

**PART 1. PROCESSABLE FLUORINATED POLYAMIDES AND POLYAMIDE-
IMIDES**

**PART 2. NOVEL PHOSPHONATED POLY(ARYLENE ETHER)S AS
POTENTIAL HIGH TEMPERATURE PROTON CONDUCTING MATERIALS**

A Dissertation Presented

By

EBRAHIM ABOUZARI-LOTF

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اساتید راهنما:

دکتر عباس شکروی

دکتر حسین قاسمی

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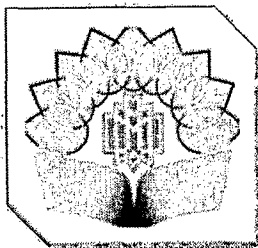
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نگارش:

ابراهیم ابوذری لطف

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PART 1: Processable Fluorinated Polyamides and Polyamide-imides
PART 2: Novel Phosphonated Poly(arylene ether)s as Potential High
Temperature Proton Conducting Materials

Supervisors

Prof. Abbas Shockravi (TMU)

Dr. Hossien Ghassemi (CWRU)

By

EBRAHIM ABOUZARI-LOTF

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DEDICATION

To my beloved family

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ABSTRACT

In the first part, two new fluorinated diamines, 2,2'-thiobis-[4-methyl(2-trifluoromethyl)4-aminophenoxy) phenyl ether] (**DAS**) and 2,2'-sulfoxide-bis[4-methyl(2-trifluoromethyl)4-aminophenoxy) phenyl ether] (**DASO**), were successfully synthesized by refluxing the dibenzosulfide (**DHS**) or dibenzosulfoxide (**DHSO**) and 2-chloro-5-nitrobenzotrifluoride in the presence of potassium carbonate, followed by catalytic reduction with zinc/ammonium chloride. Then, two series of organic-soluble polyamides (**PA_{a-g}**) and (**PA1-7**) bearing flexible ether, sulfide, and sulfoxide links, electron-withdrawing trifluoromethyl groups, and *ortho*-phenylene units were synthesized from these new diamines (**DAS** and **DASO**) with various aromatic diacids via direct polycondensation with triphenyl phosphate and pyridine. The polyamides were obtained in quantitative yields and possessed inherent viscosities in the range of 0.35-0.90 dL g⁻¹. All the polymers were noncrystalline, and showed outstanding solubility and could be easily dissolved in amide-type polar aprotic solvents (e.g., N-methyl-2-pyrrolidinone (NMP), N, N-dimethylacetamide (DMAc), and N,N-dimethylformamide (DMF)) and even dissolved in less polar solvents (e.g., pyridine and tetrahydrofuran). They were in useful levels of thermal stability: 10% weight loss in nitrogen atmosphere was in the range of 375–505 °C. These polymers showed glass transition temperatures between 160-220 °C. Also some of these polymers could be cast into flexible and tough films from DMAc solutions. The comparison of the results of thermal stability and solubility of prepared polymers with analogues sulfur containing polymers indicated that incorporation of S=O into the polymer backbone effectively enhances the thermal stability and solubility of the rigid polymer backbone.

Then, the sulfur containing diimide-diacid (**DIDA**) was prepared by condensation reaction of diamine **DAS** and trimellitic anhydride. A series of novel organic-soluble polyamide-imides (PAIs) bearing flexible ether and sulfide links, electron-withdrawing trifluoromethyl groups and *ortho*-phenylene units were synthesized from **DIDA**, by direct polycondensation with various aromatic diamines in NMP using triphenyl phosphite and pyridine as a condensing agent in the presence of dehydrating agent (LiCl). The PAIs

were obtained in high yields and possessed inherent viscosities in the range of 0.42-0.95 dL g⁻¹. All of the polymers were amorphous in nature, showed outstanding solubility and could be easily dissolved in amide-type polar aprotic solvents (NMP, DMAc, and DMF) and even dissolved in less polar solvents (e.g., pyridine and tetrahydrofuran). They showed good thermal stability with glass transition temperatures between 195-245 °C, 10% weight loss temperatures in excess of 485 °C, and char yields more than 50% at 700 °C in nitrogen atmosphere. Moreover, these PAIs possessed low refractive indexes ($n=1.57-1.59$) and low birefringence ($\Delta\approx 0.02$) due to the trifluoromethyl pendent groups and thioether bridged *ortho*-catenated aromatic rings that interrupt chain packing and increase free volume.

