

The Pennsylvania State University

The Graduate School

Department of Chemistry

**SYNTHESIS AND CHARACTERIZATION OF MIXED-SUBSTITUENT
POLY(ORGANOPHOSHAZENES)**

A Thesis in

Chemistry

by

Andrew Elessar Maher

© 2004 Andrew Elessar Maher

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

May 2004

The thesis of Andrew Elessar Maher was reviewed and approved* by the following:

Harry R. Allcock
Evan Pugh Professor of Chemistry
Thesis Advisor
Chair of Committee

Alan Benesi
Teaching Professor of Chemistry

Karl Mueller
Associate Professor of Chemistry

James Runt
Professor of Polymer Science

Andrew Ewing
J. Lloyd Huck Chair in Natural Sciences
Professor of Chemistry
Adjunct Professor of
Neuroscience and Anatomy
Head of the Department of Chemistry

*Signatures are on file in the Graduate School

ABSTRACT

This thesis focuses on the synthesis and characterization of mixed-substituent poly(organophosphazenes). The work in chapters 2 through 4 examines mixed-substituent polyphosphazenes with fluoroalkoxy side groups. Chapters 2 and 3 involve a synthetic route to mixed-substituent polyphosphazenes via side group replacement of fluoroalkoxy substituents. The thermal and mechanical properties of mixed-substituent poly(fluoroalkoxyphosphazenes) are examined through varying the ratios of two fluoroalkoxy substituents. These structure-property relationships and the potential use of these materials as fluoroelastomers are the subjects of chapter 4. The specifics of chapters 2-4 are summarized below. The work in chapter 5 concerns the synthesis and evaluation of mixed-substituent polyphosphazenes as single-ion conductors. The synthesis of a sulfonimide functionalized side group for proton conducting fuel cell applications is the subject of the appendix and is also utilized in the work in chapter 5. The specific details of the ionic conducting polymer studies are also summarized below.

In chapter 2, several poly(alkoxyphosphazenes) and poly(fluoroalkoxyphosphazenes) were synthesized and allowed to react with various organic nucleophiles. Reactions were carried out at room temperature (25 °C) and at 67 °C in tetrahydrofuran (THF) and were monitored by ^{31}P NMR spectroscopy. The possible use of single-substituent polymers as hydrolytically stable macromolecular intermediates for mixed-substituent polyphosphazene synthesis is discussed and factors that influence side group replacement in poly(organophosphazenes) are examined. In

addition, evidence for a random, irreversible S_N2 -like mechanism of side group replacement is presented. The work in chapter 3 is complementary to chapter 2 and examines the equilibrium exchange reactions of fluoroalkoxy substituents and fluoroalkoxy nucleophiles.

In chapter 4, a series of poly(fluoroalkoxyphosphazenes) containing a mixture of 2,2,3,3,4,4,5,5-octafluoropentoxy and 2,2,2-trifluoroethoxy substituents was synthesized. The series included polymers with 25-94% incorporation of the trifluoroethoxy substituent, as well as single-substituent polymers with 100% octafluoropentoxy or trifluoroethoxy side groups. The polymers were analyzed by multi-nuclear NMR spectroscopy, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and were subjected to limiting oxygen index and microtensile testing. The variation in thermal and mechanical properties as a function of the side group ratios is discussed and polymers that may be suitable for fabrication into low temperature elastomer materials are identified.

The use and evaluation of mixed-substituent polyphosphazenes as single ion conductors is described in chapter 5. Polyphosphazenes with both 2-(2-methoxyethoxy)ethoxy and lithiated sulfonimide functionalized side groups were synthesized and characterized using multi-nuclear NMR, GPC, flame atomic absorption (FAA) spectroscopy, elemental analysis (EA), and DSC. The sulfonimide functional group was lithiated via dialysis with aqueous lithium chloride solutions. Lithiation was confirmed by FAA spectroscopy and EA. The polymers were examined for their behavior as single ion conductors using impedance analysis. The dependence of the

conductivity on the macromolecular motion of the polymers and on the amount of sulfonimide functionalized side group is discussed.

Chapter 6 briefly describes potential future research directions based on the work presented in chapters 2 through 5.

The appendix describes the synthesis of the sulfonimide functionalized side group. This work also examines this side group for use in polyphosphazene proton conducting fuel cell membranes.

Table of Contents

List of Figures.....	xii
List of Schemes.....	xiv
List of Tables.....	xv
Preface.....	xvi
Acknowledgments.....	xvii
Chapter 1. General Introduction.....	1
A. Polymeric Materials.....	1
1. What is a polymer?	1
2. Brief History of Polymer Chemistry.....	1
3. Classification of Polymers	5
B. Polyphosphazenes	12
1. Introduction.....	12
2. History of Polyphosphazenes.....	12
3. Synthesis of Linear Polyphosphazenes.....	14
4. Structure-Property Relationships	16
C. Elastomers.....	21
1. General Introduction	21
2. Polyphosphazene Elastomers.....	22

D. Secondary Lithium Ion Batteries	24
1. The Lithium Ion Battery	24
2. Liquid Electrolytes	27
3. Solid Polymer Electrolytes	27
4. Single Ion Conductors	29
E. Research Objectives	30
F. References	31

**Chapter 2. Side Group Exchange in Poly(organophosphazenes) with
Fluoroalkoxy Substituents, Part 1: Alkoxide Nucleophiles34**

A. Introduction	34
B. Results and Discussion	38
1. Synthesis of Starting Macromolecules $[\text{NP}(\text{OR})_2]_n$ (2-8)	38
2. Reactions of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ (2) with Alkoxide Nucleophiles	38
3. Reactions of $[\text{NP}(\text{OCH}_2\text{CF}_2\text{CF}_2\text{H})_2]_n$ (3) with Alkoxide Nucleophiles	43
4. Reactions of $[\text{NP}(\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H})_2]_n$ (4) with Alkoxide Nucleophiles	43
5. Reactions of 5-8 with Alkoxide Nucleophiles	46
6. Characterization of Polymers 2-32	46
7. Factors Involved in Macromolecular Substitution of Polymers 2-4	49
8. Mechanism of Macromolecular Substitution	49
C. Conclusions	51
D. Experimental Section	52

1. Materials	52
2. Equipment	53
3. Synthesis of Poly[bis(fluoroalkoxyphosphazenes)] (2-4)	53
4. Synthesis of Poly[bis(alkoxyphosphazenes)] (5-8)	55
5. Synthesis of Co-substituted Polyphosphazenes (9-32)	56
6. Addition of 2,2,2-trifluoroethoxide to Polymers 9, 10, 15 , and 16	62
E. References	63

**Chapter 3. Side Group Exchange in Poly(organophosphazenes) with
Fluoroalkoxy Substituents, Part 2: Fluoroalkoxide Nucleophiles.....66**

A. Introduction.....	66
B. Results and Discussion.....	66
1. Synthesis of Co-substituted Poly(fluoroalkoxyphosphazenes).....	66
2. Reactions of Fluoroalkoxide Nucleophiles with Polymer 2	71
3. Reactions of Fluoroalkoxide Nucleophiles with Polymer 3	71
4. Reactions of Fluoroalkoxide Nucleophiles with Polymer 4	73
5. Equilibrium Exchange Reactions.....	74
C. Conclusions	75
D. Experimental Section	75
1. Materials	75
2. Equipment	76
3. Synthesis of Polyphosphazenes (2-22)	77
E. References	78

Chapter 5. Synthesis and Conductive Properties of Polyphosphazenes

Bearing Sulfonimide Functional Groups: Evaluation as Single Ion

Conductors109

A. Introduction.....	109
B. Results and Discussion.....	111
1. Synthesis of	
[NP(OCH ₂ CH ₂ OCH ₂ CH ₂ OCH ₃) _x (OC ₆ H ₄ SO ₂ N(Li)SO ₂ CF ₃) _{2-x}]	111

2. Polymer Characterization.....	113
3. Conductivity Results.....	116
4. Mechanism of Conduction.....	120
C. Conclusions.....	121
D. Experimental Section.....	121
1. Materials	121
2. Equipment.....	122
3. Synthesis of Polymers 2-5	123
4. Synthesis of Poly[bis(trifluoroethoxyphosphazene)] (6).....	126
5. Preparation of SPEs	126
E. References	127
Chapter 6. Possible Future Research Directions	128
A. Future Research Directions.....	129
Appendix. Synthesis of a Sulfonimide Side Group and Its Incorporation into	
 Polyphosphazenes	131
A. Introduction.....	131
B. Results and Discussion.....	132
1. Incorporation of Acid Groups into Polyphosphazenes	132
2. Synthesis of Sulfonimide Side Group NaOC ₆ H ₄ SO ₂ NNaSO ₂ CF ₃ (2a).....	133
3. Reactions of 2a with Partially Substituted Chlorophosphazenes.....	135
4. Membrane Characterization for Polymer 6	135

5. Mebrane Characterization for Polymer 6 Blended with PVDF	138
C. Conclusion	139
E. References	141

List of Figures

Figure 1-1. Poly(propylene).....	2
Figure 1-2. Representative Commodity Polymers.....	4
Figure 1-3. Polymer Architectures.....	6
Figure 1-4. Classification of Polymers by Monomer Residue Composition.....	8
Figure 1-5. Inorganic Backbone Polymers	13
Figure 1-6. Representative Polyphosphazenes	20
Figure 1-7. Polyphosphazene Elastomers	23
Figure 1-8. Power Density Comparison of Various Battery Systems	25
Figure 1-9. Simple Schematic of a Secondary Lithium Ion Battery.....	26
Figure 1-10. Poly(ethylene oxide)	28
Figure 2-1. Starting Polymers 2-8	39
Figure 2-2. ^1H NMR Spectra in d_6 -THF	41
Figure 3-1. ^{19}F NMR Spectrum of Polymer 8	68
Figure 4-1. Examples of Fluoroelastomers.....	80
Figure 4-2. Substituent Ratio Determination by ^1H NMR.....	86
Figure 4-3. TGA Traces of Polymers 2-9	89
Figure 4-4. DSC Traces Showing Loss of Crystallinity	91
Figure 4-5. Mechanical Properties of Polymers 2-9	95
Figure 4-6. Young's Moduli of Polymers 2-9	97
Figure 4-7. DSC Traces of Poly[bis(trifluoroethoxyphosphazene)].....	98

Figure 5-1. ^{31}P NMR of Polymer 2	116
Figure 5-2. DSC Results for Polymers 2-5 and 7	118
Figure 5-3. Conductivity Results for Polymers 2-5	106

List of Schemes

Scheme 1-1. Condensation Polymerization of Ethylene Glycol and Terephthalic Acid	10
Scheme 1-2. Chain Growth Synthesis of Poly(methyl methacrylate)	11
Scheme 1-3. Proposed Phosphazene Polymerization Mechanism.....	15
Scheme 1-4. Synthesis of Poly(organophosphazenes).....	17
Scheme 2-1. Synthesis of Co-substituted Poly(organophosphazenes)	36
Scheme 2-2. Mechanism of Side Group Exchange	50
Scheme 4-1. Synthesis of Poly(fluoroalkoxyphosphazenes)	84
Scheme 5-1. Synthetic Route for the Synthesis of Polymers 2-5	112
Scheme A-1. Synthesis of the Sulfonimide Side Group $\text{NaOC}_6\text{H}_4\text{SO}_2\text{NNaSO}_2\text{CF}_3$ (2a)	134
Scheme A-2. Reaction of 2a with Partially Substituted Chlorophosphazenes	136

List of Tables

Table 2-1. Composition of Co-substituted Polymers from $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$	42
Table 2-2. Composition of Co-substituted Polymers from $[\text{NP}(\text{OCH}_2\text{CF}_2\text{CF}_2\text{H})_2]_n$..	44
Table 2-3. Composition of Co-substituted Polymers from $[\text{NP}(\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H})_2]_n$	45
Table 2-4. GPC Results.....	48
Table 3-1. GPC Results.....	70
Table 3-2. Side Group Exchange Results	72
Table 4-1. Side Group Ratios and Molecular Weight Characterization	83
Table 4-2. Thermal Analysis of Polymers 2-9 by LOI, TGA, and DSC	88
Table 4-3. Mechanical Properties of Polymers 2-9	94
Table 5-1. Composition and Conductivity Results of Polymers 2-5	114
Table 5-2. Quantities of Reagents for Polymers 2-5	125
Table A-1. Membrane Data	137

Preface

Portions of this thesis have been adapted for publication. Chapter 2 was adapted for publication in *Macromolecules* and was coauthored by H.R. Allcock and C.M. Ambler. Chapter 4 has been accepted for publication in *Journal of Applied Polymer Science* and was coauthored by H.R. Allcock, C.M. Ambler, and E.S. Powell. The Appendix was adapted for publication in *Macromolecules* and was coauthored by M.A. Hofmann, C.M. Ambler, H.R. Allcock, E. Chalkova, and S.N. Lvov.

