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

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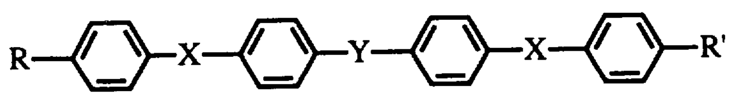
Introduction

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

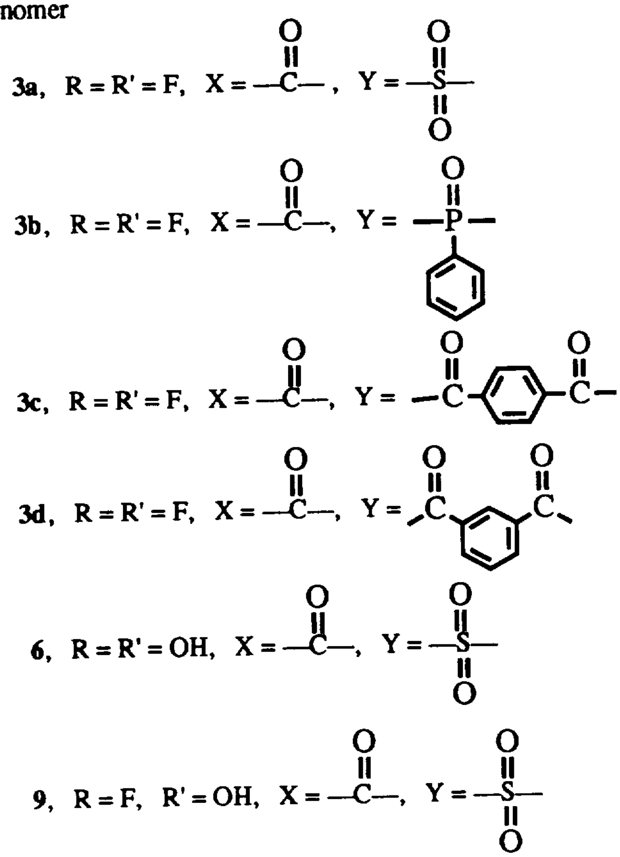
Technical Achievements

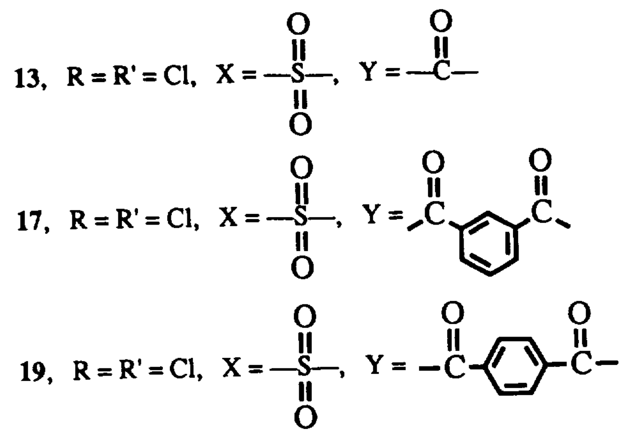
The goal of this research program was to synthesize a series of unique monomers of type I to be utilized at NASA-Langley in the preparation of new poly(arylene ether ketones), poly(arylene ether ketosulfones), and poly(arylene ether ketophosphine oxides). These A-A and A-B monomer systems, which possess 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.



