-PPVs

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

By

RYAN D. OOSTENDORP
B.S., Loras College, 2011

2013
Wright State University

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.

David A. Grossie, Ph.D.

William A. Feld, Ph.D.

R. William Ayres, Ph.D.
Interim Dean, Graduate School
ABSTRACT

Oostendorp, Ryan D. M.S., Department of Chemistry, Wright State University, 2013.
The Synthesis of Benzylxy Substituted DP-PPVs.

The alkyne 1-(benzyloxy)-4-(propargyloxy)benzene was reacted with 2,5-di(carboethoxy)3,4-diphenylcyclopentadienone to yield diethyl 5-((4-(benzyloxy)phenoxy)methyl)-2,3-diphenylterephthalate. The terephthalate was reduced with lithium aluminum hydride to produce 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(hydroxymethyl)-2,3-diphenylbenzene. The diol was reacted with thionyl chloride to yield the monomer 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(chloromethyl)-2,3-diphenylbenzene that has a pendent protected phenol function. The new compounds were characterized by melting point, IR, $^1$H NMR, $^{13}$C NMR spectroscopy and elemental analysis. Polymerization of the dichloro monomer via a Gilch polymerization yielded poly[(2,3-diphenyl-(5-((4-(benzyloxy)phenoxy)methyl)-1,4-phenylene)vinylene]. The polymer was characterized by IR, $^1$H NMR spectroscopy, TGA and DSC. The polymer was insoluble in most solvents but partially soluble in chlorinated solvents. The solid polymer fluoresced a bluish-green under UV light either in solution or in the solid state.
### TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>viii</td>
</tr>
<tr>
<td>ACKNOWLEDGMENT</td>
<td>ix</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>x</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>HISTORICAL</td>
<td>2</td>
</tr>
<tr>
<td>DP-PPVs</td>
<td>3</td>
</tr>
<tr>
<td>Sulfonium Precursor Route</td>
<td>4</td>
</tr>
<tr>
<td>Alkylated DP-PPVs</td>
<td>5</td>
</tr>
<tr>
<td>Modified Gilch method</td>
<td>5</td>
</tr>
<tr>
<td>Long Branched Alkoxy substituted DP-PPV</td>
<td>7</td>
</tr>
<tr>
<td>Liquid Crystal substituted DP-PPV</td>
<td>11</td>
</tr>
<tr>
<td>Hydrophobic and Hydrophilic Dendritic side chains</td>
<td>14</td>
</tr>
<tr>
<td>Synthesis of Phenolic Pendent Precursors</td>
<td>16</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>18</td>
</tr>
<tr>
<td>Instrumentation and Chemicals</td>
<td>18</td>
</tr>
<tr>
<td>1-(Benzyloxy)-4-(propargyloxy)benzene <strong>75</strong></td>
<td>18</td>
</tr>
<tr>
<td>Diethyl 5-((4-(benzyloxy)phenoxy)methyl)-2,3-diphenyterphthalate <strong>76</strong></td>
<td>19</td>
</tr>
</tbody>
</table>
# TABLE OF CONTENTS (CONTINUED)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-((4\text{-}(\text{benzyloxy})\text{phenoxy})\text{methyl})\text{-}1,4\text{-}di(\text{hydroxymethyl})\text{-}2,3\text{-}diphenylbenzene</td>
<td>20</td>
</tr>
<tr>
<td>5-((4\text{-}(\text{benzyloxy})\text{phenoxy})\text{methyl})\text{-}1,4\text{-}di(\text{chloromethyl})\text{-}2,3\text{-}diphenylbenzene</td>
<td>21</td>
</tr>
<tr>
<td>Poly([(2,3\text{-}diphenyl\text{-}(5\text{-}(4\text{-}(\text{benzyloxy})\text{phenoxy})\text{methyl})\text{-}1,4\text{-}phenylene)\text{vinylene}])</td>
<td>22</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td>23</td>
</tr>
<tr>
<td>1\text{-}(\text{benzyloxy})\text{-}4\text{-}(\text{propargyloxy})\text{benzene}</td>
<td>23</td>
</tr>
<tr>
<td>Diethyl 5-((4\text{-}(\text{benzyloxy})\text{phenoxy})\text{methyl})\text{-}2,3\text{-}diphenylterphthalate</td>
<td>25</td>
</tr>
<tr>
<td>5-((4\text{-}(\text{benzyloxy})\text{phenoxy})\text{methyl})\text{-}1,4\text{-}di(\text{hydroxymethyl})\text{-}2,3\text{-}diphenylbenzene</td>
<td>26</td>
</tr>
<tr>
<td>5-((4\text{-}(\text{benzyloxy})\text{phenoxy})\text{methyl})\text{-}1,4\text{-}di(\text{chloromethyl})\text{-}2,3\text{-}diphenylbenzene</td>
<td>28</td>
</tr>
<tr>
<td>poly([(2,3\text{-}diphenyl\text{-}(5\text{-}(4\text{-}(\text{benzyloxy})\text{phenoxy})\text{methyl})\text{-}1,4\text{-}phenylene)\text{vinylene}])</td>
<td>30</td>
</tr>
<tr>
<td>APPENDIX</td>
<td>42</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>49</td>
</tr>
<tr>
<td>VITAE</td>
<td>50</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Retrosynthetic scheme for the synthesis of a phenolic PPV</td>
<td>23</td>
</tr>
<tr>
<td>2.</td>
<td>TGA curve showing 5% wt. loss temperature</td>
<td>31</td>
</tr>
<tr>
<td>3.</td>
<td>DSC Trace of 79</td>
<td>32</td>
</tr>
<tr>
<td>4.</td>
<td>300 MHz $^1$H NMR Spectrum (CDCl$_3$) of 73</td>
<td>33</td>
</tr>
<tr>
<td>5.</td>
<td>300 MHz $^1$H NMR Spectrum (CDCl$_3$) of 75</td>
<td>33</td>
</tr>
<tr>
<td>6.</td>
<td>300 MHz $^{13}$C NMR Spectrum (CDCl$_3$) of 75</td>
<td>34</td>
</tr>
<tr>
<td>7.</td>
<td>300 MHz $^{13}$C NMR dept 135 Spectrum (CDCl$_3$) of 75</td>
<td>34</td>
</tr>
<tr>
<td>8.</td>
<td>IR Spectrum (NaCl) of 75</td>
<td>35</td>
</tr>
<tr>
<td>9.</td>
<td>300 MHz $^1$H NMR Spectrum (CDCl$_3$) of 76</td>
<td>35</td>
</tr>
<tr>
<td>10.</td>
<td>300 MHz $^{13}$C NMR Spectrum (CDCl$_3$) of 76</td>
<td>36</td>
</tr>
<tr>
<td>11.</td>
<td>300 MHz $^{13}$C NMR dept135 Spectrum (CDCl$_3$) of 76</td>
<td>36</td>
</tr>
<tr>
<td>12.</td>
<td>IR Spectrum (NaCl) of 76</td>
<td>37</td>
</tr>
<tr>
<td>13.</td>
<td>300 MHz $^1$H NMR Spectrum (CDCl$_3$) of 77</td>
<td>37</td>
</tr>
<tr>
<td>14.</td>
<td>300 MHz $^{13}$C NMR Spectrum (CDCl$_3$) of 77</td>
<td>38</td>
</tr>
<tr>
<td>15.</td>
<td>300 MHz $^{13}$C NMR dept135 Spectrum (CDCl$_3$) of 77</td>
<td>38</td>
</tr>
<tr>
<td>16.</td>
<td>IR Spectrum (NaCl) of 77</td>
<td>39</td>
</tr>
<tr>
<td>17.</td>
<td>300 MHz $^1$H NMR Spectrum (CDCl$_3$) of 78</td>
<td>39</td>
</tr>
<tr>
<td>18.</td>
<td>300 MHz $^{13}$C NMR Spectrum (CDCl$_3$) of 78</td>
<td>40</td>
</tr>
<tr>
<td>19.</td>
<td>300 MHz $^{13}$C NMR dept135 Spectrum (CDCl$_3$) of 78</td>
<td>40</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>20.</td>
<td>300 MHz $^1$H NMR Spectrum (CDCl$_3$) of 79</td>
<td>41</td>
</tr>
<tr>
<td>21.</td>
<td>IR Spectrum (NaCl) of 77</td>
<td>41</td>
</tr>
<tr>
<td>22.</td>
<td>300 MHz $^1$H NMR Spectrum (Acetone-d$_6$) of 80</td>
<td>44</td>
</tr>
<tr>
<td>23.</td>
<td>300 MHz $^1$H NMR Spectrum (Acetone-d$_6$) of 81</td>
<td>44</td>
</tr>
<tr>
<td>24.</td>
<td>300 MHz $^1$H NMR Spectrum (Acetone-d$_6$) of 82</td>
<td>45</td>
</tr>
<tr>
<td>25.</td>
<td>300 MHz $^1$H NMR Spectrum (DMSO-d$_6$) of 85</td>
<td>46</td>
</tr>
<tr>
<td>26.</td>
<td>300 MHz $^1$H NMR Spectrum (DMSO-d$_6$) of 86</td>
<td>47</td>
</tr>
<tr>
<td>27.</td>
<td>300 MHz $^1$H NMR Spectrum (DMSO-d$_6$) of 87</td>
<td>47</td>
</tr>
<tr>
<td>28.</td>
<td>X-ray crystal structure of 87</td>
<td>48</td>
</tr>
<tr>
<td>29.</td>
<td>X-ray crystal structure of 88</td>
<td>48</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Characterization of 1-(benzyloxy)-4-(propargyloxy)benzene</td>
<td>75</td>
</tr>
<tr>
<td>2.</td>
<td>Characterization of 5-((4-(benzyloxy)phenoxy)methyl)-2,3-diphenylterphthalate</td>
<td>76</td>
</tr>
<tr>
<td>3.</td>
<td>Characterization of 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(hydroxymethyl)-2,3-di(phenylbenzene)</td>
<td>77</td>
</tr>
<tr>
<td>4.</td>
<td>Characterization of 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(chloromethyl)-2,3-di(phenylbenzene)</td>
<td>78</td>
</tr>
</tbody>
</table>
ACKNOWLEDGMENT