Acknowledgments

I would like to thank my preceptor Harry R. Allcock for the opportunity to participate in an exciting research program. I appreciate the encouragement by Dr. Allcock to pursue application based research in polymer chemistry and to develop important professional skills. The experiences I have gained in his research group have helped me to attain the ability and the confidence necessary for success in my future endeavors. I would also like to thank The Pennsylvania State University and the U.S. Navy for financial support of my research.

I am also indebted to my collaborators and co-workers here at Penn State who have worked with me on various research projects. These include Catherine Ambler, Eric Powell, Dr. Michael Hofmann, Dan Welna, Rich Wood, Dr. Robbyn Prange, Dr. Serguei Lvov, and Dr. Elena Chalkova. I would also like to thank all the present and past members of the Allcock research group who have contributed to my academic and professional development. Special thanks go to: Dr. Jonathan Taylor, Dr. Angela Cannon, Dr. Thomas Hartle, Dr. Clay Kellam, Dr. Robert Morford, Dr. Youngkyu Chang, and Jared Bender. I would also like to thank Dr. Alan Benesi, Dr. James Runt, Dr. Timothy Glass, and Dr. Daniel Jones for helpful scientific discussions.

I would like to thank my father and mother (John and Mary) and my sister and brother (Jessica and Jonathan) for support and encouragement. I also thank Brent

England, Mike Stout, Jayson Ewer, Keith Martel and Charlie Munro who I met while studying here and whose friendship I will cherish for a lifetime.

I would especially like to thank my wife and best friend Anna and our daughter Aria. Their love and support is a tremendous source of encouragement and joy. Finally I would like to acknowledge the Lord Jesus Christ for life and strength to carry out my responsibilities and scientific endeavors (Jeremiah 9:23-24).

Chapter 1

General Introduction

A. Polymeric Materials

1. What is a polymer?

The word polymer is composed of two classical Greek words and simply means many (poly) parts (meres). Polymers are large molecules that have units of identical structure (monomers) covalently bonded in a long chain.¹ Many polymers, such as polypropylene (figure 1-1), consist of a single repeating unit structure. Other polymers have two or more different repeating units. Proteins, for example, are polymers that are composed of amino acids. A single protein could have ten or twenty different repeating unit structures linked together in a long chain.² Polymers, such as proteins, cellulose and Hevea (natural rubber), occur in nature. However, many polymers must be produced synthetically.² During the past 100 years, these synthetic polymers have come to hold a position of great technological importance for the industrialized world.

2. Brief History of Polymer Chemistry

Natural polymers, such as wood and horn, have been used for shelter, weapons and tools for thousands of years.² However, scientific use of the word polymer only started with J. J. Berzelius in 1827.³ Important discoveries were made throughout the nineteenth century that brought about new and unusual uses for polymeric materials. For

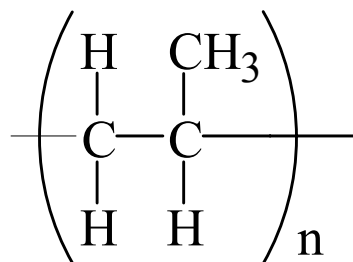
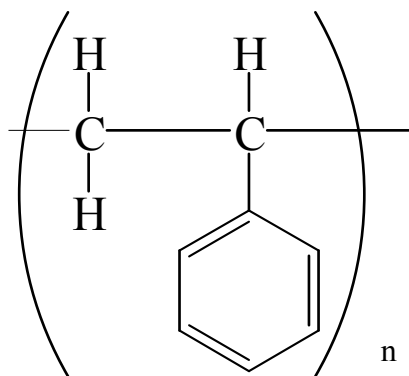


Figure 1-1: Poly(propylene)

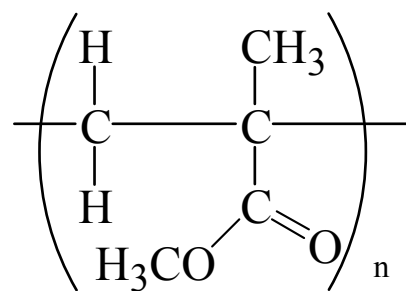
example, Goodyear discovered ways to improve the mechanical properties of natural rubber by using heat and sulfur to introduce cross-links into the rubber (i.e. vulcanization).¹ Other examples include the modification of cellulose materials to produce polymers such as celluloid, rayon, and cellophane.² After the turn of the nineteenth century, several fully synthetic polymers were developed, including Bakelite and methyl rubber.²

All of the above discoveries and inventions occurred without a proper understanding of the physical structure of the polymers. Until 1920, polymers were believed to be small molecule aggregates and not large, covalently bonded molecules. Staudinger then proposed the hypothesis that polymers were very large molecules composed of simpler structural units (monomers) attached by covalent bonds and coined the term “macromolecule”.^{2,4} Careful experimental work by Staudinger, Carothers and others convinced the scientific community of the validity of the macromolecular hypothesis.^{2,5} The field of polymer science became well established over the next two decades. Paul Flory, for example, greatly contributed to the understanding of polymer properties and behavior. He was awarded the Nobel Prize in Chemistry in 1974. Researchers during this period also developed polystyrene, poly(methyl methacrylate), poly(tetrafluoroethylene), poly(vinyl chloride) (figure 1-2) and many other polymers.²

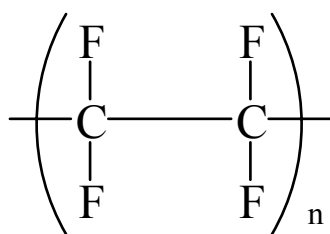
Over the past fifty years, new polymeric materials have been discovered that have greatly impacted modern technology. Thermoplastic elastomers such as polystyrene-polybutadiene-polystyrene (SBS) rubber are used widely in the automotive industry.⁶ Poly(acetylene), poly(p-phenylene) and poly(aniline) are examples of electrically conductive polymers useful in solar cells and batteries.⁷ Other examples of progress in



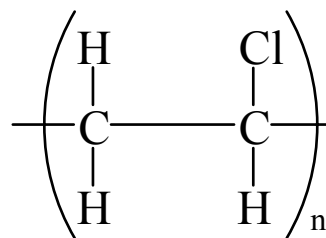
Poly(styrene)



Poly(methyl methacrylate)



Poly(tetrafluoroethylene)



Poly(vinyl chloride)

Figure 1-2: Representative Commodity Polymers

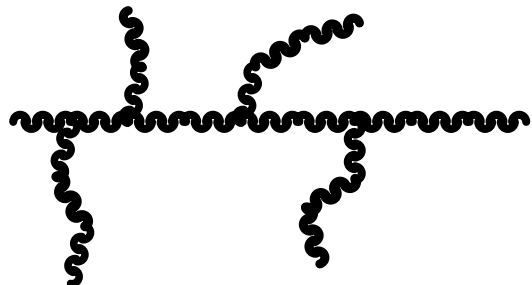
polymer science include liquid-crystalline polymers, such as polyesters (with high aromatic content), and high performance fibers such as Kevlar.³ Although a well-developed field of study, polymer science continues to be an important and highly active area of research.

3. Classification of Polymers

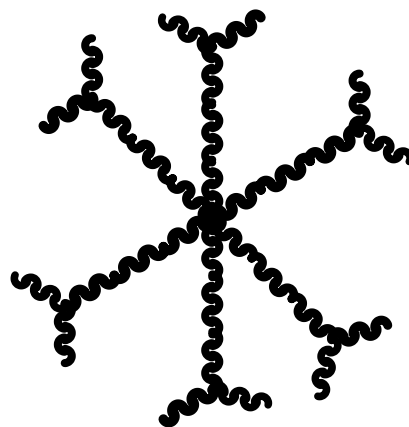
There are many ways to classify polymeric materials. These include classification by polymer architecture, monomer composition, and polymerization mechanism.⁸ Different classification schemes can aid in understanding the relationship between structure and property in polymeric materials. For example, the three dimensional architecture of a polymer can greatly impact its properties. Several polymer architectures are shown in figure 1-3.^{8,9} The simplest polymer architecture is a linear chain. Polymers with side chains of significant length attached to the main linear chain are termed branched polymers. Introduction of branches into a polymer can have a great effect on the thermal properties such as melting points and glass transition temperatures. Network polymers consist of many chains connected to each other.^{8,9} These connections are called cross-links. Unlike many linear and branched polymers, cross-linked polymers are insoluble materials. The number and density of the cross-links can impact a polymer's mechanical properties. For example, low cross-link density in natural rubber yields an elastomer but high cross-link density gives rigid, non-elastomeric materials. Two more recently discovered polymer architectures are dendrimer and star polymers.⁸ Both architectures involve chains of polymer attached to a core. In a dendrimer, the chains



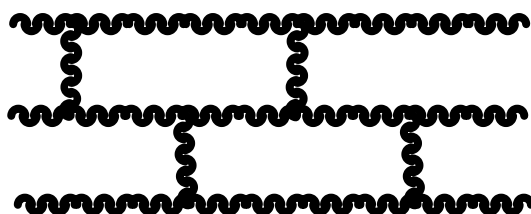
Linear



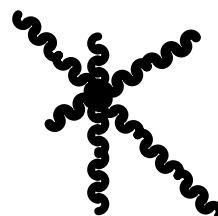
Branched



Dendrimer



Network



Star

Figure 1-3: Polymer Architectures

are of equal length. Dendrimers have a high degree of symmetry and controlled branching. Star polymers have chains of many different lengths and are not symmetrical.⁸ Dendrimers also have lower solution viscosities than an equal molecular weight linear polymer due to the shape of the dendrimer because the linear polymer has a larger hydrodynamic radius and can undergo entanglement.⁸

Polymer properties also depend on the chemical identity of the monomers that compose them. Figure 1-4 shows some of the common monomer compositions of polymers. The simplest composition contains a single monomer and these polymers are called homopolymers. Co-polymers have two or more monomer moieties. Random co-polymers have randomly distributed monomer residues. If the monomer residues are alternating then the polymer is an alternating co-polymer. Polymers that have a chain of one monomer residue followed by a chain of another residue are called block co-polymers. If the chain(s) of the second monomer is not attached to the end of the first monomer chain, but along the chain, then the polymer is a graft co-polymer. Obviously, the polymer properties can change greatly depending on the composition. Block copolymers, for example, can form micelles and can also compatibilize the blending of two different homopolymers. In contrast, random or alternating co-polymers do not form micelles.^{8,9}

A third way to classify polymers is by the polymerization mechanism.⁸ The three main mechanisms are (1) condensation or step-growth polymerization, (2) addition or chain-growth polymerization and (3) ring-opening polymerization. Formation of poly(ethylene terephthalate) from ethylene glycol and terephthalic acid shown in scheme