I

Monomer

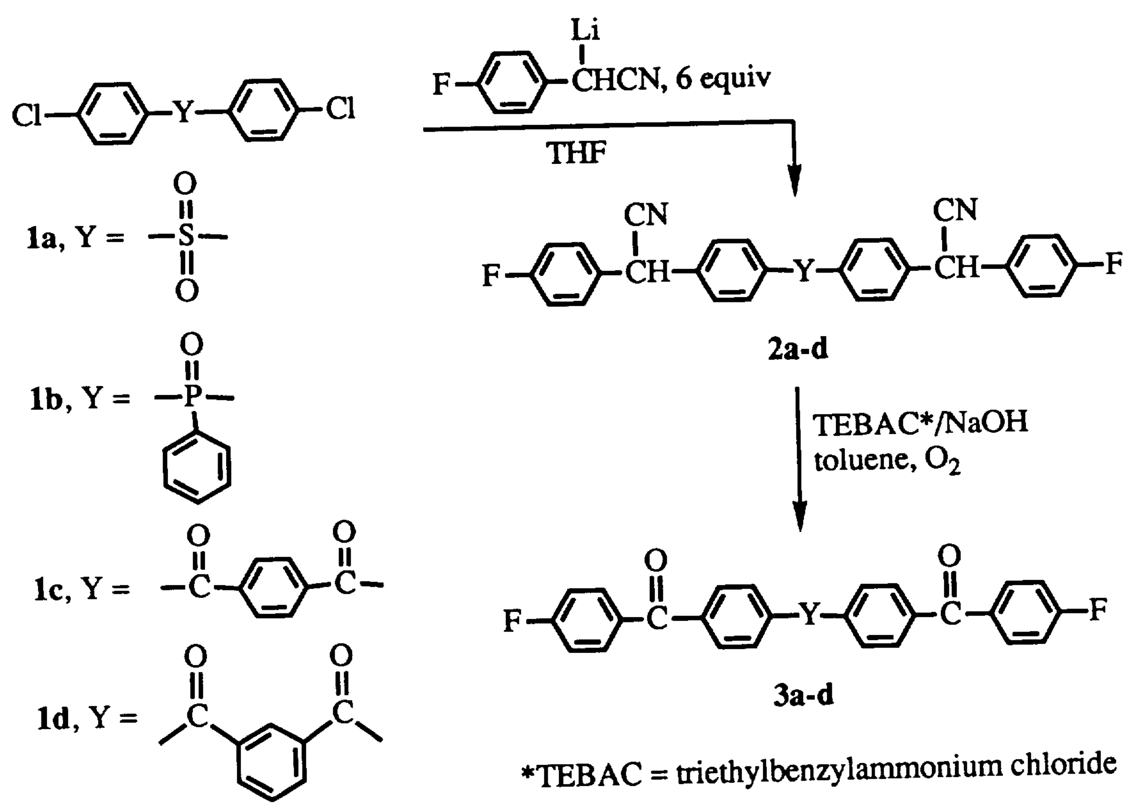




I. Synthesis of Monomers **3a-d**

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



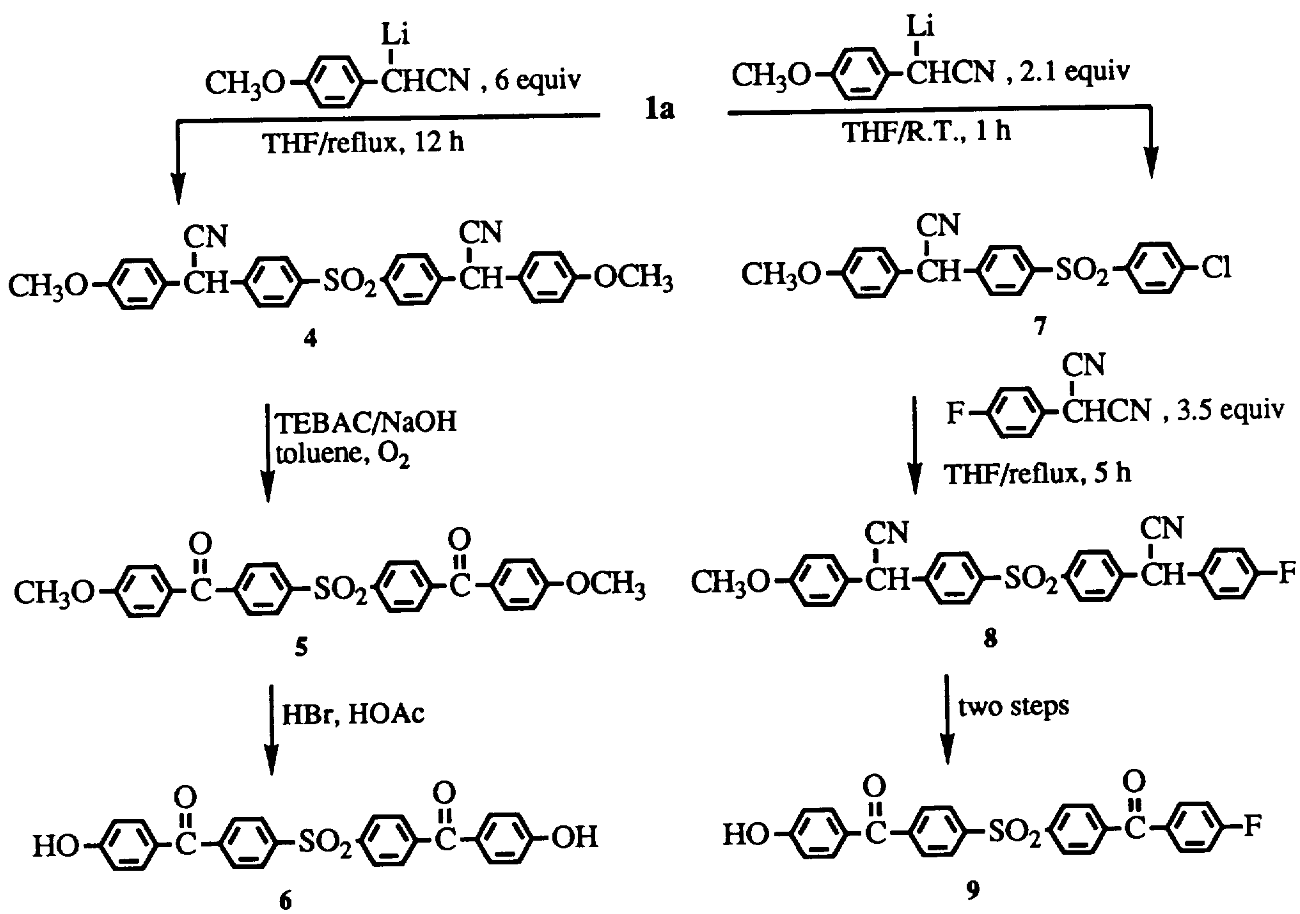
*TEBAC = triethylbenzylammonium chloride

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 (**1 a**) and α -lithio-4-methyoxyphenylacetonitrile. (Scheme II).