Second part of this dissertation focuses on proton conducting materials that could be used at high operating temperatures. Higher operating temperatures are desirable as they will increase fuel cell efficiency, reduce cost, and simplify the heat management system. Because of sulfonated polyelectrolytes are sensitive to dehydration at elevated temperatures, research is shifting to alternative protogenic groups, such as phosphonic acid ($-\text{PO}_3\text{H}_2$) functionalized derivatives.

Organophosphorus compounds, dichlorophenylphosphonic acid diethyl esters (**M 3** and **M 4**) were synthesized through the reaction of dichloro iodobenzenes (**M 1** and **M 2**) and triethyl phosphite in the presence of NiCl_2 . Then these compounds were hydrolyzed to the corresponding acids (**M 5** and **M 6**) and finally the corresponding potassium salts (**M 7** and **M 8**) were prepared. They were characterized by elemental analysis, and ^1H , ^{13}C and ^{31}P NMR spectroscopies as well as CHN analysis. These monomers were used in the polymerization reactions for the preparation of the appropriate phosphonated polyethers. Unfortunately, none of the *para*- or *meta*-linked phosphonated esters, acids, or bispotassium salts was active enough in the reaction to yield the appropriate polymers.

In continue, aromatic diphosphonate monomers based on hydroquinone were prepared (**M 10**, **M 11**, and **M 12**). The synthesis of the **M 10** monomer carried out in two steps: the reaction of diethyl phosphate with hydroquinone, and the second step was involved the rearrangement of the resulting phosphate derivative into hydroxyaryl phosphonate

with lithium diisopropylamide. Aromatic polyethers or poly(ether sulfone)s were synthesized using this hydroxyaryl phosphonate ester or corresponding acid, or bispotassium salt with decafluorobiphenyl and 4,4'-difluorodiphenyl sulfone. A novel membrane was prepared from the reaction of phosphonated bisphenol (**M 10**) and decafluorobiphenyl. The polymer has moderate molecular weights as indicated by the inherent viscosity around 0.45 g/dL. End group analysis of ^{19}F NMR was also used for the estimation of the number average molecular weight M_n (g/mol). The calculated polymer M_n^{NMR} value was around 28400 g/mol, which corresponds to a block length of $n = 42$. The polymer showed outstanding solubility and could be dissolved in amide-type polar aprotic solvents (e.g., NMP, DMSO, DMAc, and DMF) and even dissolved in less polar solvents (e.g., THF and ethanol). Flexible, tough, and clear films (20-40 μm in thickness) were obtained from the casting of appropriate polymer amount in THF, DMF, or even ethanol.

The TGA data indicated that **P 23** polymer loss around 15 % weights in the range of 200–300 $^{\circ}\text{C}$, because of the loss of -Et segments. Therefore, it is evidence that corresponding acid polymer will be thermally stable with no significant weight loss up to approximately 500 $^{\circ}\text{C}$. From ^1H and ^{31}P NMR spectrum of **P 23** it can be implied that there was partial hydrolysis in the polymerization reaction in the presence of potassium carbonate and produced water.

None of the hydrolysis methods (acidic or alkaline) were appropriate to obtain almost quantitative conversions to the diacid phosphonate **M 11**.

The use of masked bisphenol may possibly leads to the useful hydrolyzed polymers (polymerization in the absence of water). Therefore, in the third section, hydroxyaryl phosphonate ester **M 10** was converted into the corresponding biscarbamate **M 12**.