I would like to acknowledge my advisor, Dr. William Feld for the opportunity to work in his group and for all of his guidance and support. I would also like to acknowledge the Chemistry Department faculty and graduate students for their support.
DEDICATION

I would like to dedicate this work to my family; my parents, Dave and Kim, and my sisters, Amanda, Alison and Nicole for encouraging me throughout my life.
INTRODUCTION

Poly(phenylene vinylene) (PPV) 1 and its derivatives have been used in recent years in polymer, light-emitting diodes (PLEDs)1 because they have excellent electroluminescent properties and are thermally stable but they do have limited solubility. To enhance processing and performance, alkoxy groups have been added to the backbone of the polymer as in MEH-PPV 2.2 Other derivatives include DP-PPV 3 that exhibits a higher photoluminescence than PPV.3 DP-PPV derivatives having alkoxy substituents on the pendent phenyl rings have been reported and are all synthesized by the reaction of a cyclopentadienone with an alkyne.4,5,6 The generation of hydroxyl-substituted, phenylated derivatives DP-PPVOH 4 would potentially provide enhanced properties as well as water solubility by reaction with base.

The objectives of this research were to investigate the synthesis of phenolic substituted PPV derivatives by using benzyloxy protected precursors in the synthesis of 1) cyclopentadienones that can be used in DP-PPV monomer preparation and/or 2) alkynes that can be used in monomer preparation.
HISTORICAL

DP-PPVs

The first synthesis of oligomeric poly(2,3-diphenylphenylene vinylene) 3 was reported in 1982 by Ganesan. The polymer has been called DP-PPV and has been used in many studies.

One monomer was prepared by a multistep procedure that began with the base-catalyzed aldol reaction of benzil 5 and 3-pentanone 6 to produce 3,4-diphenyl-2,5-dimethylcyclopent-2-en-4-ol-one 7 which was dehydrated to 2,5-dimethyl-3,4-diphenylcyclopentadienone 8 (exists as a disassociating dimer) with acetic anhydride.

The Diels-Alder reaction of cyclopentadienone 8 with norbornadiene 9 yields 3',6'-dimethyl-o-terphenyl 10. The dimethyl compound 10 was brominated with N-bromosuccinimide to form 3',6'-biscbromomethyl-o-terphenyl 11.
The dibromo compound 11 was converted to the monomer 2,3-diphenylterephthalaldehyde 13 with hexamethylene tetramine (HMTA) 12 by use of the Sommelet reaction.

The preparation of the second monomer was carried out by reaction of 3',6'-bisbromomethyl-o-terphenyl 11 with triphenylphosphine 14 to yield 2,3-diphenyl-p-xylenebis(triphenylphosphonium bromide) 15.

Oligomeric DP-PPV 3 was produced by the Wittig reaction of the monomers 2,3-diphenylterephthalaldehyde 13 and 2,3-diphenyl-p-xylenebis(triphenylphosphonium bromide) 15. The DP-PPV 1 produced by this method was determined to have an average
molecular weight of 1470, a pale green color, and was soluble in chlorinated nonpolar solvents.

![Chemical structures](image)

**Sulfonium Precursor Route**

An alternate approach was reported by Paulvannan. The reaction of 3',6'-bisbromomethyl-o-terphenyl 11 with excess dimethyl sulfide was used to prepare the 2,3-diphenyl-p-xylenebis(dimethylsulfonium bromide) 16.

![Chemical structures](image)

The polymerization was a two-step process. It has been proposed that the reaction of 16 with base involves a proton removal at the benzylic position of the sulfonium halide 16 to form a sulfur ylid 17. The ylid could undergo an elimination reaction to form the sulfonium halide 18 which could undergo the polymerization.
The second step involves the thermal elimination of hydrogen bromide and dimethyl sulfide to form a double bond. The presence of the trans configuration was shown by a strong absorption at 970 cm\(^{-1}\) that is characteristic of a trans double bond configuration. The DP-PPV 3 formed under these conditions was a brittle, yellow-orange material.

**Modified Gilch Method**

Poly(2,3-diphenyl-5-hexyl-p-phenylene vinylene) (DP6-PPV) 25 was first synthesized by Feld and Hsieh\(^3\) through a series of steps, including two key steps, a Diels Alder reaction and a modified Gilch route. A Diels-Alder reaction was carried out using 2,5-bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone 20 and 1-octyne to yield 5-hexyl-2,3-diphenylterphthalate 21. Reduction of the two ester groups with LiAlH\(_4\) yields the diol 22 which can be reacted with SOCl\(_2\) to give the bis(chloromethyl) monomer 23. The
polymerization was carried out using a modified Gilch technique. Using the typical Gilch method of only using excess of t-BuOK the product came out as insoluble DP-PPV gels, but by also using an acidic additive with the t-BuOK such as 4-tert-butylbenzyl chloride \(24\) the gelling was prevented.