Scheme II

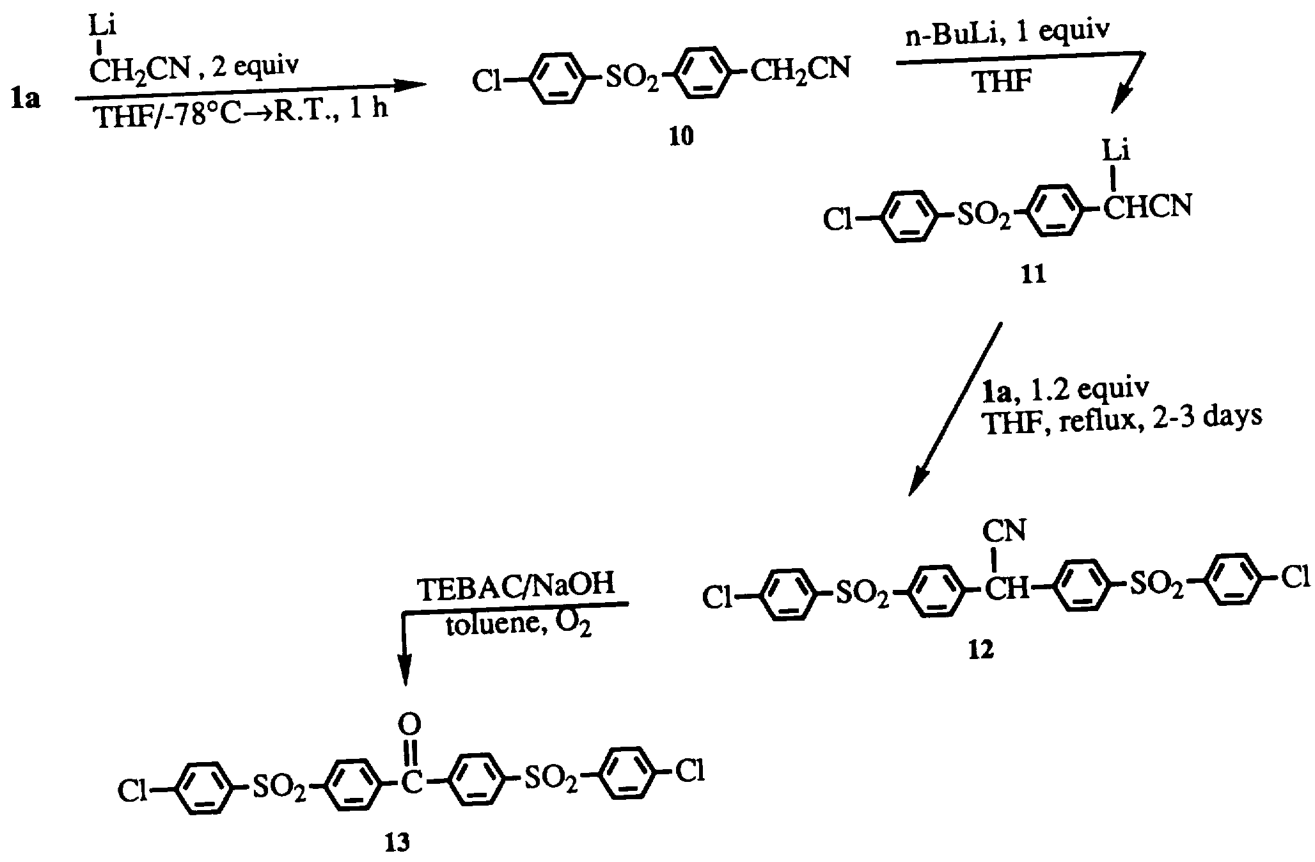


Although an alternative synthesis of monomer **9** was also accomplished beginning with condensation of **1a** with α-lithio-4-fluorophenylacetonitrile, overall yields of **9** by this route were lower than with α-lithio-4-methoxyphenyacetontirile.

III. <u>Synthesis of Monomer 13</u>

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 *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