AAAAAAAAAAAAAAAAAAAAA

Homopolymer

AAAAAAAAAABBBBBBBB

Block Co-Polymer

ABBABBBBAABAABAAABBABA

Random Co-Polymer

B
B
B
B
AAAAAAAAAAAAAAAAAAAAA
B **B**
B **B**
B **B**
B **B**
B **B**

ABABABABABABABABABABA

Alternating Co-Polymer

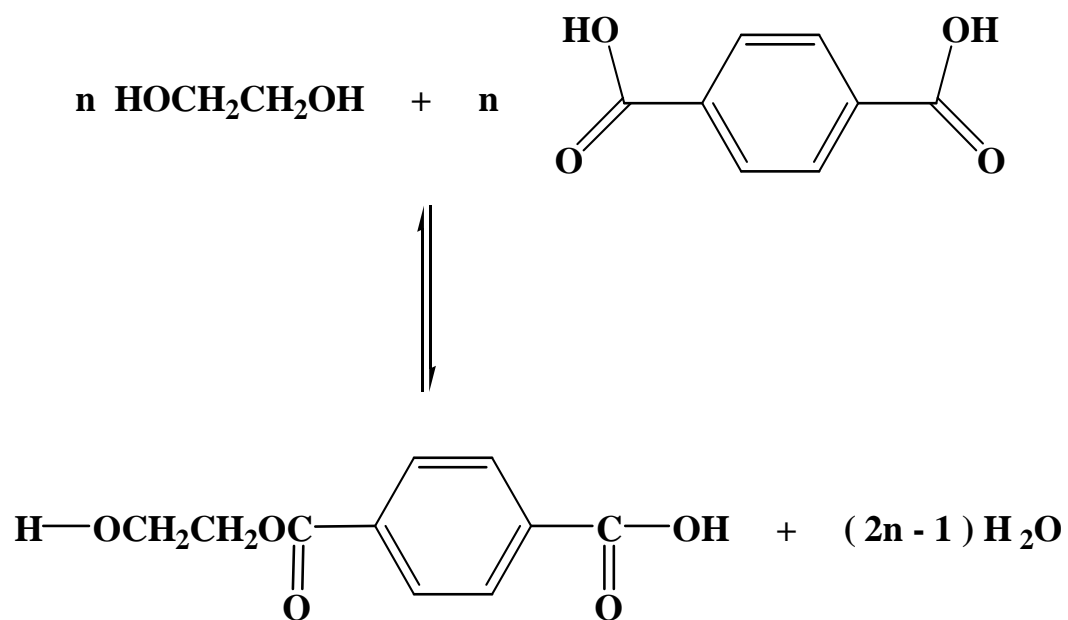
Graft Co-Polymer

Figure 1-4: Classification of Polymers by Monomer Residue Composition

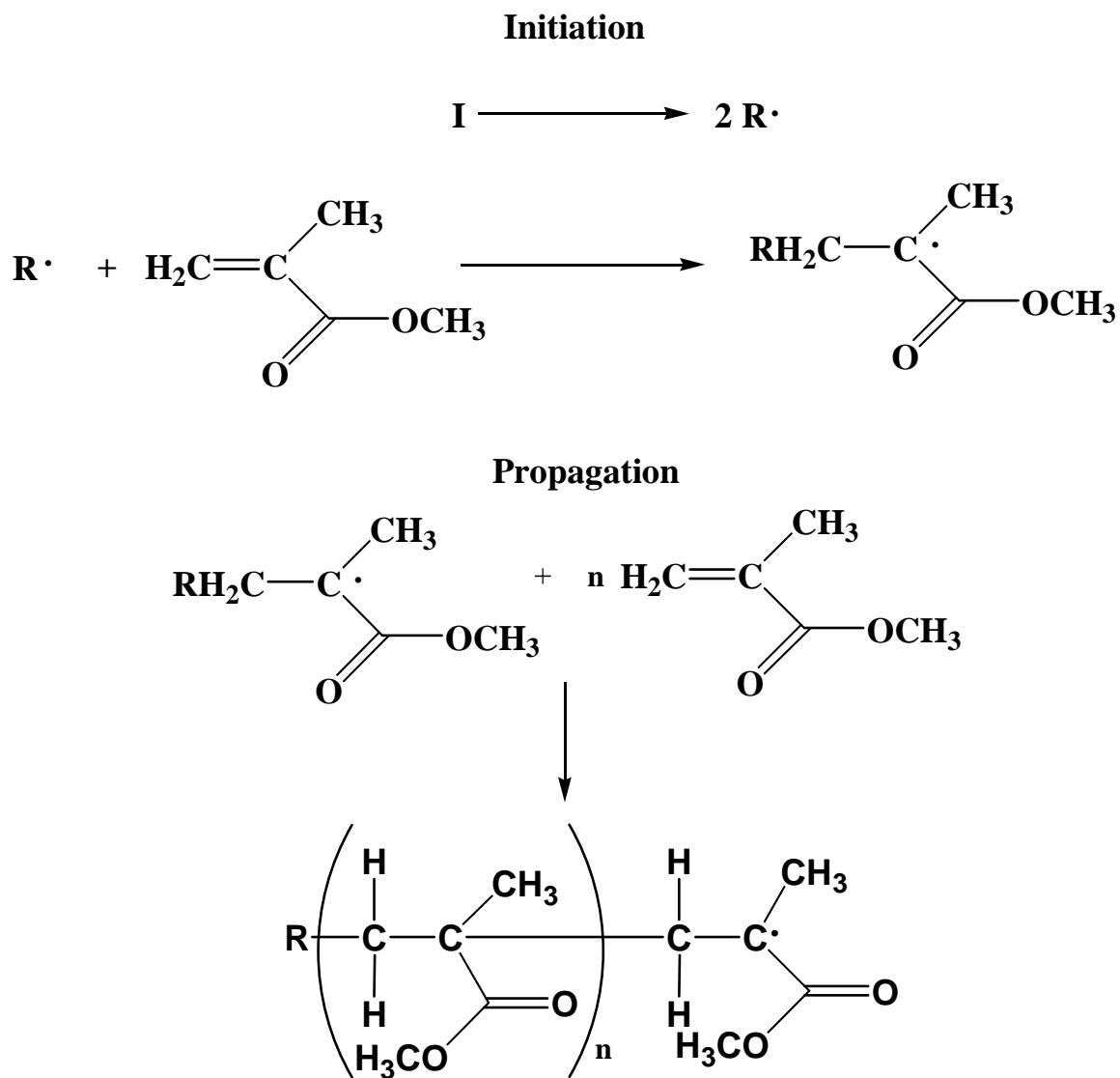
1-1 is an example of a step-growth polymerization.⁸ In step-growth polymerizations, two functional groups at growing chain ends condense to form a covalent linkage and propagate to form the polymer. Near the beginning of the polymerization, many short chains of varying lengths (dimers, trimers, etc.) are quickly formed. All chain ends can react with their complementary functional group and propagate over the whole time of reaction. This means that the average degree of polymerization also increases with reaction time.^{8,9}

In contrast, chain-growth polymerization involves an initiated, active chain end that adds monomer at the active site. An example is the free radical synthesis of poly(methyl methacrylate) (scheme 1-2). In chain-growth polymerization high molecular weight chains are formed very quickly and chain termination occurs. Thus, longer reaction times may yield more polymer chains but decrease the overall degree of polymerization. Also, an initiator such as 2,2'-azo-bis-isobutyronitrile (AIBN) is necessary to begin the polymerization.^{8,9}

A third mechanism is ring opening polymerization. In this type of polymerization, an initiated monomer can react with the cyclic monomers to open the ring and regenerate an active chain end that can continue chain propagation. The chain propagation mechanism of ring opening polymerization is similar to chain-growth polymerization but the polymers produced are often condensation polymers. An example of this is the synthesis of Nylon 6. This polymer can be obtained by condensation polymerization of hexamethylene diamine and adipic acid or by ring opening polymerization of ϵ -caprolactam.^{8,9}



Scheme 1-1: Condensation Polymerization of Ethylene Glycol and Terephthalic Acid



Scheme 1-2: Chain Growth Synthesis of Poly(methyl methacrylate)

B. Polyphosphazenes

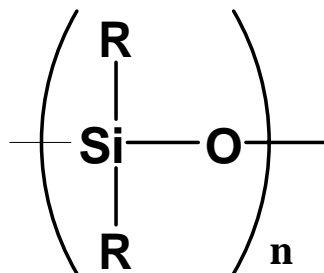
1. Introduction

Thus far, the discussion has dealt mainly with organic backbone polymers such as poly(propylene) and Nylon 6. Inorganic backbone polymers are materials with atoms other than carbon, oxygen or nitrogen in the main polymer chain. Two important examples of polymers with inorganic backbones are polysiloxanes and polyphosphazenes (figure 1-5).⁸ Polysiloxanes consist of a silicon-oxygen backbone with two organic side groups attached to each silicon atom. The most important example is poly(dimethylsiloxane). Polysiloxanes have undergone significant commercialization and are used as elastomers, sealants and biomedical materials.⁸

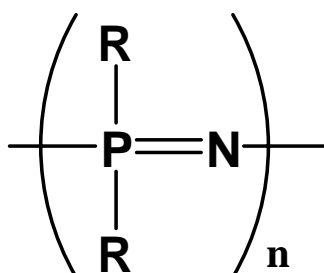
Polyphosphazenes are polymers that have a backbone of alternating nitrogen and phosphorus atoms. Each phosphorus atom has two side groups covalently attached. Poly(dichlorophosphazene) is the key intermediate in polyphosphazene chemistry. Most of the known polyphosphazenes have been synthesized through macromolecular substitution of the labile chlorine atoms of poly(dichlorophosphazene).¹⁰ Polysiloxanes have been developed and commercialized since the 1950's. Polyphosphazenes are newer polymers and are still in the research and development phase.

2. History of Polyphosphazenes

In the 1890's, H. N. Stokes carried out a series of experiments that identified several cyclic homologues of hexachlorocyclotriphosphazene.¹¹⁻¹³ These experiments also yielded an elastomeric material later called "inorganic rubber". However, "inorganic



Polysiloxane



Polyphosphazene

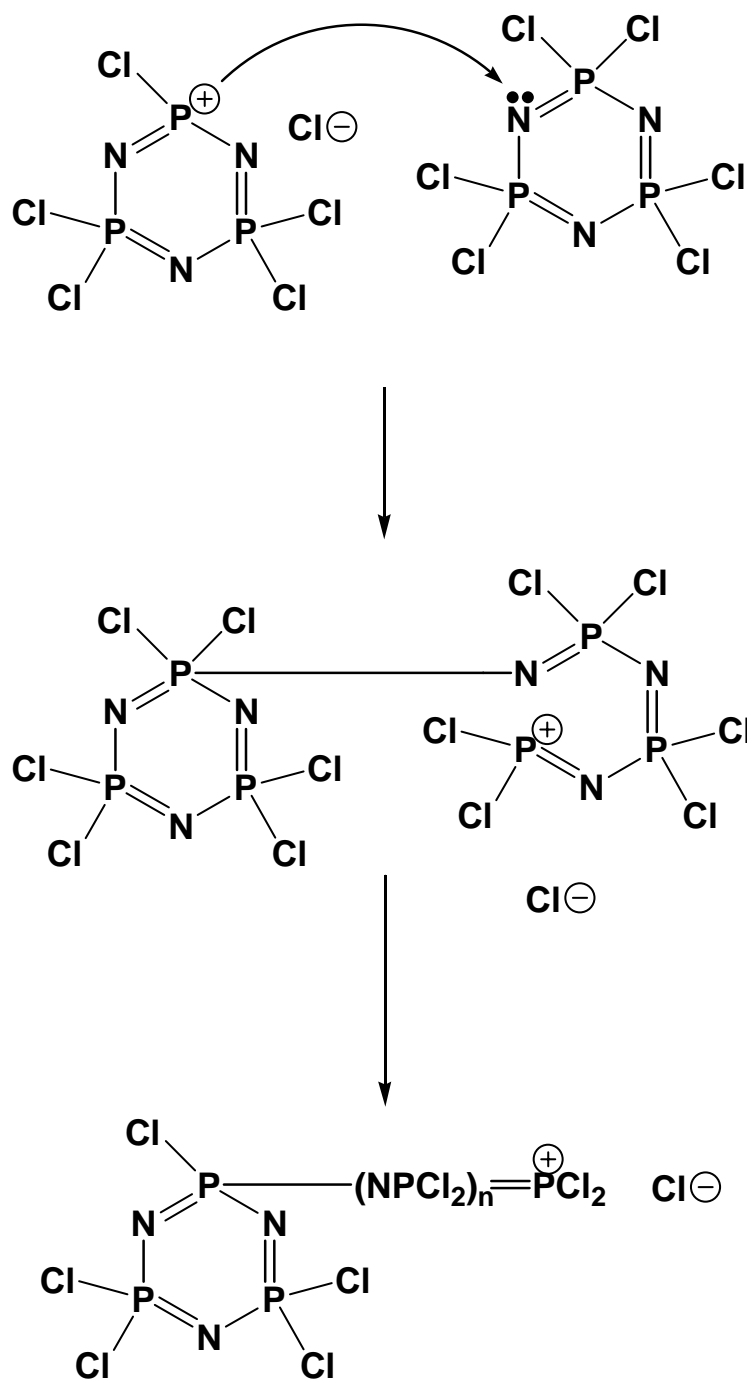
Figure 1-5: Inorganic Backbone Polymers

rubber” was not a very useful material. The polymer was readily hydrolyzed to ammonia, phosphate and hydrochloric acid in the presence of atmospheric moisture and

was insoluble in all known solvents. It took about 70 years before the key discovery was made that uncrosslinked “inorganic rubber” could undergo macromolecular substitution reactions to yield hydrolytically stable high polymers. In the 1960’s, Allcock, Kugel, and Valan demonstrated that in suitable solvents this uncrosslinked polymeric material could react with organic nucleophiles to yield hydrolytically stable polymers.¹⁴⁻¹⁶ Since that time, hundreds of polyphosphazenes have been synthesized, studied from a fundamental viewpoint and developed for a wide variety of applications.¹⁰