![Chemical structures](attachment:image.png)

It was found that the molecular weight of DP6-PPV \(25\) decreased as the ratio of 4-tert-butylbenzyl chloride \(24\) to monomer \(23\) increases. The UV-VIS and photoluminescence (PL) spectra of the DP6-PPV film gave bluish-green emission peak at 490 nm which is blue shifted by 10 nm compared to DP-PPV. The shift was attributed to the steric effects of the hexyl group in conjunction with the phenyls in limiting conjugation length.

**Long Branched Alkoxy Substituted DP-PPV**

DP-PPV derivatives with long branched alkoxy pendent groups have been reported to improve solubility by increasing steric hindrance thereby preventing polymeric close-chain packing. It is also thought to reduce the electroluminescence (EL) efficiency by spreading out polymer chains and decreasing π-π interactions.
One process for adding alkoxy chains to the phenyl rings of DP-PPV was a seven-step process. The synthesis began with a Sonogashira coupling of phenylacetylene 26 with 4-iodoanisole 27 to yield 28.

\[
\text{Ph} - \text{C} = \text{C} - \text{Ph} + \text{Ph} - \text{I} \rightarrow \text{Ph} - \text{C} = \text{C} - \text{Ph} - \text{OMe}
\]

The alkyne 28 was oxidized using potassium permanganate to yield 4-methoxybenzil 29. A condensation reaction of 29 with diethyl 1,3-acetonedicarboxylate 30 produces 2,5-di(carboethoxy)-3-(4'-methoxyphenyl)-4-phenylcyclopentadienone 31.

The cyclopentadienone 31 underwent a Diels-Alder reaction with norbornadiene 9 to yield diethyl 2-(4’-methoxyphenyl)-3-phenylterephthalate 32. The terephthalate 32 was then reduced with LiAlH₄ to yield 1,4-bis(hydroxymethyl)-2-(4’methoxyphenyl)-3-phenylbenzene 33.
Diol 33 was reacted with boron tribromide which caused bromination and demethylation to yield 1,4-bis(bromomethyl)-2-(4-hydroxyphenyl)-3-phenylbenzene 34. The synthesis of the monomer was then finished by a Mitsunobu reaction of the dibromo compound 34 using 3,7-dimethyloctanol 35 and diethyl azodicarboxylate to yield 1,4-bis(bromomethyl)-2-[4’-(3,7-dimethyloctoxy)phenyl]-3-phenylbenzene 36.

The second monomer was synthesized in a six-step process also beginning with a Sonogashira coupling using phenylacetylene 26 and 2-bromo-9,9-dihexylfluorene 37 to yield 9,9-dihexyl-2-(2’-phenyl-1-ethynyl)fluorene 38 followed by oxidation using
potassium permanganate to yield 1-(9,9-dihexyl-2-fluorenyl)-2-phenyl-1,2-ethanedione 39.4

The next three steps of the reaction were performed in the same manner as for the previous monomer. A condensation reaction of 39 with 30 produced diethyl 4-(9,9-dihexyl-2-fluorenyl)-2-oxo-5-phenyl-3,5-cyclopentadiene-1,3-dicarboxylate 40. This was followed by the Diels-Alder reaction of 40 with norbornadiene 9 to yield diethyl 4-(9,9-dihexyl-2-fluoren-2-yl)terephthalate 41. The next step was to reduce the terephthalate 41 with LiAlH4 to yield 1,4-bis(hydroxymethyl)-2-phenyl-3-(9,9-dihexylfluorene-2-yl)benzene 42. The last step was the reaction of the diol 42 with thionyl chloride to yield the monomer 1,4-bis(chloromethyl)-2-phenyl-3-(9,9-dihexylfluoren-2-yl)benzene 43.
The monomers 36 and 43 were polymerized through a Gilch method using excess \(t\)-BuOK as a base in excess. The monomers 36 and 43 were also copolymerized with 2,5-dimethoxy-1,4-bis(bromomethyl)benzene 44 or 2-methoxy-5-(2’-ethylhexoxy)-1,4-bis(bromomethyl)benzene 45 to yield polymers P1-P7.

Often in the Gilch the method, gelation of the polymeric product may occur during polymerization, but bulky groups in the monomers help prevent gelation and improve solubility during the process. The molecular weights of these polymers ranged from 3.97 x 10^5 kDa to 7.09 x 10^5 kDa and had a polydispersity index of less than 2. The synthesized polymers were thermally stable with glass temperature \((T_g)\) over 140°C and decomposition temperatures \((T_d)\) over 400°. Thin films of the polymers had a maximum PL emission band from 498-564 nm. Double-layer light-emitting diodes with a configuration order of indium-tin oxide/poly(ethylenedioxythiophene)/polymer/Ca/Al emitted green \((P_1, P_4, P_6)\), green-yellow \((P_2, P_5, P_7)\), and yellow-orange \((P_3)\) light under a charge with the maximum brightness of 16910 cd/m^2 was produced.
**Liquid Crystal Substituted DP-PPV**

Other soluble DP-PPVs with alkoxy pendent groups or a charge transport group have been synthesized and characterized.\(^5\) The synthesis of one liquid crystal pendant group began with the monoalkylation of 4,4’-biphenol 46 with 1-bromoheptane to yield 47 which was then alkyated with 5-chloro-1-pentyne to give 48.
The second one was prepared using a similar alkylation of 49 using 5-chloro-1-pentyne to yield 50.

\[
\text{49} \xrightarrow{\text{K}_2\text{CO}_3, \text{KI}} \text{5-chloro-1-pentyne} \rightarrow \text{50}
\]

The electron transport group was synthesized by a condensation reaction of salicylaldehyde 51, benzil 5 and aniline 52 to yield 53. It was then alkylated with 5-chloro-1-pentyne to yield 54.

\[
\text{51} + \text{5} + \text{52} \xrightarrow{\text{EtOH}} \text{53}
\]

The synthesis of the monomers were carried out by the same pathway as that reported by Feld and Hsieh et al., all three of the alkynes 48, 50, and 54 underwent a Diels-Alder reaction with cyclopentadienone 20 to yield the terephthalates 55a-c. These were reduced with LiAlH₄ to yield the diols 56a-c. The formation of the dichloro compound 57a-c was accomplished by reacting 56a-c with thionyl chloride.
The polymerization of 57a-c was carried out using a large excess of potassium tert-butoxide to give polymers 58a-c. No gelation was observed in these polymerizations.

Polymers 58a-c were found to be highly soluble in common organic solvents like THF, chloroform, dichloromethane, and toluene. The weight-average molecular weight and polydispersity for each was 58a 226x10^3 kDa and 1.53, for 58b 401x10^3 kDa and 1.97, and for 58c 418x10^3 kDa and 2.91. All three were shown to have a blue shift and
high PL efficiency when compared to a typical PPV and DP-PPV polymer that is probably due to the bulky substituents that reduce the conjugation length.

**Hydrophobic and Hydrophilic Dendritic Side Chains**

Other DP-PPV derivatives that were synthesized via Gilch polymerization include several that contain hydrophobic and hydrophilic dendritic side chains. These branched side chains show effects on the photophysical properties of the polymers due to their bulkiness and hydrophobic and hydrophilic properties.

