Final Technical Report

NASA Project (NAG-1-1250)

"New Aromatic Activated Dihalides and Bisphenol Monomers for the Preparation of Novel Poly(arylene ethers)"

Prepared for

Materials Division and Structures and Dynamics Division
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**Introduction**

This final report summarizes the technical achievements resulting from research activities supported during the tenure of this grant (06/01/91 - 09/30/92).

**Technical Achievements**

The goal of this research program was to synthesize a series of unique monomers of type I to be utilized at NASA-Langley in the preparation of new poly(arylene ether ketones), poly(arylene ether ketosulfones), and poly(arylene ether ketophosphine oxides). These A-A and A-B monomer systems, which possess activated aryl halide and/or phenolic end groups, are accessible via condensation reactions of appropriately substituted aryl acetonitrile carbanions with activated aryl dihalides followed by oxidative decyanation.

\[ R - X - Y - X - R' \]

Monomer

3a, \( R = R' = F, \) \( X = \text{---C---}, \) \( Y = \text{---S---} \)

3b, \( R = R' = F, \) \( X = \text{---C---}, \) \( Y = \text{---P---} \)

3c, \( R = R' = F, \) \( X = \text{---C---}, \) \( Y = \text{---C---} \)

3d, \( R = R' = F, \) \( X = \text{---C---}, \) \( Y = \text{---C---} \)

6, \( R = R' = OH, \) \( X = \text{---C---}, \) \( Y = \text{---S---} \)

9, \( R = F, \) \( R' = OH, \) \( X = \text{---C---}, \) \( Y = \text{---S---} \)
I. Synthesis of Monomers 3a-d

The general synthetic route for the preparation of monomers 3a-d involved the condensation of excess α-lithio-4-fluorophenylacetonitrile, prepared from the nitrile and n-BuLi, with the appropriate activated aryl dihalide to give intermediate bis-nitriles 2a-d, followed by phase transfer-catalyzed oxidative decyanation. (Scheme I).

Scheme I

\[ \text{Cl-} \text{Y-} \text{Cl} \]

1a, \( Y = \text{S} \)

1b, \( Y = \text{P} \)

1c, \( Y = \text{C-C} \)

1d, \( Y = \text{C-CN} \)

\[ \text{F-CHCN, 6 equiv} \]

\[ \text{THF} \]

\[ \text{CN} \]

\[ \text{CN} \]

2a-d

\[ \text{TEBAC*/NaOH} \]

\[ \text{toluene, O}_2 \]

3a-d

*TEBAC = triethylbenzylammonium chloride
Overall yields in this two step process were >80% and satisfactory combustion analyses were obtained for all but phosphine oxide monomer 3b. In reactions to prepare dinitrile 2b, an inseparable mixture of 2b along with some of the monosubstitution product was invariably obtained. This same nitrile mixture persisted even when the difluoro analogue of 1b was treated with excess α-lithio-4-fluorophenylacetonitrile for 12 h in refluxing THF. Surprisingly, a similar reaction using excess α-lithio-4-fluorophenylacetonitrile, generated using lithium diisopropylamide (LDA) as the base, gave only the monosubstitution product. Subsequent oxidative decyanation of this mixture afforded a mixture of ketone monomers from which it was impossible to obtain pure 3b by column chromatography.

II. Synthesis of Monomers 6 and 9

Monomers 6 and 9 were prepared in overall yields of 90% and 73%, respectively, starting with, condensation of bis-(4-chlorophenyl)sulfone (1a) and α-lithio-4-methoxyphenylacetonitrile. (Scheme II).

Scheme II

```
\begin{tikzpicture}
  \node (a) at (0,0) {CH₃O-CH-CHCN, 6 equiv \text{THF/reflux, 12 h}};
  \node (b) at (4,0) {CH₃O-CH-CHCN, 2.1 equiv \text{THF/R.T., 1 h}};
  \node (c) at (0,-4) {CH₃O-CH-CN-SO₂-C-OC₃H₃};
  \node (d) at (4,-4) {CH₃O-CH-CN-SO₂-C-Cl};
  \node (e) at (2,-8) {CH₃O-CH-CN-SO₂-C-OC₃H₃};
  \node (f) at (6,-8) {CH₃O-CH-CN-SO₂-C-CH₃};
  \node (g) at (2,-12) {CH₃O-CH-CN-SO₂-C-OC₃H₃};
  \node (h) at (6,-12) {CH₃O-CH-CN-SO₂-C-CH₃};
  \node (i) at (4,-16) {\text{TEBAC/NaOH, toluene, O₂}};
  \node (j) at (4,-20) {\text{HBr, HOAc}};
  \node (k) at (6,-20) {\text{two steps}};
  \node (l) at (2,-24) {CH₃O-CH-CN-SO₂-C-OC₃H₃};
  \node (m) at (6,-24) {CH₃O-CH-CN-SO₂-C-CH₃};

  \draw[->, thick] (a) to (b);
  \draw[->, thick] (b) to (c);
  \draw[->, thick] (b) to (d);
  \draw[->, thick] (c) to (e);
  \draw[->, thick] (d) to (f);
  \draw[->, thick] (e) to (i);
  \draw[->, thick] (i) to (j);
  \draw[->, thick] (j) to (k);
  \draw[->, thick] (k) to (l);
  \draw[->, thick] (l) to (m);
\end{tikzpicture}
```
Although an alternative synthesis of monomer 9 was also accomplished beginning with condensation of 1a with α-lithio-4-fluorophenylacetonitrile, overall yields of 9 by this route were lower than with α-lithio-4-methoxyphenylacetonitrile.