Scheme III

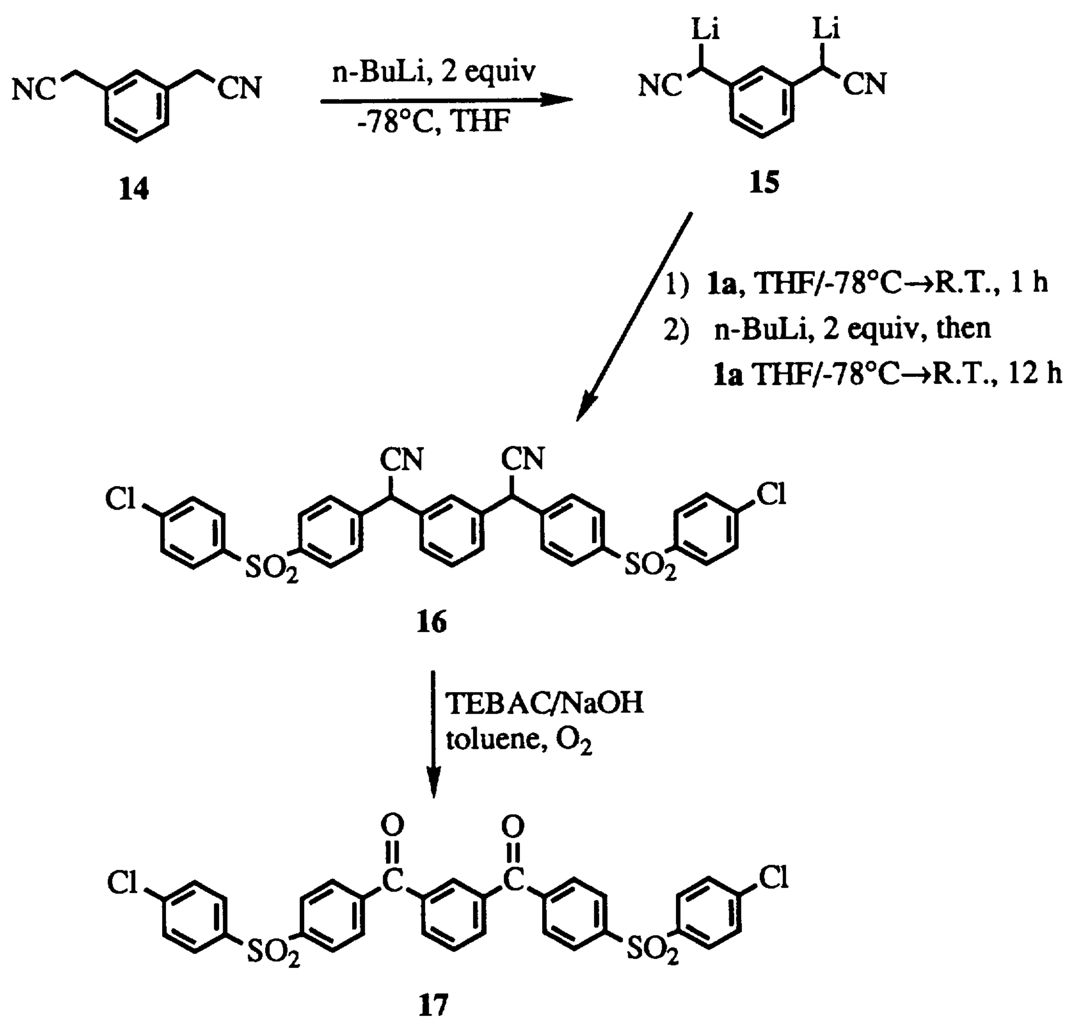


in 80% yield from the reaction of **1a** with α-lithioacetonitrile. The subsequent condensation reaction to prepare **12** which proceeded very sluggishly due to the weakly nucleophilic nature of carbanion **11**, afforded nitrile **12** in yields ranging from 70-75% based on reacted **10**. When an 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

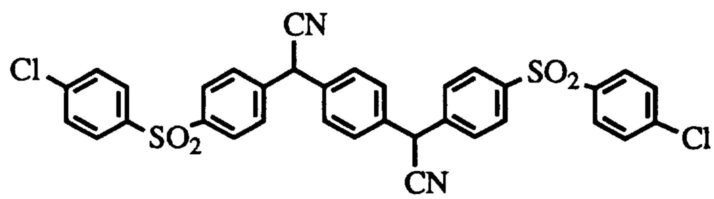
The synthesis of monomer **17** from sulfone **1a** and 1,3-phenylenediacetonitrile (**14**) is outlined in Scheme IV.

Scheme IV

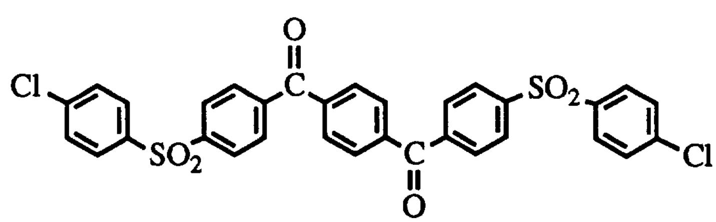


Stepwise condensation of 2 equiv of **1a** with α,α'-dilithio-1,3-phenylenediacetonitrile (**15**) afforded a 72% yield of dinitrile **16**. Phase transfer-catalyzed oxidative decyanation of **16**, which required a two day reaction period, gave analytically pure monomer **17** in 76% yield.

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



18



19

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

Monomer*	Quantity (g)	M.P.°C
3a	13	183-184
3c	13	342-343
3d	20	309-310
6	18	226-227
9	20	198-199
13	14	226-227
17	20	232-233

* Combustion analyses for all monomers were within 0.4% of theoretical values. ^{1}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