The process of synthesizing the monomers occurred over several steps. The first step was the alkylation of the alcohol groups of methyl gallate 59 using a Williamson etherification with two different alkyl halides 60a-b to yield compounds 61a-b. A reduction of the ester in 61 using LAH yields the dendritic alcohols 62a-b.

The alcohols 62a-b were reacted with thionyl chloride to obtain the dendritic chlorides 63a-b. The chloro compounds 63a-b underwent a Mitsonobu reaction with pent-4-yn-1-ol to yield 3,4,5-tris(dodecyloxy)benzylloxypent-4-yne 64a and 3,4,5-tris(2-(2-ethoxyethoxy)ethoxy)benzylloxypent-4-yne 64b.
Alkynes 64a-b were used in a Diels-Alder reaction with the cyclopentadienone 20 to yield the terephthalates 65a-b.

\[
\begin{align*}
\text{64a-b} & \quad \text{EtO}_2\text{C} - \text{CO}_2\text{Et} + \text{65a-b} \\
\text{Toluene} & \quad \text{64a-b} \\
\text{R}^\prime & = \quad \text{(RCH}_2\text{CH}_2\text{O)}_2\text{C}_2\text{H}_5 \\
\text{65a-b} & \quad \text{R}^\prime \\
\end{align*}
\]

Reduction of the terephthalates 65a-b with LAH yields the diols 66a-b which then underwent a reaction with thionyl chloride to give the dichloro monomers 67a-b.

\[
\begin{align*}
\text{65a-b} & \quad \text{LAH} \rightarrow \text{66a-b} \\
\text{66a-b} & \quad \text{SOCl}_2 \rightarrow \text{67a-b} \\
\end{align*}
\]

The polymerization of the monomers 67a-b carried out by the Gilch method with THF and potassium tert-butoxide. To obtain the yellow polymers 69a-b, a capping agent 2,6-di-tert-butylphenol 68, was added.
Polymers $69\text{a-b}$ were found to be highly soluble in common organic solvents, including chloroform, toluene, and chlorobenzene. They also were polymerized with high molecular weights. The number-average molecular weight and PDI for $69\text{a}$ were found to be 135 kDa and 2.88 and for $69\text{b}$ the molecular weight and PDI was 58.8 kDa and 2.50. In TGA analysis the 5% weight loss was found to be above 310° for both of the polymers. The maximum absorption of the polymers dissolved in chloroform was located between 352 and 362 nm and the PL emission was located from 477 to 481 nm. In thin-films a red shift was observed which was suggested to be due to closer intermolecular distances and stronger intermolecular interactions of the chains in the film form compared to being in a solution.

**Synthesis of Phenolic Pendant Precursors**

The introduction of phenolic pendent functions in DP-PPV systems requires the protection of the phenol during monomer construction. The benzyl group appeared to be a good choice for a protective function as it can be removed either by reduction or reaction with hydrogen bromide in acetic acid.
The synthesis of 4,4’-di(benzyloxy)benzil 72 has been reported.\textsuperscript{12}

\begin{center}
\begin{tikzpicture}
  \node (a) at (0,0) {\includegraphics[width=0.5\textwidth]{70-71-72.png}};
  \node at (0,1.5) {70};
  \node at (1.5,1.5) {71};
  \node at (3,1.5) {72};
\end{tikzpicture}
\end{center}

An alternative method for introducing the benzyloxy pendent is illustrated below.

The reaction of 4-(benzyloxy)phenol 73 with propargyl bromide 74 yields 1-(benzyloxy)-4-(propargyloxy)benzene 75.\textsuperscript{13}

\begin{center}
\begin{tikzpicture}
  \node (a) at (0,0) {\includegraphics[width=0.5\textwidth]{73-74-75.png}};
  \node at (0,1.5) {73};
  \node at (1.5,1.5) {74};
  \node at (3,1.5) {75};
\end{tikzpicture}
\end{center}

The objectives of this research were to investigate the synthesis of phenolic substituted PPV derivatives by using benzyloxy protected precursors in the synthesis of 1) cyclopentadienones that can be used in DP-PPV monomer preparation and/or 2) alkynes that can be used in monomer preparation.
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. Gel permeation chromatography (GPC) spectra were obtained with a Viscotek Model 270 Dual Detector and OmniSEC 4.0 software. Infrared (IR) spectra were recorded as thin films (NaCl) with a Nicolet 6700 FT-IR spectrometer. X-ray crystallographic data was obtained using a Bruker SMART X2S Diffractometer.

Structures were solved using OSCAIL (McArdle, 1995);$^{34}$ data collection: SMART (Bruker 2002); cell refinement: SAINT-Plus (Bruker, 2003) and CRYSTALS (Betteridge et. al., 2003); program used to solve structures: SHELXS97 (Sheldrick, 2008); program used to refine structure: SHELXS97 (Sheldrick, 2008); molecular graphics: Mercury (Macrae et al., 2006); computing publication material: CRYSTALS (Betteridge et. al., 2003). Elemental analyses were obtained through Midwest Microlab, LLC, Indianapolis, IN. Chemicals were purchased from Aldrich and used as received.

1-(Benzyloxy)-4-(propargyloxy)benzene 75

In a round-bottomed flask, $p$-(benzyloxy)phenol (4.000 g, 20 mmol), potassium carbonate (7.95 g, 57.5 mmol), and propargyl bromide (3.8 mL, 50 mmol) were dissolved
in 30 mL acetone. The solution was stirred at rt for 1 h. The excess potassium carbonate was then filtered off and distilled water was added to the filtrate. The mixture was extracted with ether. The extracts were evaporated and the residue was dried under reduced pressure. The resulting brown solid was recrystallized from ethanol to yield 1-(benzyloxy)-4-(propargyloxy)benzene as a light-tan solid (2.898 g, 62%); (lit. mp 45-46°; found 46.5-47.8°); IR (NaCl, cm\(^{-1}\)) 3280 (Ar CH), 2903 (Ali CH), 2360 (C≡C), 1510 (Ar C=C); \(^1\)H NMR (300 MHz, CDCl\(_3\), δ) 2.53 (t, 1 H, J = 2.4 Hz, ROCH\(_2\)CCH), 4.66 (d, 2H, J = 2.37 Hz, ROCH\(_2\)CCH), 5.04 (s, 2H, PhCH\(_2\)OR), 6.95 (s, 4H, Ar CH), 7.33-7.46 (m, 5H, PhCH\(_2\)OR); \(^1^3\)C NMR (75 MHz, CDCl\(_3\), ppm) 56.6 (ROCH\(_2\)CCH), 70.7 (CH\(_2\)), 75.3 (ROCH\(_2\)CCH), 78.9 (ROCH\(_2\)CCH), 115.8 (Ar CH), 116.2 (Ar CH), 127.5 (Ar CH), 127.9 (Ar CH), 128.6 (Ar CH), 137.2 (Ar CH), 152.0 (Ar CH), 153.7 (Ar CH).