III. Synthesis of Monomer 13

The preparation of the nitrile precursor, 12, of monomer 13 turned out to be rather difficult. Attempted one-pot syntheses of 12 involving the stepwise addition of two 1-equiv portions of 1a, first to 2 equiv of α-lithioacetonitrile and then to α-lithionitrile 11, formed \textit{in situ}, gave a mixture of nitrile products consisting of 10, 12 and bis-(4-cyanomethylphenyl) sulfone, which made the isolation of 12 very inefficient. Ultimately, the two step reaction shown in Scheme III proved to be satisfactory for the preparation of 12. Thus, nitrile 10 was isolated in 80% yield from the reaction of 1a with α-lithioacetonitrile. The subsequent condensation reaction to prepare 12 which proceeded very sluggishly due to the weakly nucleophilic nature of carbanion 11, afforded nitrile 12 in yields ranging from 70-75% based on reacted 10. When an
additional equivalent of $n$-BuLi was employed in this reaction to improve the conversion of 10 by regenerating carbanion 11 consumed during the course of the reaction via protonation by 12, a complex reaction mixture resulted, which still contained a substantial quantity of unreacted 10. Similar results were obtained when 2 equiv of lithium diisopropylamide (LDA) was used as the base in place of $n$-BuLi. Oxidative decyanation of 12 required inordinately long reaction times (three to four days) for completion (87% yield of 13) presumably as a result of the low reactivity of the highly delocalized nitrile carbanion with oxygen.

IV. **Synthesis of Monomers 17 and 19**

The synthesis of monomer 17 from sulfone 1a and 1,3-phenylenediacetonitrile (14) is outlined in Scheme IV.

![Scheme IV](attachment:SchemeIV.png)
Stepwise condensation of 2 equiv of 1a with α,α'-dilithio-1,3-phenylenediacetonitrile (15) afforded a 72% yield of dinitrile 16. Phase transfer-catalyzed oxidative decyanation of 16, which required a two day reaction period, gave analytically pure monomer 17 in 76% yield.

When the same synthetic approach used to synthesize monomer 17 was applied to the preparation of monomer 19, some unexpected difficulties were encountered. Attempted synthesis of intermediate dinitrile 18 by addition of sulfone 1a to a solution of α,α'-dilithio-1,4-phenylenediacetonitrile at -78°C yielded a solid material (polymer?) which was essentially insoluble in organic solvents. By reversing the order of addition and thus maintaining an excess of 1a, this problem was avoided and pure dinitrile 18 was obtained in 67% yield. The conversion of 18 to monomer 19, however, also proved to be problematical. Unlike its dinitrile analogue 16, 18 was virtually insoluble in toluene, the organic solvent employed in all previous oxidative decyanation reactions in this study. As a result, this reaction proceeded very slowly and after several days gave a solid product mixture having very limited solubility in organic solvents. Subsequently, several other solvent/base systems were employed, including THF/n-BuLi, DMSO/LDA, DMSO/NaOH, and dioxane/LDA, but the same intractable reaction mixture persisted in each case. Regrettably, after about a three month effort, we were unable to obtain monomer 19 in the high degree of purity required for use in polymer synthesis. The purest material we were able to isolate melted at 297-300°C and analyzed 0.7% high in hydrogen.

Samples of the seven monomers listed in Table I whose syntheses are previously described in this report were submitted to Paul Hergenrother at the NASA-Langley Research Center for the
preparation of new poly(arylene ethers). Several moderately high molecular weight polymers of this type have been prepared and evaluation of these materials is continuing.

Table I

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Quantity (g)</th>
<th>M.P. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>13</td>
<td>183-184</td>
</tr>
<tr>
<td>3c</td>
<td>13</td>
<td>342-343</td>
</tr>
<tr>
<td>3d</td>
<td>20</td>
<td>309-310</td>
</tr>
<tr>
<td>6</td>
<td>18</td>
<td>226-227</td>
</tr>
<tr>
<td>9</td>
<td>20</td>
<td>198-199</td>
</tr>
<tr>
<td>13</td>
<td>14</td>
<td>226-227</td>
</tr>
<tr>
<td>17</td>
<td>20</td>
<td>232-233</td>
</tr>
</tbody>
</table>

* Combustion analyses for all monomers were within 0.4% of theoretical values. 'H NMR spectrum were in agreement with assigned structures and purity.

Personnel Supported

Dr. Graciela Bariberi, Ph.D. Virginia Tech, Research Associate, 02/01/91 - 08/31/91
Dr. Phuoc Nguyen, Ph.D. Northeastern University, Research Associate, 10/01/91 - 11/30/92