3. Synthesis of Linear Polyphosphazenes

As stated above, the initial synthetic challenge for polyphosphazene chemistry involved the synthesis of an uncrosslinked, soluble poly(dichlorophosphazene).¹⁴⁻¹⁶ Synthesis of poly(dichlorophosphazene) can be accomplished by ring opening polymerization or condensation polymerization.¹⁰ The classical method is the thermal ring opening polymerization of hexachlorocyclotriphosphazene. The most widely accepted polymerization mechanism is shown in scheme 1-3.¹⁷ The initial step involves ionization of the phosphorus chlorine bond followed by attack of the nitrogen lone pair electrons of an adjacent hexachlorocyclotriphosphazene molecule on the electropositive phosphorus atom. This continues until a high polymer is formed.¹⁷ It should also be noted that ring expansion could also be a contributor to the polymerization mechanism.¹⁰ Ring-opening polymerizations can be carried out in the bulk in an evacuated sealed glass tube at 250 °C or with a Lewis acid catalyst such as BF_3 .¹⁸



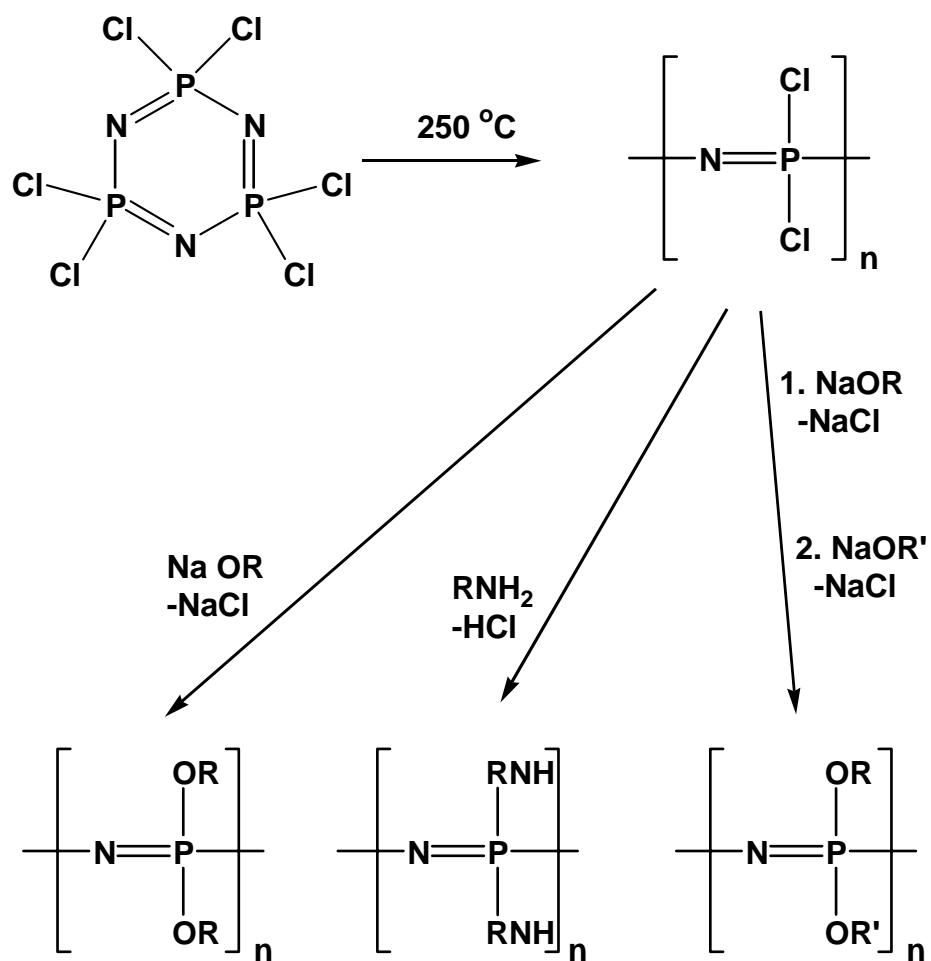
Scheme 1-3: Proposed Phosphazene Polymerization Mechanism

Condensation methods for obtaining polyphosphazenes are varied. These methods include condensation of phosphorus pentachloride with ammonium chloride,¹⁹⁻²² condensation polymerization of the phosphoranimine $\text{Cl}_3\text{P}=\text{NP}(\text{O})\text{Cl}_2$,²³⁻²⁵ and the living cationic condensation polymerization of $\text{Me}_3\text{SiN}=\text{PCl}_3$.^{26,27}

Most conventional organic polymer systems involve polymerization of monomer to polymer without a reactive intermediate. Thus, if changes in polymer properties are desired, changes must be made to the monomers and new polymerizable monomers employed. The versatility of polyphosphazene chemistry that sets it apart from most other polymer syntheses is the utilization of a reactive polymeric intermediate. Although the intermediate is hydrolytically unstable it can be reacted in solution with many different organic nucleophiles to yield hundreds of polymers with different property combinations (scheme 1-4).¹⁰ Some advantages of macromolecular substitution include: 1) the synthesis of polymers that are not accessible through direct polymerization, 2) a wide range of polymers and properties obtainable without new monomer synthesis, 3) facile mixed-substituent polymer preparation, 4) the utilization of small molecule analogues to model macromolecular reactions, and 5) the incorporation of reactive side groups for secondary modification.¹⁰

4. Structure-Property Relationships

The properties of polyphosphazenes depend on both the backbone of the polymer and on the side groups attached to the phosphorus atoms. The backbone of alternating phosphorus and nitrogen atoms has a unique chemical bonding structure that is



Scheme 1-4: Synthesis of Poly(organophosphazenes)

responsible for properties such as flexibility, thermo-oxidative stability, and high refractive indices.¹⁰

The polyphosphazene backbone has very little resistance to torsional motion. The barrier to torsion is lower than 1 kcal/bond/repeat unit and glass transition temperatures (T_g s) can be less than -100 °C for some polyphosphazenes.¹⁰ Although the electronic bonding structure of polyphosphazenes is not universally agreed upon, a reason for this high flexibility can be related to the electronic structure of the chemical bonds. Three possibilities for the electronic structure are: 1) d_{π} - p_{π} bonding interactions between the nitrogen p orbital and the phosphorus 3d orbitals, 2) zwitterionic arrangements of alternating positive and negative charges on the phosphorus and nitrogen atoms, respectively, and 3) a polarized sigma bond framework with backbonding from nitrogen to a sigma anti-bonding orbital on the phosphorus.¹⁰ The d_{π} - p_{π} bonding structure of polyphosphazenes is the most accepted structure. In this proposed bonding structure, the nitrogen p orbital always overlaps a diffuse, 3d phosphorus orbital irrespective of bond torsion. Also, electron delocalization is disrupted by a node at each phosphorus (the polyphosphazene backbone is not electronically conductive).¹⁰

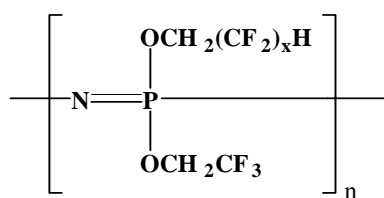
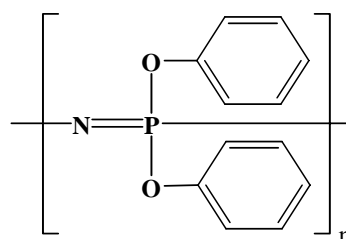
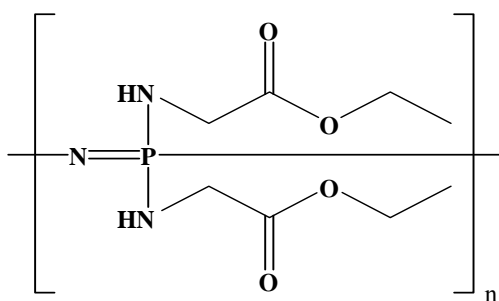
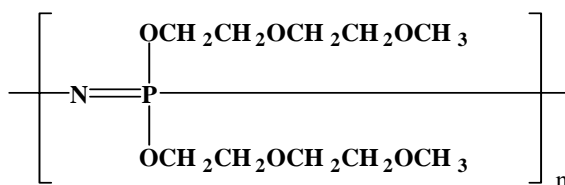
The polyphosphazene backbone bond angles are also important when considering backbone flexibility since side group interactions can create barriers to torsion. The skeletal bond angles are wider in polyphosphazenes than in most organic polymers. In addition, side groups are only present on the phosphorus atoms and not on each atom of the backbone. Thus, the polyphosphazene platform can give some of the lowest T_g materials known.¹⁰

Unlike most organic polymers, many polyphosphazenes are stable at high temperatures and do not decompose or fragment when exposed to ultraviolet, X-ray or gamma-ray radiation. The thermo-oxidative stability of the polyphosphazene backbone is attributed to resistance to homolytic cleavage of the phosphorus-nitrogen bond. In addition, high bond energy is associated with the phosphorus- nitrogen bond. Polyphosphazenes are also resistant to free radical decomposition processes.¹⁰

The high refractive index associated with the polyphosphazene system is due to the relatively high electron density of the polyphosphazene backbone. The polyphosphazene backbone has 45 electrons per repeat unit compared to 24 for a polyalkane.¹⁰ The estimated molar refractivity of 14.36 cm³/mol is significantly greater than that of many linear organic polymers.²⁸

The properties of polyphosphazenes can also be manipulated through the side groups attached to the phosphorus atoms (figure 1-6). For example, polymers with two different fluoroalkoxy groups are low-temperature, hydrophobic elastomers. Poly[bis(phenoxy)phosphazene] is hydrophobic and forms excellent films and fibers. Polyphosphazenes with amino acid side groups are excellent for bioerodible materials and polymers with oligoethyleneoxy side groups are water soluble, and suitable for use as solid polyelectrolytes.¹⁰

The polyphosphazene platform is well suitable for a wide variety of applications. The ability to tailor the side groups opens up a vast range of property-tunable materials. Optimization of material properties can often be accomplished by incorporation of different side groups or by varying side group ratios in mixed substituent systems. Several potential applications include tissue engineering, drug delivery systems, low

**Hydrophobic elastomers****Hydrophobic; fire resistant****Biodegradable****Water soluble; polymer electrolyte
"MEEP"****Figure 1-6: Representative Polyphosphazenes**

temperature elastomers,²⁹ fire resistant materials,²⁹ ion conductive polymers,^{30,31} gas transport membranes, and non-linear optical materials.¹⁰ In this thesis, the two applications that will be examined are low temperature elastomer materials and ion conductive materials.

C. Elastomers

1. General Introduction

An elastomer is a polymeric material that returns substantially to its original dimensions following the release of an applied stress that causes deformation of the material.¹ As an elastomer is deformed, the polymer chains are forced into a chain extended conformation. When the deformation force is removed, the polymer chains return to an entropically favored arrangement in which the chains are contracted.