**Diethyl 5-((4-(benzyloxy)phenoxy)methyl)-2,3-diphenyterephthalate 76**

In a 50 mL, round-bottomed flask, 2,5-dicarboethoxy-3,4-diphenylcyclopenta- dinone (2.000 g, 5.31 mmol) and 1-(benzyloxy)-4-(propargyloxy)benzene (1.2662 g, 5.31 mmol) were dissolved in 20 mL of toluene. The solution was stirred and refluxed for 12 h, cooled to rt and the solvent was removed under reduced pressure to yield diethyl 5-((4-(benzyloxy)phenoxy)methyl)-2,3-diphenylterephthalate as a reddish-brown oil (2.917 g, 4.97 mmol, 93.6%): mp 97.2-99.1°; IR (NaCl, cm\(^{-1}\)) 3058 (Ar CH), 2981 (Ali CH), 1714 (C=O Ester) 1614 (Ar C=C); \(^1\)H NMR (300 MHz, CDCl\(_3\), δ) 0.89 (t, 3H, J = 7.14 Hz, CH\(_3\)), 0.96 (t, 3H, J = 7.12 Hz, CH\(_3\)), 3.93 (q, 2H, J = 7.14 RCOCH\(_2\)CH\(_3\)), 4.01 (q, 2H, J = 7.11 RCOCH\(_2\)CH\(_3\)), 5.05 (s, 2H, CH\(_2\)), 5.16 (s, 2H, CH\(_2\)), 6.94-7.14 (m, 14H, Ar CH), 7.34-7.47 (m, 5H, Ar CH), 7.98 (s, 1H, Ar CH); \(^1^3\)C NMR (75 MHz, CDCl\(_3\), ppm) 13.49 (RCOCH\(_2\)CH\(_3\)), 13.53 (RCOCH\(_2\)CH\(_3\)), 61.12 (RCOCH\(_2\)CH\(_3\)), 61.25
(RCOCH₂CH₃), 68.25 (CH₂), 70.69 (CH₂), 115.82 (Ar CH), 115.87 (Ar CH), 116.14 (Ar CH), 126.71 (Ar CH), 126.96 (Ar CH), 127.24 (Ar CH), 127.26 (Ar CH), 127.29 (Ar CH), 127.47 (Ar CH), 127.89 (Ar CH), 127.90 (Ar CH), 128.55 (Ar CH), 129.73 (Ar CH), 130.08 (Ar CH), 133.81 (Ar CH), 133.94 (Ar CH), 135.88 (Ar CH), 137.27 (Ar CH), 137.96 (Ar CH), 138.67 (Ar CH), 140.43 (Ar CH), 140.94 (Ar CH), 151.53 (Ar CH), 152.90 (Ar CH), 153.46 (Ar CH), 168.08 (Ar CH), 168.13 (Ar CH); Anal. Calcd. for C₃₉H₃₆O₄; C, 77.80; H, 5.84. Found: C, 77.74; H, 5.82.

5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(hydroxymethyl)-2,3-diphenylbenzene

In a 250 mL, round-bottomed flask, lithium aluminum hydride (0.9703 g, 25.56 mmol) was added to 60 mL THF in increments and the solution was placed in an ice bath. Diethyl 5-((4-(benzyloxy)phenoxy)methyl)-2,3-diphenylterephthalate (3.000 g, 5.11 mmol) in 60 mL THF was added dropwise to the grey slurry at 0º. The solution was then warmed to rt and stirred for 1 h then heated to 70º for 8 h. After cooling the solution to rt, 1 mL H₂O was added dropwise with stirring. A sodium hydroxide solution (0.9 g in 6 mL H₂O) was slowly added followed by a 2 mL aliquot of H₂O. The THF was evaporated. A 120 mL solution of 10% H₂SO₄ was added and the mixture was stirred for 12 h. The resulting product was filtered, dried and recrystallized from ethanol to yield 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(hydroxymethyl)-2,3-diphenylbenzene (2.12 g, 82%): mp 161.7-162.3º; IR (NaCl, cm⁻¹) 3306 (OH), 3056 (Ar CH), 2922 (Ar CH), 2882 (Ali CH), 1592 (Ar C=C); ¹H NMR (300 MHz, CDCl₃, δ) 2.32 (s), 4.48 (m, 4H, RCOCH₂OH), 5.07 (s, 2H, CH₂), 5.27 (s, 2H, CH₂), 6.84-7.18 (m, 14H, Ar CH) 7.32-7.56 (m, 5H, Ar CH) 7.74 (s, 1H, Ar CH); ¹³C NMR (75 MHz, CDCl₃, ppm) 59.82 (CH₂), 63.27 (CH₂), 70.35 (RCOCH₂OH), 70.73 (RCOCH₂OH), 116.07 (Ar CH), 126.58 (Ar CH), 126.65 (Ar CH),
127.41 (Ar CH), 127.46 (Ar CH), 127.66 (Ar CH), 127.92 (Ar CH), 128.57 (Ar CH),
129.82 (Ar CH), 130.31 (Ar CH), 135.43 (Ar CH), 137.08 (Ar CH), 137.23 (Ar CH),
138.71 (Ar CH), 138.83 (Ar CH), 138.93 (Ar CH), 141.13 (Ar CH), 143.08 (Ar CH),
152.78 (Ar CH), 153.68 (Ar CH); Anal. Calcd. For C\textsubscript{34}H\textsubscript{30}O\textsubscript{4}; C, 81.25; H, 6.02. Found
C, 81.3; H, 6.09.

**5-((4-(benzylxy)phenoxy)methyl)-1,4-di(chloromethyl)-2,3-diphenylbenzene 78**

In a 25 mL round-bottomed flask, thionyl chloride (0.866 mL, 11.94 mmol) was
added dropwise to 5-((4-(benzylxy)phenoxy)methyl)-1,4-di(hydroxymethyl)-2,3-diphenylbenzene (0.3074 g, 0.5969 mmol). The solution was stirred at rt for 1 h then the
temperature was increased to 50º for 1 h then brought down to rt for 12 h. The product
was slowly added to 25 mL of water and stirred for 12 h. The light green solid was
filtered and dried then purified by column chromatography to yield 5-((4-(benzylxy)-
phenoxy)methyl)-1,4-di(chloromethyl)-2,3-diphenylbenzene (0.2575 g, 0.4773 mmol,
80% yield) as a white solid: mp 108.0-109.3°; IR (NaCl, cm\textsuperscript{-1}) 3059 (Ar CH), 2869 (Ali
CH), 1506 (Ar C=C); \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, $\delta$) 4.38 (s, 2H, RCOCH\textsubscript{2}Cl), 4.50 (s, 2H, RCOCH\textsubscript{2}CH\textsubscript{3}), 5.07 (s, 2H, CH\textsubscript{2}), 5.30 (s, 2H, CH\textsubscript{2}), 6.96-7.21 (m, 14H, Ar CH),
7.34-7.50 (m, 5H, Ar CH), 7.77 (s, 1H, Ar CH); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}, ppm) 41.0
(CH\textsubscript{2}), 44.4 (CH\textsubscript{2}), 68.5 (CH\textsubscript{2}), 70.73 (CH\textsubscript{2}), 115.9 (Ar CH), 116.0 (Ar CH), 127.0 (Ar
CH), 127.46 (Ar CH), 127.49 (Ar CH), 127.56 (Ar CH), 127.9 (Ar CH), 128.56 (Ar CH),
129.97 (Ar CH), 130.11 (Ar CH), 130.19 (Ar CH), 134.16 (Ar CH), 136.15 (Ar CH),
136.41 (Ar CH), 137.25 (Ar CH), 137.92 (Ar CH), 138.08 (Ar CH), 143.5 (Ar CH),
153.04 (Ar CH), 153.54 (Ar CH); Anal. Calcd. For C\textsubscript{34}H\textsubscript{28}Cl\textsubscript{2}O\textsubscript{2}; C, 75.69; H, 5.23.
Found C, 74.89; H, 5.22.
Poly[(2,3-diphenyl-5-((4-(benzyloxy)phenoxy)methyl)-1,4-phenylene)vinylene] 79