CHEMICAL STRUCTURES OF ANALYZED COMPOUNDES

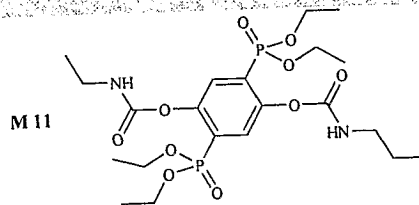
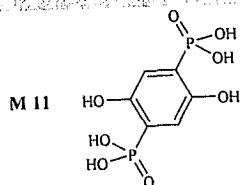
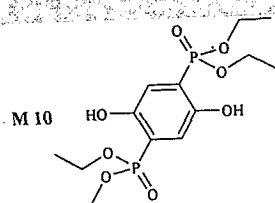
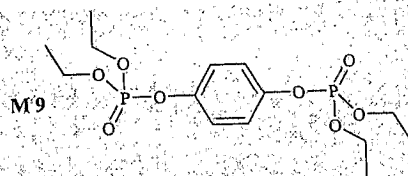
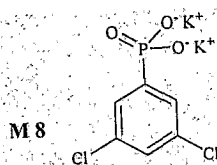
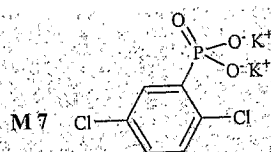
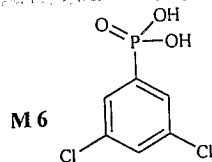
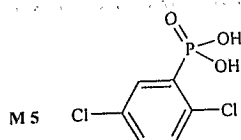
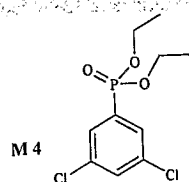
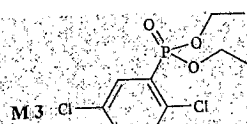
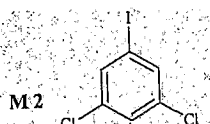
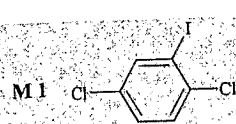
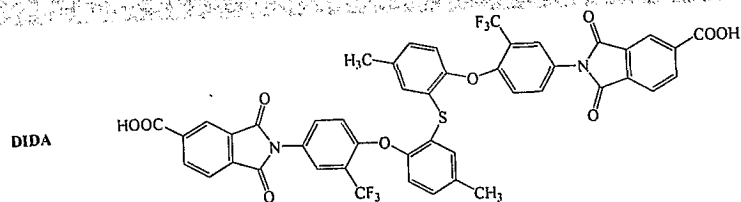
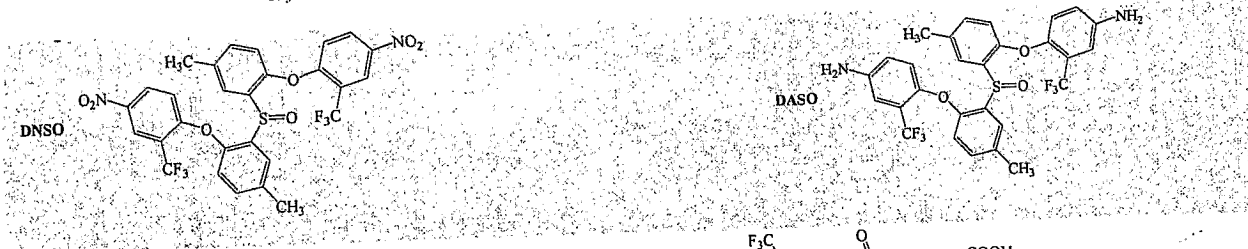
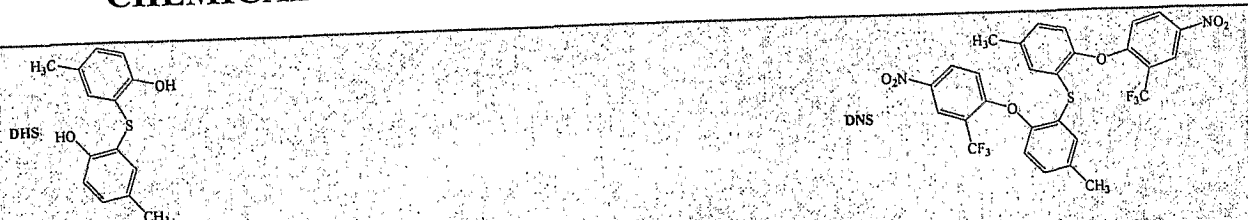


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