In the 1800s the discovery of vulcanization of natural rubber had a profound impact on the properties of the material. The cross-linking imparted strength and resilience to the natural rubber making it a useful material.^{32,33} In the early 1900s many synthetic rubbers, such as poly(2,3-dimethylbutadiene) (“methyl rubber”) and poly(1,4-butadiene) began to be developed.³³ Later in the century, Bayer began production of styrene butadiene rubber (SBR) and butadiene acrylonitrile rubber (NBR). These were different from previous synthetic elastomers in that two monomers were mixed prior to polymerization.³³ Other developments in synthetic rubber synthesis include the stereoregular polymerization catalysts developed by Ziegler and Natta,⁴ silicone rubber⁴ and thermoplastic elastomers.⁶

Although rubber and elastomer are often used interchangeably, it should be noted that elastomers are usually cross-linked materials.² Cross-linking improves mechanical properties and converts rubbery polymers to a more useable form. Often the rubbers are fabricated into desired shapes and are then cross-linked and compounded with suitable materials.¹

2. Polyphosphazene Elastomers

“Inorganic rubber” was the term used for cross-linked poly(dichlorophosphazene) because of the elastomeric properties of the polymer. Many poly(organophosphazenes) also possess elastomeric properties. Two of the more important polyphosphazene elastomers will be discussed here.¹⁰

Mixed substituent polyphosphazenes with phenoxy and para-ethyl phenoxy side groups are important as materials for fire resistant elastomer applications (figure 1-7). The base polymers are self-extinguishing in air and have limiting oxygen index (LOI) values of 28 (any value over 20 indicates resistance to combustion in air). In addition, compounding the materials can raise the LOI to over 40. These polymers also yield fewer toxic combustion products than many fire resistant materials and do not have halogens incorporated into the materials. This type of material was commercialized by Ethyl Corporation under the name Eypel-A.²⁹

Mixed-substituent polyphosphazenes with fluoroalkoxy side groups (figure 1-7) are important as low temperature elastomers for aerospace and petrochemical applications, such as hydraulic seals and O-rings. The base polymers are soft gum rubbers. Incorporation of a small amount of unsaturated cross-linkable side group allows

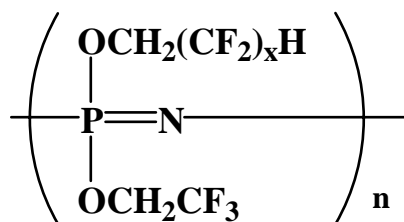
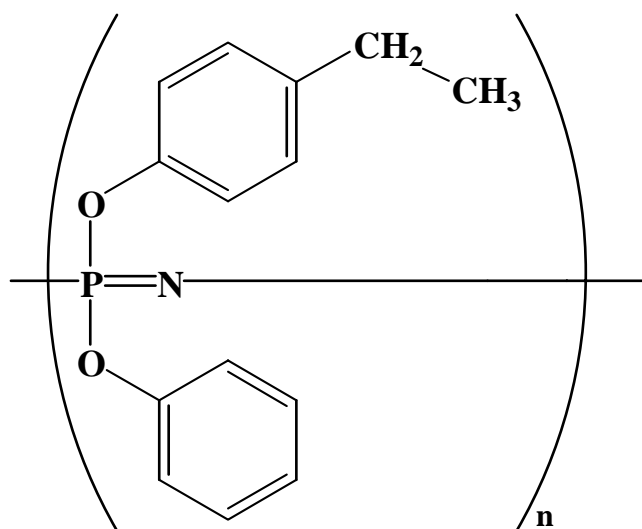


Figure 1-7: Polyphosphazene Elastomers

for cross-linking. Compounding of the polymers to commercial materials involves the use of several materials, such as metal oxides, carbon blacks and silicas. Mixed substituent fluoroalkoxy polyphosphazenes also have excellent resistance to fuels, oils and hydraulic fluids. This type of polyphosphazene material was developed commercially by Firestone as PNF and by Ethyl Corporation as Eypel-F.²⁹

D. Secondary Lithium Ion Batteries

1. The Lithium Ion Battery

Industrialized societies have created an ever-growing demand for portable, lightweight power sources. One area of intense research that seeks to meet these demands is secondary (rechargeable) lithium ion battery systems.³⁴ Lithium ion batteries can achieve high power densities because lithium metal has a high standard potential and is lightweight. Figure 1-8 shows a comparison of the range of power densities available for several rechargeable energy systems in terms of both weight and volume.³⁵ Secondary lithium ion batteries show greater potential for development and use than the other systems shown.³⁶

A simple secondary lithium ion battery consists of a lithium metal anode, an electrolyte and an intercalation cathode (figure 1-9). Oxidation of a lithium atom at the anode yields a lithium cation and an electron. Transport of the lithium ion to the cathode takes place through an electrolyte layer. The electrolyte must have high ionic conductivity in order to efficiently transport the ions. The cathode reversibly intercalates

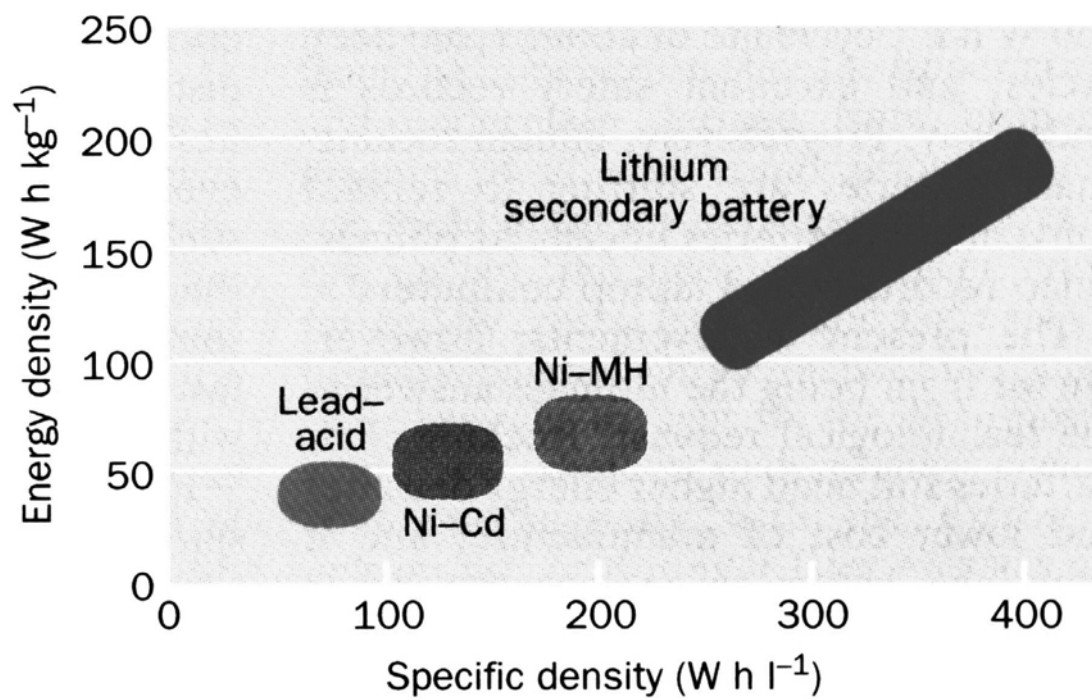


Figure 1-8: Power Density Comparison of Various Battery Systems

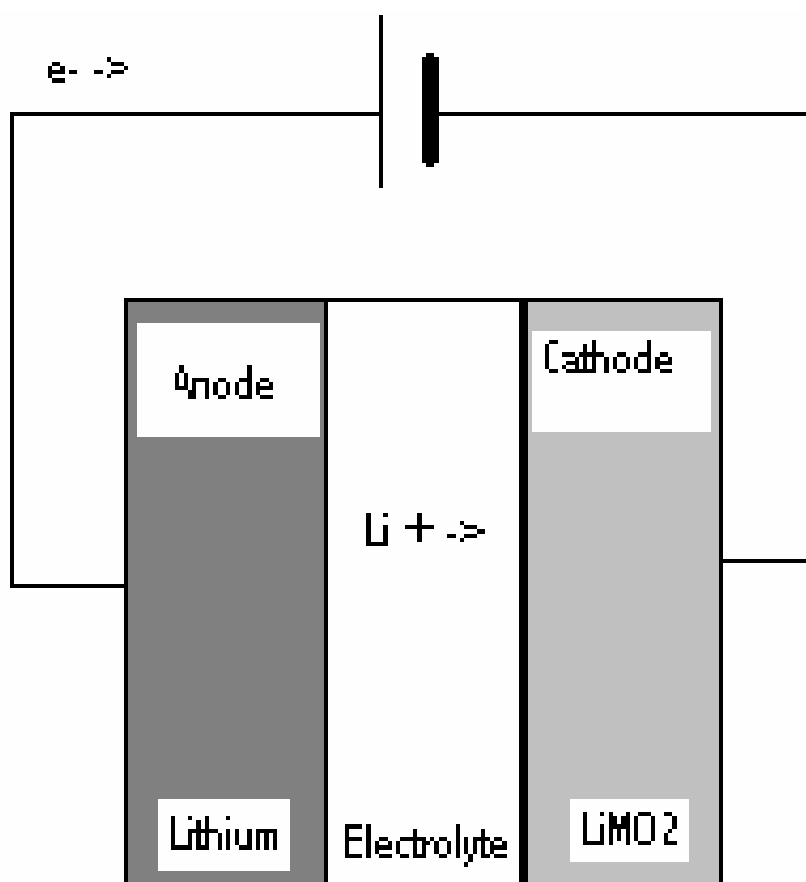


Figure 1-9: Simple Schematic of a Secondary Lithium Ion Battery

the lithium ion and reduction occurs.³⁴ Chapter 5 of this thesis focuses on the synthesis and conductivity behavior of polymer electrolytes.

2. Liquid Electrolytes

A solution of lithium salt in a polar, aprotic solvent is one of the two common electrolyte systems under development in secondary lithium ion batteries. Considerations affecting solvent choice include solubility of the lithium salts in the solvent, stability of the solvent towards the electrodes, and toxicity of the solvent.³⁴ Flammable solvents such as ethylene carbonate and dimethyl carbonate are usually used for commercial systems. Some commonly used lithium salts include LiClO_4 and LiPF_6 . Recently, salts such as $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ and $\text{LiC}(\text{SO}_2\text{CF}_3)_3$ have been developed.³⁴ These new salts have better stability and conductivity than previous generation lithium salts. In the work in this thesis, a derivative of the $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ salt is covalently linked to a polymer electrolyte and tested for ionic conductivity.

3. Solid Polymer Electrolytes

Polymer electrolytes are also being developed for rechargeable lithium batteries. Use of solid polymer electrolytes offers several advantages over the liquid electrolyte system. Some of these advantages are: 1) electrode separation without use of an inert, porous component, 2) less corrosiveness, 3) less toxicity, 4) low flammability, 5) easy device fabrication, and 6) no vapor pressure (i.e. easy packaging).³⁴ The classical example of a polymer electrolyte is poly(ethylene oxide) (figure 1-10). This polymer acts as a high molecular weight solvent in which ionic salts can be dissolved. The ions can

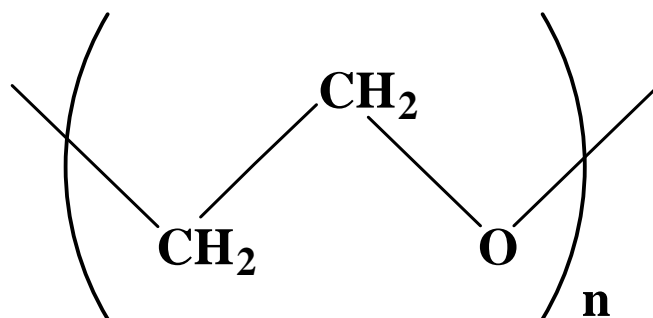


Figure 1-10: Poly(ethylene oxide)

then move about due to segmental motion of the polymer electrolyte and coordination of the ions with the polymer.³⁴

In 1984, Blonsky, Shriver, Austin, and Allcock, published results on the first polymer electrolyte based on the highly flexible polyphosphazene system.³⁰ Poly[bis(2,2-methoxyethoxyethoxy)phosphazene] (MEEP) is a highly flexible, amorphous polymer with a glass transition temperature of -84 °C. In MEEP, lithium ions are transported by coordination to the oxygen lone pair electrons on the ethyleneoxy side groups. In addition, recent studies have shown a limited participation of nitrogen lone pairs of the polyphosphazene backbone in the lithium ion conduction mechanism. Since MEEP first appeared, several new mixed substituent polymers and several different structured oligoethyleneoxy side groups have been synthesized to improve ionic conductivities.³⁰

4. Single Ion Conductors

Several research groups have attempted to improve lithium ion conductivity via single-ion conduction. In this type of polyelectrolyte, either the anion or the cation is chemically bound to the polymer. Two advantages offered by single-ion conduction are that the salt is directly incorporated into the electrolyte (i.e. no mixing of the lithium salt into the polymer is necessary) and electrical polarization is reduced at the cathode.¹⁰

Some single-ion conducting polymers based on the polyphosphazene platform have been synthesized by Shriver and co-workers.³⁷ One of these polymers included the immobilization of a sulfate anion as a sodium ion conductor. Conductivities on the order of 10^{-7} S/cm were obtained for this system.³⁷ A similar polymer bearing oligoethyleneoxy and sulfate functionalized oligoethyleneoxy side groups was

synthesized by Tada and coworkers. However, maximum ambient temperature lithium ion conductivities of only 8×10^{-8} S/cm were obtained.³⁸

E. Research Objectives

There are two main research goals of the work in this thesis. The first is the study of fluoroalkoxy substituted polyphosphazenes as hydrolytically stable intermediates for the synthesis of mixed substituent polyphosphazenes. This is the subject of chapter 2 and 3. Chapter 4 examines structure-property relationships of mixed-substituent poly(fluoroalkoxyphosphazenes) and their potential use as low temperature elastomers.