To a stirred solution of 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(chloromethyl)-2,3-diphenylbenzene (0.20 g, 0.3707 mmol) in 10 mL anhydrous THF was added 3.0 mL t-BuOK (1.0 M in THF) at 0º. The resulting solution was stirred for 24 h at rt before it was poured into 100 mL of methanol. The bright yellow solid was collected and air dried to yield poly[(2,3-diphenyl-5-((4-(benzyloxy)phenoxy)methyl)-1,4-phenylene)vinylene] (0.107 g, 0.215 mmol, 58.0%). IR (NaCl, cm) 3056 (Ar CH), 2918 (Al CH), 1505 (Ar C=C); 1H NMR (300 MHz, CDCl3, δ) 4.71 (s, 2H, CH2), 5.00 (s, 2H, CH2), 6.15 (s, 1H, CH), 6.80-7.11 (m, 14H, Ar CH), 7.26-7.52 (m, 6H, Ar CH).
RESULTS AND DISCUSSION

As shown in Figure 1, hydroxyl precursor functions (benzyloxy groups) in DP-PPV can be introduced either by way of the benzil component in the construction of a cyclopentadienone or by way of the use of 4-benzyloxyphenol in the construction of an alkyne to be used in a Diels-Alder reaction.

Figure 1. Retrosynthetic scheme for the synthesis of a phenolic PPV.

1-(Benzyloxy)-4-(propargyloxy)benzene

The propargylation of a phenol compound was the first step in producing a phenolic pendent group for a DP-PPV derivative. This was accomplished by a nucleophilic substitution on propargyl bromide \( \text{74} \) by \( p \)-(benzyloxy)phenol \( \text{73} \) to yield 1-
(benzyloxy)-4-(propargyloxy)benzene 75 and was characterized by melting point, IR, $^1$H NMR, and $^{13}$C NMR.

The $^1$H NMR spectrum (Figure 2) of $p$-(benzyloxy)phenol 73 exhibits a methylene absorption at 5.04 $\delta$ integrating to 2H. The para-substituted aromatic ring absorptions appear as a pair of doublets at 6.79 and 6.88 $\delta$ integrating to a total of 4H. The benzyl aromatic absorption appears as a multiplet between 7.28-7.47 $\delta$. A singlet appears at 4.72 $\delta$, integrating to 1H, which is assumed to be due to the hydroxyl proton.

In the $^1$H NMR spectrum (Figure 3) of 1-(benzyloxy)-4-(propargyloxy)benzene 75, the absorption of the acetylenic hydrogen is observed at 2.53 $\delta$ integrating to 1H and appears as a triplet due to long range coupling with the methylene of the propargyl group. The methylene absorption appears as a doublet at 4.66 $\delta$ integrating to 2H. The benzylic methylene absorption appears as a singlet at 5.05 $\delta$ integrating to 2H. The para-substituted aromatic absorptions appear as a singlet at 6.95 $\delta$ integrating to 4H. The benzyl aromatic proton absorption appears as a multiplet between 7.33-7.46 $\delta$ with an integration of 5H. The IR spectrum (Figure 6) of 75 exhibits a weak absorption at 2360 cm$^{-1}$ and a strong absorption at 3300 cm$^{-1}$ associated with the triple bond.

The $^{13}$C NMR spectrum (Figure 4) of 75 exhibits a propargyl methylene carbon absorption at 56.6 ppm and a benzylic methylene carbon absorption at 70.7 ppm. The alkyne carbon absorptions appear at 75.3 and 78.9 ppm. A summary of properties of 1-(benzyloxy)-4-(propargyloxy)benzene 75 is shown in Table 1.
Table 1. Characterization of 1-(benzyloxy)-4-(propargyloxy)benzene 75.

<table>
<thead>
<tr>
<th>Compound</th>
<th>mp (°C)</th>
<th>Yield (%)</th>
<th>IR (cm⁻¹) (NaCl)</th>
<th>¹H NMR (δ) (CDCl₃)</th>
<th>¹³C NMR (ppm) (CDCl₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Compound Image" /></td>
<td>46.5-47.8</td>
<td>62</td>
<td>3280 (Ar CH), 2903 (Ali CH), 2360 (C≡C), 1510 (Ar C=C)</td>
<td>2.53 (t, 1 H, J = 2.4 Hz, ROCH:CCH), 4.66 (d, 2H, J = 2.37 Hz, ROCH:CCH), 5.04 (s, 2H, PhCH:OR) 6.95 (s, 4H, Ar CH), 7.33-7.46 (m, 5H, PhCH:OR)</td>
<td>56.6, 70.7, 75.3, 78.92, 115.8, 116.2, 127.5, 127.9, 128.6, 137.2, 152.0, 153.7</td>
</tr>
</tbody>
</table>

Diethyl 5-((4-(benzyloxy)phenoxy)methyl)-2,3-diphenylterephthalate

A Diels-Alder reaction was carried out using 1-(benzyloxy)-4-(propargyloxy)benzene 75 and 2,5-bis(ethoxycarbonyl-3,4-diphenylcyclopentadienone 20 to yield diethyl 5-((4-(benzyloxy)phenoxy)methyl)-2,3-diphenylterephthalate 76. The product was characterized by IR, ¹H NMR, and ¹³C NMR.

![Chemical Structures](image2.png)

In the ¹H NMR spectrum (Figure 7), the absorption of the ester methyls appear at 0.89 and 0.96 δ. Both appear as triplets and each integrates to 3H. The absorptions of the ester methylenes appear at 3.93 and 4.01 δ as quartets both integrating to 2H. Two
methylene absorptions from the pendent protected phenol group appear as singlets at 5.05 and 5.16 δ each integrating to 2H. The aromatic proton absorptions appear as two multiplets, one between 6.94-7.14 δ and another between 7.34-7.47 δ, integrating to 14H and 5H, respectively. A third aromatic proton absorption appears as a singlet at 7.74 δ with the integration of 1H.

The $^{13}$C NMR spectrum (Figure 8) shows the absorption of the ester methyl carbon at 13.49 and 13.53 ppm and the ester methylene carbon at 61.12 and 61.25 ppm. The two aliphatic methylene carbons from the pendent protected phenol group appear at 68.25 and 70.69 ppm. The IR spectrum (Figure 10) of diethyl 5-((4-(benzyl oxy)-phenoxy)methyl)-2,3-diphenylterephthalate 76 shows an absorption at 1714 cm$^{-1}$ associated with the ester carbonyls in 76. A summary of properties of diethyl 5-((4-(benzyl oxy)phenoxy)methyl)-2,3-diphenylterephthalate 76 is shown in Table 2.