The second research goal involves the design and synthesis of mixed-substituent polymers with oligoethyleneoxy and sulfonimide functionalized side groups for use as single-ion conductors. This is the main focus of the material in chapter 5. Chapter 6 briefly summarizes the work in this thesis and suggests possible future research directions. Appendix A gives the synthetic details of the sulfonimide functionalized side group and its use in polyphosphazene membranes for proton conducting fuel cells.

F. References

- 1) Fried, J.R. *Polymer Science and Technology*; Prentice Hall: Englewood Cliffs, 1995.
- 2) Young, R.J.; Lovell, P.A. *Introduction to Polymers*, 2nd ed.; Chapman & Hall: New York, 1996.
- 3) Campbell, I.M. *Introduction to Synthetic Polymers*; Oxford University Press: New York, 1994.
- 4) Staudinger, H. *Ber.* **1920**, 53, 1073.
- 5) Mark, H; Whitby, G.S. *Collected Papers of Wallace Hume Carothers on High Polymeric Substances*; Interscience Publishers: New York, 1940.
- 6) Holden, G. *Understanding Thermoplastic Elastomers*; Hanser-Gardner Publications: Cincinnati, 2000.
- 7) Wallace, G.G.; Spinks, G.M.; Teasdale, P.R. *Conductive Electroactive Polymers: Intelligent Materials Systems*; Technomic Publishing Company: Lancaster, 1997.
- 8) Challa, G. *Polymer Chemistry: An Introduction*; Ellis Horwood Limited: New York, 1993.
- 9) Allcock, H.R.; Lampe, F.W. *Contemporary Polymer Chemistry*, 2nd ed.; Prentice Hall: Englewood Cliffs, 1990.
- 10) Allcock, H.R. *Chemistry and Applications of Polyphosphazenes*; John Wiley & Sons: Hoboken, 2003.
- 11) Stokes, H.N. *Am. Chem. J.* **1895**, 17, 275.
- 12) Stokes, H.N. *Am. Chem. J.* **1896**, 18, 629.

- 13) Stokes, H.N. *Am. Chem. J.* **1897**, *19*, 782.
- 14) Allcock, H.R.; Kugel, R.L. *J. Am. Chem. Soc.* **1965**, *87*, 4216-4217.
- 15) Allcock, H.R.; Kugel, R.L.; Valan, K.J. *Inorg. Chem.* **1966**, *5*, 1709-1715.
- 16) Allcock, H.R.; Kugel, R.L. *Inorg. Chem.* **1966**, *5*, 1716-1718.
- 17) Allcock, H.R.; Best, R.J. *Can. J. Chem.* **1964**, *42*, 447-455.
- 18) Kolich, C.H.; Meltsner, B.R.; Braxton, H.G. *US Patent* 2,006,324, 1991.
- 19) Allen, G.; Lewis, C.J.; Todd, S.M. *Polym.* **1970**, *11*, 31-43.
- 20) *Japanese Patents* 80/56,130, 1980; 80/60,528, 1980.
- 21) Li, H.M. *US Patents* 4,374,815, 1983; 4,447,408, 1984; 4,551,317, 1985.
- 22) Pettigrew, F.A.; Li, H.M.; Lum, G.S. *US Patents* 4,522,797, 1983; 4,522,798, 1983.
- 23) D'Halluin, G.; De Jaeger, R.; Chambrette, J.P.; Potic, P. *Macromol.* **1992**, *25*, 1254.
- 24) De Jaeger, R.; Potin, P. *Phosphorus, Sulfur, Silicon, Relat. Elem.* **1993**, *76*, 483.
- 25) Potin, P.; De Jaeger, R. *Phosphorus, Sulfur, Silicon, Relat. Elem.* **1993**, *76*, 487.
- 26) Honeyman, C.H.; Manners, I.; Morrissey, C.T.; Allcock, H.R. *J. Am. Chem. Soc.* **1995**, *117*, 7035-7036.
- 27) Allcock, H.R.; Crane, C.A.; Morrissey, C.T.; Nelson, J.M.; Reeves, S.D.; Honeyman, C.H.; Manners, I. *Macromol.* **1996**, *29*, 7740-7747.
- 28) Olshavsky, M.; Allcock, H.R. *Macromol.* **1997**, *30*, 4179-4183.
- 29) Lohr, D.F.; Penton, H.R. In *Handbook of Elastomers*, 2nd ed.; Bhowmick, A.K.; Stephens, H.L., Ed.; Marcel Dekker: New York, 2001; Chapter 21.

- 30) Blonsky, P.M.; Shriver, D.F.; Austin, P.; Allcock, H.R. *J. Am. Chem. Soc.* **1984**, *106*, 6854-6855.
- 31) Hofmann, M.A.; Ambler, C.M.; Maher, A.E.; Chalkova, E.; Zhou, X.Y.; Lvov, S.N.; Allcock, H.R. *Macromol.* **2002**, *35*, 6490-6493.
- 32) *Science and Technology of Rubber*, 2nd ed.; Mark, J.E.; Erman, B.; Elrich, F.R., Ed.; Academic Press: New York, 2001.
- 33) Blackley, D.C. *Synthetic Rubbers: Their Chemistry and Technology*; Applied Science Publishers: New York, 1983.
- 34) Vincent, C.; Scrosati, B. *Modern Batteries: An Introduction to Electrochemical Power Sources*, 2nd ed.; John Wiley and Sons: New York, 1997.
- 35) Scrosati, B. *Nature*, **1995**, *373*, 557.
- 36) Tarascon, J.M.; Armand, M. *Nature* **2001**, *414*, 359-367.
- 37) Shriver, D.F.; Siska, D.P. *Chem. Mater.* **2001**, *13*, 4698-4700.
- 38) Tada, Y.; Sato, M.; Takeno, N.; Nakacho, Y.; Shigehara, K. *Chem. Mater.* **1994**, *6*, 27-30.

Chapter 2

Side Group Exchange in Poly(organophosphazenes) with Fluoroalkoxy Substituents, Part 1: Alkoxide Nucleophiles

A. Introduction

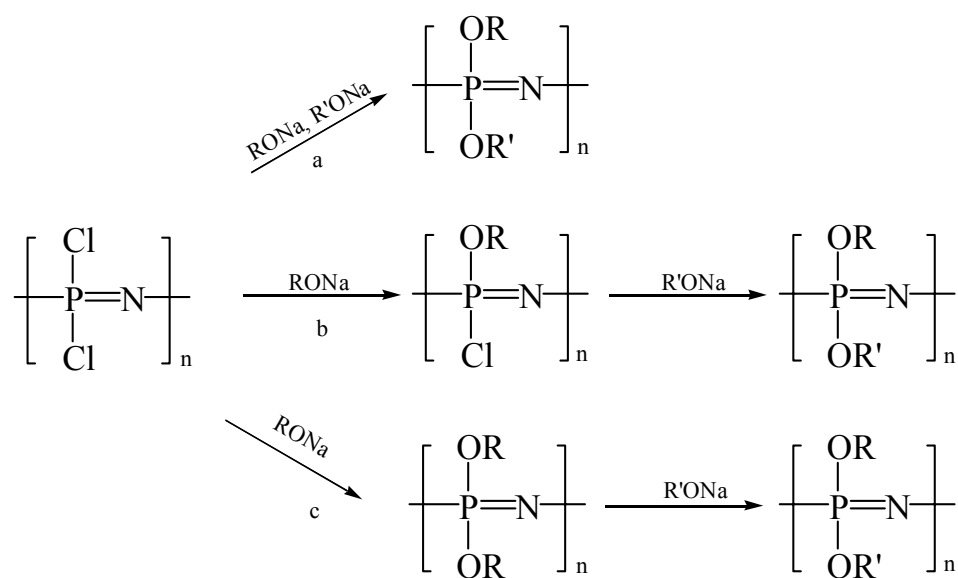
Polyphosphazenes are inorganic backbone polymers that have a skeleton of alternating phosphorus and nitrogen atoms.¹ Two organic or organometallic side groups are linked to each phosphorus atom. They are of interest as biomedical materials,^{2,3} fire-retardants,^{4,5} low temperature elastomers,⁶ and are under development as fuel cell membranes⁷ and solid polymer lithium ion conductors.⁸ A distinctive feature of polyphosphazenes is the ease with which polymer properties can be tuned through changes in the side groups linked to the phosphorus atoms.^{9,10}

Several methods have been developed previously for the synthesis of poly(organophosphazenes). The most widely explored method is based on the ring-opening polymerization of hexachlorocyclotriphosphazene, $(\text{NPCl}_2)_3$, to poly(dichlorophosphazene), $(\text{NPCl}_2)_n$ (**1**), followed by the replacement of the labile chlorine atoms in this macromolecular intermediate by organic groups – typically alkoxy, aryloxy, or amino groups.^{1,11,12} A second category of synthetic process involves the preparation of **1** by condensation methods, such as, the thermal condensation reaction of $\text{OPCl}_2\text{--N=PCl}_3$ ^{13,14} and the living cationic polymerization of $\text{Me}_3\text{Si--N=PCl}_3$.^{15,16} These various approaches provide access to several hundred different polymer systems, each with specific and often unique chemical and physical property combinations. In addition,

several methods exist for the modification of these polymers by secondary reactions such as sulfonation,¹⁷ lithiation,¹⁸ hydrolysis,¹⁹ etc.

An alternative method for structural modification involves the replacement of one organic side group linked to a phosphazene chain by another.²⁰ This is a secondary reaction that offers the prospect that single-substituent poly(organophosphazenes) can be converted readily to mixed-substituent species, especially for the preparation of mixed-substituent elastomers which are of broad technological interest. It also raises the possibility that an organophosphazene polymer that is stable for long periods of time in the atmosphere might be employed as a general macromolecular intermediate for the preparation of other poly(organophosphazenes). For some situations this would be an improvement over the use of **1** for this purpose because the chloro-derivative is sensitive to moisture, must be stored under carefully controlled conditions, and can be used as a macromolecular intermediate only in a limited number of organic solvents.⁵

Co-substituted poly(organophosphazenes) have traditionally been prepared through the sequential or simultaneous reaction of two or more nucleophiles with $(\text{NPCl}_2)_n$ (scheme 2-1 (a) and (b)). Alternatively, displacement of organic side groups on poly(organophosphazenes) by various nucleophiles would be an effective route to the same types of polymers (scheme 2-1 (c)).²⁰ Allcock, Kugel and Walsh reported a series of side group exchange reactions between cyclic small molecule model organophosphazenes and organic nucleophiles.²¹ Another study examined the exchange reactions of cyclophosphazene trimers that have phenoxy, chlorophenoxy, or nitrophenoxy side groups.²² Although side group displacement was induced in these small molecule systems by nucleophiles such as 2,2,2-trifluoroethoxide, some side



Scheme 2-1. Synthesis of Co-substituted Poly(organophosphazenes)

a) Simultaneous addition of nucleophiles

b) Sequential addition of nucleophiles

c) Macromolecular substitution of poly(organophosphazene)

reactions also occurred. For example, α -carbon attack on the aryl group in the nitro-substituted rings has been detected, and ring degradation occurs in some cases.²² In other work, *o*-nitrophenoxy groups were displaced from high polymeric poly[bis(*o*-nitrophenoxyphosphazene)] by sodium trifluoroethoxide. Although some side-group displacement was detected, polymer degradation occurred again through α -carbon attack on the aryl group.²³

Earlier preliminary work has shown that fluorinated alkoxy units²⁴ and phenoxy side groups can be displaced from polyphosphazenes.²⁰ The surface modification of poly[bis(trifluoroethoxy)phosphazene] (**2**) by displacement of trifluoroethoxy groups has also been studied.²⁵ For polyphosphazenes that bear both trifluoroethoxy and phenoxy side groups, replacement of phenoxy side groups by 2,2,2-trifluoroethoxide occurs only on non-geminally substituted phosphorus atoms. The reverse reaction, exchange of the trifluoroethoxy group by phenoxide ions, was not detected.²⁰

In the present study, co-substituted polyphosphazenes have been synthesized by macromolecular side group exchange reactions between poly[bis(fluoroalkoxy)phosphazenes] and several alkoxide nucleophiles. Stereo-electronic effects were investigated through varying both the reaction conditions and the type of nucleophile for each poly(organophosphazene).

B. Results and Discussion

1. Synthesis of Starting Macromolecules $[\text{NP}(\text{OR})_2]_n$ (2-8)

Poly(dichlorophosphazene) readily undergoes macromolecular replacement of the chlorine atoms to yield poly(organophosphazenes).^{1,9} The course of these reactions can be followed by ^{31}P NMR spectroscopy. Fluoroalkoxy substituted polymers **2-4** (Figure 2-1) were obtained via this route in good yields and at room temperature over 3-10 hours reaction time. However, the preparation of polymers **5** and **8** (Figure 2-1) required slightly elevated temperatures ($\sim 40^\circ\text{C}$) for longer times (~ 18 hrs) to obtain complete substitution. Formation of polymer **6** (Figure 2-1) required heating for 36 hrs. The synthesis of polymer **7** (Figure 2-1) required heating to reflux for 48 hrs. The ease of macromolecular substitution can be affected by alkoxide solubility, but this low reactivity is probably due more to the steric bulk and lower nucleophilicity of the isopropoxide ion than to the low solubility of the nucleophile.

2. Reactions of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ (**2**) with Alkoxide Nucleophiles

Solutions of each of the fluoroalkoxy substituted polymers (**2-4**) in THF were treated with solutions of sodium ethoxide, sodium propoxide, sodium isopropoxide and sodium hexoxide at 25°C and at the solvent reflux temperature (67°C). These reactions were monitored using ^{31}P NMR spectroscopy. Although ^{31}P NMR chemical shifts change with side group replacement, the spectral changes could not be used to obtain quantitative information about the composition of the resultant polymers because of overlap of the phosphorus signals. Similarly, ^{19}F NMR spectra showed peak broadening with side

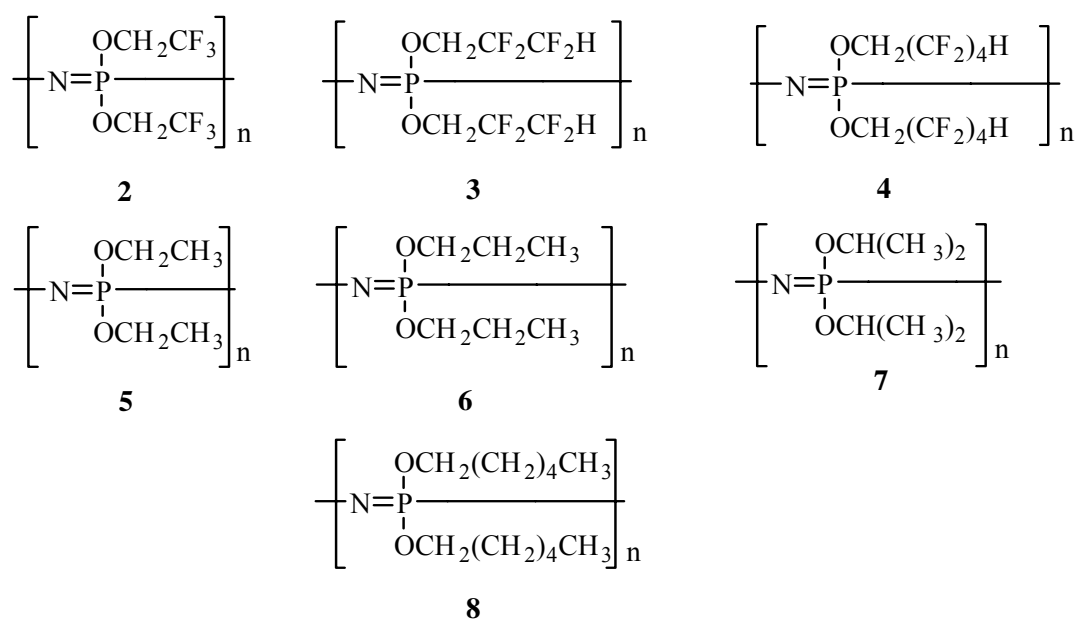


Figure 2-1: Starting Polymers 2-8

group exchange, but these changes yielded little information that would allow monitoring of the side group ratios. However, ^1H NMR spectroscopy was utilized to ascertain the ratio of different side groups by integration of the proton signals from the α -carbon atoms of the alkoxy and fluoroalkoxy side-groups (figure 2-2).²⁶

The results from the reaction of **2** with several different alkoxide nucleophiles at ambient temperature and at reflux are shown in table 2-1. The highest degree of displacement at 25 °C was found for the formation of polymer **9**, where the ethoxide ion displaced 41% of the 2,2,2-trifluoroethoxy side groups. Reactions of polymer **2** with other nucleophiles at 25 °C gave less displacement, probably due to the larger size of the propoxide, isopropoxide, and hexoxide nucleophiles. The same trend was found for reactions at 67 °C, with sodium ethoxide displacing the largest percentage of 2,2,2-trifluoroethoxide groups, followed by sodium hexoxide and then the other alkoxides. The degree of substitution increased 15-20% with the 42 °C increase in reaction temperature. It might be expected, based on steric hindrance considerations, that sodium propoxide would give more substitution than sodium hexoxide at 25 °C and at 67 °C. However, this did not occur, possibly due to the lower solubility of sodium propoxide in THF. The similar side group ratios that were generated in polymers **11** and **13** and in **12** and **14** after reactions of polymer **2** with sodium propoxide and sodium isopropoxide, suggest that the isopropoxide group is not seriously sterically hindered in its attack on the phosphorus atoms of **2**.

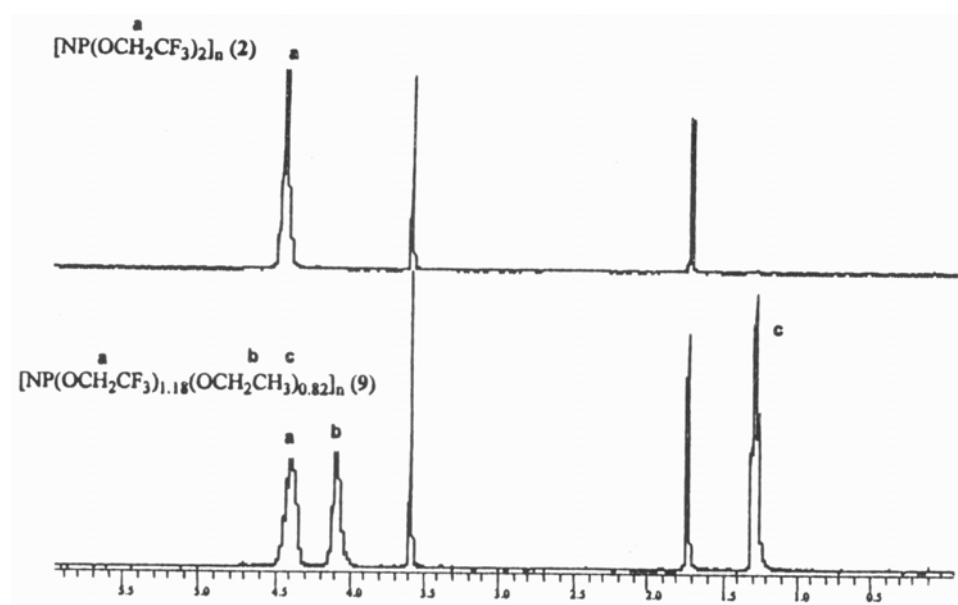


Figure 2-2: ^1H NMR spectra in $\text{d}_8\text{-THF}$

Table 2-1: Composition of Co-substituted Polymers From 2 [NP(OCH₂CF₃)₂]_n

<i>Resultant</i>	<i>Reaction</i>	<i>% Sub.</i>
<i>Polyphosphazene</i>	<i>T (°C)</i>	<i>¹H NMR</i>
[NP(OCH ₂ CF ₃) _{1.18} (OCH ₂ CH ₃) _{0.82}] _n (9)	25	41
[NP(OCH ₂ CF ₃) _{0.82} (OCH ₂ CH ₃) _{1.18}] _n (10)	67	59
[NP(OCH ₂ CF ₃) _{1.48} (OCH ₂ CH ₂ CH ₃) _{0.52}] _n (11)	25	26
[NP(OCH ₂ CF ₃) _{1.34} (OCH ₂ CH ₂ CH ₃) _{0.66}] _n (12)	67	33
[NP(OCH ₂ CF ₃) _{1.52} (OCH(CH ₃) ₂) _{0.48}] _n (13)	25	24
[NP(OCH ₂ CF ₃) _{1.22} (OCH(CH ₃) ₂) _{0.78}] _n (14)	67	39
[NP(OCH ₂ CF ₃) _{1.42} (OCH ₂ (CH ₂) ₄ CH ₃) _{0.58}] _n (15)	25	29
[NP(OCH ₂ CF ₃) _{0.92} (OCH ₂ (CH ₂) ₄ CH ₃) _{1.08}] _n (16)	67	54

3. Reactions of $[\text{NP}(\text{OCH}_2\text{CF}_2\text{CF}_2\text{H})_2]_n$ (**3**) with Alkoxide Nucleophiles

^1H NMR spectroscopy was also used to determine the ratio of side groups present in co-substituted polyphosphazenes **17-24** (table 2-2). The results followed similar trends to those found for polymer **2**, but fewer fluoroalkoxy side groups were displaced from polymer **3**. The highest degree of substitution was 33-36% for reaction with the ethoxide nucleophile at 67 °C (**18**), compared to 59-62% for **2** with the same nucleophile under the same conditions (**10**). Reactions of **3** in THF at 67 °C yielded an increase of only ~5-10% in the extent of substitution for reactions using the same nucleophiles at 25 °C. This is in contrast to increases of ~10-20% for reactions of polymer **2** carried out at 67 °C. The isopropoxide nucleophile displaced marginally fewer (4-5%) 2,2,3,3-tetrafluoropropoxide groups than the primary propoxide nucleophile. This is illustrated by a comparison of polymers **18** and **19** with polymers **20** and **21**. This suggests that (surprisingly) the isopropoxide ion has roughly the same access to the backbone phosphorus atoms of polymer **3** as does the n-propoxide ion.

4. Reactions of $[\text{NP}(\text{OCH}_2(\text{CF}_2)_4\text{H})_2]_n$ (**4**) with Alkoxide Nucleophiles

Similar trends were apparent for reactions of polymer **4** with the same four alkoxides as used with polymers **2** and **3** (table 2-3). Almost all of the co-substituted polymers had ~20% side group exchange after reactions at both 25 °C and at 67 °C. The extent of displacement was ~5-10% less than for **3** and 20-30% less than the reactions of the same nucleophiles with **2**. Very little increase in the degree of displacement was detected with increased temperature for the reactions of **4**, especially with respect to the hexoxide substitutions that gave polymers **31** and **32** as compared to polymers **22** and **23**.