**Table 2. Characterization of 5-((4-(benzyl oxy)phenoxy)methyl)-2,3-diphenylterephthalate 76.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>mp (°C)</th>
<th>Yield (%)</th>
<th>IR (cm$^{-1}$) (NaCl)</th>
<th>$^1$H NMR (δ) (CDCl$_3$)</th>
<th>$^{13}$C NMR (ppm) (CDCl$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="structure" /></td>
<td>97-99</td>
<td>93.6</td>
<td>3058 (Ar CH), 2981 (Ali CH), 1714 (C=O Ester), 1614 (Ar C=C)</td>
<td>0.89 (t, 3H, J = 7.14 Hz, CH$_3$), 0.96 (t, 3H, J = 7.12 Hz, CH$_3$), 3.93 (q, 2H, J = 7.14 RCOCH$_2$CH$_3$), 4.01 (q, 2H, J = 7.11 RCOCH$_2$CH$_3$), 5.05 (s, 2H, CH$_2$), 5.16 (s, 2H, CH$_2$) 6.94-7.14 (m, 14H, Ar CH), 7.34-7.47 (m, 5H, Ar CH) 7.98 (s, 1H, Ar CH)</td>
<td>13.49, 13.53, 61.12, 61.25, 68.25, 70.69, 115.82, 115.87, 116.14, 126.71, 126.96, 127.24, 127.26, 127.29, 127.47, 127.89, 127.90, 128.55, 129.73, 130.08, 133.81, 133.94, 135.88, 137.27, 137.96, 138.67, 140.43, 140.94, 151.53, 152.90, 153.46, 168.08, 168.13</td>
</tr>
</tbody>
</table>
Reduction of 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(hydroxymethyl)-2,3-diphenylbenzene with LiAlH₄ yields 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(hydroxymethyl)-2,3-diphenylbenzene 77. The diol 77 was characterized by IR, ¹H NMR and ¹³C NMR spectroscopy.

The ¹H NMR spectrum (Figure 11) of 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(hydroxymethyl)-2,3-diphenylbenzene 77 exhibits a broad multiplet absorption for the benzylic alcohol methylenes at 4.48 δ which give a total integration of 4H. The cause of the broadening could be due to the asymmetry of the compound causing a slight overlap of the two absorptions and a possible coupling with the hydroxyl absorption which appears at 2.32 δ and is likewise broad. The two methylene absorptions from the pendent protected phenol group appear at 5.07 and 5.27 δ. The three sets of aromatic proton absorption appear at 6.84-7.18 δ integrating to 14H, 7.32-7.56 δ integrating to 5H and 7.74 δ integrating to 1H.

The ¹³C NMR spectrum (Figure 12) of 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(hydroxymethyl)-2,3-diphenylbenzene 77 exhibits four absorptions for the four
methylene groups, two in the pendant group at 70.35 and 70.73 ppm and two for the benzylic hydroxyl groups at 59.82 and 63.27 ppm.

The IR spectrum (Figure 14) of 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(hydroxymethyl)-2,3-diphenylbenzene 77 exhibits a hydroxyl stretch at 3306 cm$^{-1}$ as a broad absorption. An absorption at 3056 cm$^{-1}$ can be associated with an aromatic C-H stretch, that at 2882 cm$^{-1}$ with the aliphatic C-H streach and that at 1592 cm$^{-1}$ shows the absorption of aromatic C=C bonds.

A summary of properties of diethyl 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(hydroxymethyl)-2,3-diphenylbenzene 77 is shown in Table 3.

Table 3. Characterization of 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(hydroxymethyl)-2,3-diphenylbenzene 77

<table>
<thead>
<tr>
<th>Compound</th>
<th>mp (°C)</th>
<th>Yield (%)</th>
<th>IR (cm$^{-1}$) (NaCl)</th>
<th>$^1$H NMR (δ) (CDCl$_3$)</th>
<th>$^{13}$C NMR (ppm) (CDCl$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Compound Structure" /></td>
<td>161.7-162.3</td>
<td>82</td>
<td>3306 (OH), 3056 (Ar CH), 2882 (Ali CH), 1592 (Ar C=C)</td>
<td>2.32 (s), 4.48 (overlap, 4H, RCOCH$_2$OH), 5.07 (s, 2H, CH$_2$), 5.27 (s, 2H, CH$_2$), 6.84-7.18 (m, 14H, Ar CH) 7.32-7.56 (m, 5H, Ar CH) 7.74 (s, 1H, Ar CH)</td>
<td>59.82, 63.27, 70.35, 70.73 116.07, 126.58, 126.65, 127.41, 127.46, 127.66, 127.92, 128.57, 129.82, 130.31, 135.43, 137.08, 137.23, 138.71, 138.83, 138.93, 141.13, 143.08, 152.78, 153.68</td>
</tr>
</tbody>
</table>
5-((4-(benzyloxy)phenoxy)-methyl)-1,4-di(chloromethyl)-2,3-diphenylbenzene

The reaction of 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(hydroxymethyl)-2,3-diphenylbenzene 77 with thionyl chloride smoothly yielded 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(chloromethyl)-2,3-diphenylbenzene 78.

![Chemical Structures]

The $^1$H NMR spectrum (Figure 15) of 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(chloromethyl)-2,3-diphenylbenzene 78 exhibits four methylene absorptions. The two absorptions of the benzylic chloride methylene groups are observed as singlets at 4.38 and 4.50 δ, each integrating to 2H. The two methylene absorptions of the pendent protected phenol group are observed at 5.07 and 5.30 δ, both integrating to 2H.

The $^{13}$C NMR spectrum (Figure 16) of 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(chloromethyl)-2,3-diphenylbenzene 78 exhibits the absorption of the benzylic chloride methylene carbons at 41.0 and 44.4 ppm. The methylene carbon absorption of the pendent protected phenol group are observed at 68.5 and 70.7 ppm. The IR spectrum (Figure 17) of 78 exhibits a aromatic C-H stretch at 3059 cm$^{-1}$, a aliphatic C-H stretch at 2869 and a aromatic C=C bond absorption at 1506. A summary of properties of 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(chloromethyl)-2,3-diphenylbenzene 78 is shown in Table 4.
Table 4. Characterization of 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(chloromethyl)-2,3-diphenylbenzene 78.

<table>
<thead>
<tr>
<th>Compound</th>
<th>mp (°C)</th>
<th>Yield (%)</th>
<th>IR (cm(^{-1})) (NaCl)</th>
<th>(^1)H NMR (δ) (CDCl(_3))</th>
<th>(^{13})C NMR (ppm) (CDCl(_3))</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Chemical Structure" /></td>
<td>108.0-109.3</td>
<td>80</td>
<td>3059 (Ar CH), 2869 (Ali CH), 1506 (Ar C=C)</td>
<td>4.38 (s, 2H, RCOCH(_2)Cl), 4.50 (s, 2H, RCOCH(_2)CH(_3)), 5.07 (s, 2H, CH(_2)), 6.96-7.21 (m, 14H, Ar CH)</td>
<td>41.0, 44.4, 68.5, 70.73, 115.9, 116.0, 127.0, 127.46, 127.49, 127.56, 127.9, 128.56, 129.7, 130.11, 130.19, 134.16, 136.15, 136.41, 137.25, 137.92, 138.08, 143.5, 153.04, 153.54</td>
</tr>
</tbody>
</table>

Poly[(2,3-diphenyl-(5-((4-(benzyloxy)phenoxy)methyl)-1,4-phenylene)vinylene]-1,4-phenylene)vinylene]

Polymerization of 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(chloromethyl)-2,3-diphenylbenzene 78 was carried out by the Gilch method using an excess of \(t\)-BuOK to yield poly[(2,3-diphenyl-(5-((4-(benzyloxy)phenoxy)methyl)-1,4-phenylene)vinylene]-1,4-phenylene)vinylene] 79. The polymer 79 was characterized by IR, \(^1\)H NMR and TGA.

The IR spectrum (Figure 19) of poly[(2,3-diphenyl-(5-((4-(benzyloxy)phenoxy)-methyl)-1,4-phenylene)vinylene]-1,4-phenylene)vinylene] 79 exhibits an aromatic C-H stretch at 3056 cm\(^{-1}\), a
aliphatic C-H stretch at 2918 and an aromatic C=C bond absorption at 1505. The $^1$H NMR spectrum (Figure 18) of 79 exhibits the two methylene absorptions of the pendent protected phenol group at 4.71 and 5.00 $\delta$, each integrating to 2H. The three sets of aromatic proton absorption appear at 6.80-7.11 $\delta$ integrating to 14H, 7.26-7.52 $\delta$ integrating to 6H and 6.15 $\delta$ integrating to 1H.

Figure 2. TGA curve showing 5% wt. loss temperature.

The TGA curve in Figure 2 indicates the thermo stability of poly[(2,3-diphenyl-(5-((4-(benzyloxy)phenoxy)methyl)-1,4-phenylene)vinylene] 79 with a 5% wt. loss at a temperature of 349.23°. The decomposition begins at 300° and levels off at 475° where it degrades at a constant rate.
**Figure 3.** DSC trace of 79.

The DSC trace **Figure 3** indicates the glass transition temperature of 79 at 149.71°. An impurity in the instrument gives us a peak at 95°.
Figure 4: 300 MHz $^1$H NMR Spectrum (CDCl$_3$) of 73.

Figure 5: 300 MHz $^1$H NMR Spectrum (CDCl$_3$) of 75.
Figure 6: 300 MHz $^{13}$C NMR Spectrum (CDCl$_3$) of 75.

Figure 7: 300 MHz $^{13}$C NMR dept135 Spectrum (CDCl$_3$) of 75.
Figure 8: IR Spectrum (NaCl) of 75.

Figure 9: 300 MHz $^1$H NMR Spectrum (CDCl$_3$) of 76.
Figure 10: 300 MHz $^{13}$C NMR Spectrum (CDCl$_3$) of 76.

Figure 11: 300 MHz $^{13}$C NMR dept135 Spectrum (CDCl$_3$) of 76.
Figure 12: IR Spectrum (NaCl) of 76.

Figure 13: 300 MHz $^1$H NMR Spectrum (CDCl$_3$) of 77.
**Figure 14:** 300 MHz $^{13}$C NMR Spectrum (CDCl$_3$) of 77.

**Figure 15:** 300 MHz $^{13}$C NMR dept135 Spectrum (CDCl$_3$) of 77.
Figure 16: IR Spectrum (NaCl) of 77.

Figure 17: 300 MHz $^1$H NMR Spectrum (CDCl$_3$) of 78.
**Figure 18:** 300 MHz $^{13}$C NMR Spectrum (CDCl$_3$) of 78.

**Figure 19:** IR Spectrum (NaCl) of 78.
Figure 20: 300 MHz $^1$H NMR Spectrum (CDCl$_3$) of 79

Figure 21: IR Spectrum (NaCl) of 79
APPENDIX

The work described in this section was performed early in the author’s time at Wright State. It is included for completeness and the inclusion of x-ray crystal structures..
ADDITIONAL WORK

Originally, the objective of the research was the preparation of bis(benzyloxy)-
benzils for use in a condensation reaction with diethyl 1,3-acetonedicarboxylate 30.

4,4'-Benzyloxybenzil

The demethylation of 4,4’-dimethoxybenzil 80 was carried out using 48% hydrobromic acid in acetic acid to yield 4,4’-dihydroxybenzil 81. Considerable problems were encountered in the purification of 81. However, the alkylation of 81 with benzyl chloride could be used to synthesize 4,4’-benzyloxybenzil 82. The condensation reaction of 82 with 30 resulted only in a small amount of the cyclopentadienone 83 which was unable to be separated from the unreacted 82.
The $^1$H NMR spectrum (Figure 22) of 4,4’-methoxybenzil 80 exhibits a single methyl absorption at 3.94 $\delta$ integrating to 6H. The substituted aromatic ring absorptions appear as a pair of doublets at 7.13 and 7.93 $\delta$ integrating to 4H each.

Figure 23. 300 MHz $^1$H NMR Spectrum (Acetone-d$_6$) of 81.
The $^1$H NMR spectrum (Figure 23) of 4,4'-hydroxybenzil 81 exhibits the para-substituted aromatic ring absorption as a pair of doublets at 7.01 and 7.84 δ integrating to 4H each. The hydroxyl absorption appears at 9.6 δ as a broad singlet.

![NMR Spectrum of 4,4'-hydroxybenzil 81](image)

**Figure 24.** 300 MHz $^1$H NMR Spectrum (Acetone-d$_6$) of 82

The $^1$H NMR spectrum (Figure 24) of 4,4'-benzylxybenzil 82 exhibits the two methylene absorptions at 5.29 δ integrating to 4H. The aromatic proton absorption appears at 7.10-7.97 δ integrating to 18H.

3,3'-Benzyloxybenzil

![Chemical Reactions](image)
The demethylation of 3,3’-dimethoxybenzil 85 was carried out using 48% hydrobromic acid in acetic acid to yield 4,4’-dihydroxybenzil 86. Alkylation of 86 with benzyl chloride yielded 4,4’-benzyloxybenzil 87. The condensation reaction of 87 with 30 resulted only in a small amount of the cyclopentadienone 88 which was unable to be separated from the unreacted 87.

Figure 25. 300 MHz $^1$H NMR Spectrum (DMSO-d$_6$) of 85.

The $^1$H NMR spectrum (Figure 25) of 3,3’-methoxybenzil 85 exhibits a single methyl absorption at 3.84 δ integrating to 6H. The aromatic absorption appears between 7.34-7.54 integrating to 8H.
Figure 26. 300 MHz $^1$H NMR Spectrum (DMSO-$d_6$) of 86.

The $^1$H NMR spectrum (Figure 26) of 3,3'-hydroxybenzil 86 exhibits an aromatic absorption between 7.12-7.43 δ integrating to 8H. The hydroxyl absorption appears as a singlet at 10.08 δ integrating to 2H.

Figure 27. 300 MHz $^1$H NMR Spectrum (DMSO-$d_6$) of 87.
The $^1$H NMR spectrum (Figure 28) of 3,3′-hydroxybenzil 87 exhibits the two methylene absorptions at 5.20 δ as a singlet integrating to 4H. The aromatic absorptions appear between 7.33-7.54 δ integrating to 18H.

![Figure 28. X-ray crystal structure of 87.](image1)

![Figure 29. X-ray crystal structure of 88.](image2)

The crystal structure of 87 was determined with a $R_1 = 4.28\%$ for the observed data. It has a monoclinic unit cell with the dimensions $a = 24.388 \, \text{Å}$, $b = 7.7768 \, \text{Å}$, $c = 12.0284 \, \text{Å}$, $\beta = 107.683^\circ$, $V = 2173.5 \, \text{Å}^3$.

The crystal structure of 88 was determined with a $R_1 = 5.32\%$ for the observed data. It has a monoclinic unit cell with the dimensions $a = 8.0124 \, \text{Å}$, $b = 7.5909 \, \text{Å}$, $c = 14.0927 \, \text{Å}$, $\beta = 95.011^\circ$, $V = 853.86 \, \text{Å}^3$. 

88
REFERENCES


VITAE

Ryan David Oostendorp was born in Dubuque, Iowa on March 23, 1989. He graduated from Hempstead High School in 2007. He attended Loras College for four years and received his Bachelor of Science in Chemistry in 2011. He then began working towards his Master of Science Degree in Chemistry at Wright State University working under Dr. William Feld and expects to receive his degree in August 2013.