Table 2-2: Composition of Co-substituted Polymers From 3 [NP(OCH₂CF₂CF₂H)₂]_n

<i>Resultant</i> <i>Polyphosphazene</i>	<i>Reaction</i> <i>T (°C)</i>	<i>% Sub.</i> <i>¹H NMR</i>
[NP(OCH ₂ CF ₂ CF ₂ H) _{1.50} (OCH ₂ CH ₃) _{0.50}] _n (17)	25	25
[NP(OCH ₂ CF ₂ CF ₂ H) _{1.34} (OCH ₂ CH ₃) _{0.66}] _n (18)	67	33
[NP(OCH ₂ CF ₂ CF ₂ H) _{1.62} (OCH ₂ CH ₂ CH ₃) _{0.38}] _n (19)	25	19
[NP(OCH ₂ CF ₂ CF ₂ H) _{1.54} (OCH ₂ CH ₂ CH ₃) _{0.46}] _n (20)	67	23
[NP(OCH ₂ CF ₂ CF ₂ H) _{1.72} (OCH(CH ₃) ₂) _{0.28}] _n (21)	25	14
[NP(OCH ₂ CF ₂ CF ₂ H) _{1.62} (OCH(CH ₃) ₂) _{0.38}] _n (22)	67	19
[NP(OCH ₂ CF ₂ CF ₂ H) _{1.60} (OCH ₂ (CH ₂) ₄ CH ₃) _{0.40}] _n (23)	25	20
[NP(OCH ₂ CF ₂ CF ₂ H) _{1.40} (OCH ₂ (CH ₂) ₄ CH ₃) _{0.60}] _n (24)	67	30

Table 2-3: Composition of Co-substituted Polymers From 4**[NP(OCH₂CF₂CF₂CF₂CF₂H)₂]_n**

<i>Resultant</i> <i>Polyphosphazene</i>	<i>Reaction</i> <i>T (°C)</i>	<i>% Sub.</i> <i>¹H NMR</i>
[NP(OCH ₂ (CF ₂) ₄ H) _{1.66} (OCH ₂ CH ₃) _{0.34}] _n (25)	25	17
[NP(OCH ₂ (CF ₂) ₄ H) _{1.54} (OCH ₂ CH ₃) _{0.46}] _n (26)	67	23
[NP(OCH ₂ (CF ₂) ₄ H) _{1.58} (OCH ₂ CH ₂ CH ₃) _{0.42}] _n (27)	25	21
[NP(OCH ₂ (CF ₂) ₄ H) _{1.52} (OCH ₂ CH ₂ CH ₃) _{0.48}] _n (28)	67	24
[NP(OCH ₂ (CF ₂) ₄ H) _{1.66} (OCH(CH ₃) ₂) _{0.34}] _n (29)	25	17
[NP(OCH ₂ (CF ₂) ₄ H) _{1.60} (OCH(CH ₃) ₂) _{0.40}] _n (30)	67	20
[NP(OCH ₂ (CF ₂) ₄ H) _{1.70} (OCH ₂ (CH ₂) ₄ CH ₃) _{0.30}] _n (31)	25	15
[NP(OCH ₂ (CF ₂) ₄ H) _{1.66} (OCH ₂ (CH ₂) ₄ CH ₃) _{0.34}] _n (32)	67	17

The size of the 2,2,3,3,4,4,5,5-octafluoropentoxy side groups provides better shielding of the phosphorus atoms from nucleophilic attack, which leads to a decreased degree of displacement when compared with the displacement of 2,2,2-trifluoroethoxy or 2,2,3,3-tetrafluoropropoxy groups.

5. Reactions of 5-8 with Alkoxide Nucleophiles

No side group exchange was detected when poly[bis(ethoxy)phosphazene] (**5**), poly[bis(propoxy)phosphazene] (**6**), poly[bis(isopropoxy)phosphazene] (**7**), or poly[bis(hexoxy)phosphazene] (**8**) were treated with alkoxide nucleophiles. The non-fluorinated alkoxy groups are less electron withdrawing than the fluoroalkoxy units, and this renders the backbone phosphorus atoms less susceptible to nucleophilic attack than in the case of poly[bis(fluoroalkoxy)phosphazenes]. Thus, the electron withdrawing ability of the initial side group appears to be a key factor that determines if side group displacement can occur. The degree of substitution is also affected by shielding of the backbone phosphorus as seen in the earlier work of Allcock and Kim²⁶ and confirmed by the current work.

6. Characterization of Polymers 2-32

³¹P NMR spectroscopy was used to monitor all the reactions. The side group replacement reactions were allowed to continue for 48 hours, although no change in the phosphorus spectra was detected after 36 hours for most of the polymers studied. The absence of peaks around 0 ppm indicated that no rearrangement of the polyphosphazene to a phosphazane had occurred. However, it is possible that substitution was accompanied

by some chain cleavage because lower molecular weight polymers were detected from GPC plots of the co-substituted polymers.

^{19}F NMR spectra were also obtained for each polymer. Peak-broadening and unresolved splitting were present in each spectrum. No fluorine-fluorine coupling was detected in these polymers because the coupling constants are <1 Hz for vicinal fluoroalkyl species.²⁷

Elemental analysis was used to confirm the composition of the polymers after side group displacement had occurred. The fluorine percentages obtained from this method were significantly lower than those calculated for each polymer. However, the differences between the calculated and found weight percentages for each of the other elements are minimal. It is known that high fluorine content can decrease the accuracy of fluorine elemental analysis.²⁸ Therefore, it is believed that elemental analysis adequately verifies the composition of our materials. Side group ratios based on the nitrogen to fluorine ratios from elemental analysis are included in tables 2-1, 2-2, and 2-3 for comparison.

The molecular weights of the starting polymers and the co-substituted products were markedly different (table 2-4). Decreases in molecular weight were detected following the substitution reactions. Three explanations seem plausible. First, most of the introduced side groups have lower molecular weights than the fluorinated side groups displaced from the starting polymers. Second, the hydrodynamic radii of the resultant polymers could be very different from those of the starting polymers and this could affect elution from GPC columns.²⁹ Third, some chain cleavage could accompany macromolecular substitution reactions. For all the polymers except **14**, there is little

Table 2-4: GPC Results

Polymer	M_n	Polymer	M_n	Polymer	M_n
2	552,000	13	136,000	24	76,000
3	140,000	14	36,000	25	180,000
4	627,000	15	423,000	26	206,000
5	172,000	16	180,000	27	125,000
6	540,000	17	126,000	28	122,000
7	134,000	18	92,000	29	111,000
8	577,000	19	98,000	30	130,000
9	475,000	20	70,000	31	180,000
10	231,000	21	54,000	32	172,000
11	312,000	22	31,000		
12	202,000	23	97,000		

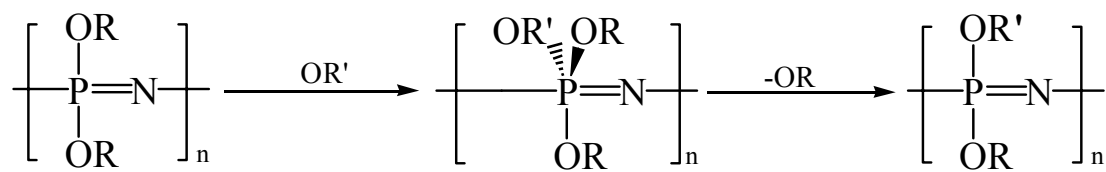
change in the shape of the peaks in the GPC traces. For polymer **14**, synthesized via reaction of the trifluoroethoxy single substituent polymer (**2**) with the isopropoxide nucleophile in refluxing THF, the GPC trace contained an unresolved bimodal peak indicative of chain cleavage. The isopropoxide ion is a stronger base than the other alkoxides and at reflux conditions could attack the backbone of polymer **2**. This is not observed for polymers **3** and **4** because the phosphorus-nitrogen backbone is better protected by the bulkier tetrafluoropropoxy and octafluoropentoxy side groups.

7. Factors Involved in Macromolecular Substitution of Polymers 2-4

As already noted, a key factor that determines if side group displacement occurs in poly(organophosphazenes) is the electron-withdrawing ability of the initial side groups. Electron-withdrawing side-groups make the phosphorus to which they are linked more susceptible to nucleophilic attack. However, the ability of the initial side groups to shield the backbone phosphorus atoms also plays an important role in determination of the degree of substitution.²⁰ Thus, while the 2,2,3,3-tetrafluoropropoxy and 2,2,3,3,4,4,5,5-octafluoropentoxy side groups are more electron-withdrawing than 2,2,2-trifluoroethoxy side group, they also shield the skeletal phosphorus atoms from nucleophilic attack to a greater degree. This results in a lower level of side group substitution.

8. Mechanism of Macromolecular Substitution

The reactions are believed to proceed via an S_N2-like addition-elimination reaction at the phosphorus atoms as shown in scheme 2-2. If the reaction proceeded in an



Scheme 2-2: Mechanism of Side Group Exchange

S_N1 -like fashion, the polymers with the more ionizable side groups, such as poly[bis(tetrafluoropropoxy)phosphazene] and poly[bis(octafluoropentoxy)phosphazene], would presumably be more prone to side group exchange than poly[bis(trifluoroethoxy)phosphazene].

Another question to consider is whether the mechanism consists of an equilibrium reaction of incoming and displaced nucleophiles or whether side group substitution is irreversible. To this end, polymers **9**, **10**, **15**, and **16** were exposed to 1 eq/side group of sodium 2,2,2-trifluoroethoxide in THF for 48 hours at 67 °C. No changes in the NMR spectra were detected and this suggests the irreversibility of the side group displacement.

Multinuclear NMR spectroscopy provided evidence for a random disposition of side groups in the modified polymers. ^{31}P NMR spectra showed no evidence of sharp peaks that would be indicative of blocky structures but instead gave broad peaks. ^1H NMR spectra contained unresolved multiplets instead of sharp multiplets.

C. Conclusions

An alternative way to prepare co-substituted poly[(fluoroalkoxy-alkoxy)phosphazenes] through side group exchange has been investigated. The degree of displacement of organic side groups in the poly[bis(alkoxy)phosphazene] system depends on both the electron withdrawing ability of the side groups and the ability of the side group to protect the backbone phosphorus atoms from nucleophilic attack. The highest degree of replacement of side groups was ~60%. Thus, none of the polymers examined

here could be completely converted to derivative single-substituent polymers in one reaction.

Although none of the starting polymers were found to be universal macromolecular intermediates with the broad versatility of **1**, the information obtained here is valuable for the synthesis of many co-substituted polyphosphazenes. For example, it can be used to determine the order in which nucleophiles should be added to **1** to obtain specific side group ratios without side group exchange taking place during macromolecular substitution. It is also important for designing new high performance elastomers with properties that differ from those of the existing fluoroalkoxyphosphazene commercial materials.

D. Experimental Section

1. Materials

Ethanol, 1-propanol, 2-propanol, 1-hexanol, 2,2,2-trifluoroethanol, 2,2,3,3-tetrafluoropropanol and 2,2,3,3,4,4,5,5-octafluoropentanol from Aldrich were dried over CaH_2 and distilled before use. Sodium hydride (60% in mineral oil) was obtained from Aldrich and was weighed into Schlenk flasks in an argon filled glove box. Poly(dichlorophosphazene) (**1**) was prepared via thermal ring-opened polymerization as reported previously.¹ Tetrahydrofuran was distilled from sodium benzophenone under a dry argon atmosphere.

All glassware was flame-dried under vacuum or dried overnight in an oven before use. The reactions were carried out using standard Schlenk techniques under an atmosphere of dry argon.

2. Equipment.

^1H and ^{31}P spectra were recorded on a Bruker AMX-360 NMR spectrometer operated at 360 and 90.27 MHz, respectively. ^1H NMR spectra were referenced to external tetramethylsilane. ^{31}P and ^{19}F NMR (Bruker DPX-300, 282 MHz) proton decoupled chemical shifts were relative to external 85% phosphoric acid standard and trichlorofluoromethane, respectively. Molecular weights and polydispersities were estimated using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector, Phenomenex Phenogel 10 μm linear columns, and calibrated versus polystyrene standards. Sample elution was carried out at 40 $^{\circ}\text{C}$ with a 0.1 wt % solution of tetra-*n*-butylammonium nitrate (Aldrich) in THF (OmniSolv). Elemental analyses were obtained from Quantitative Technologies of Whitehouse, New Jersey.

3. Synthesis of Poly[bis(fluoroalkoxyphosphazenes)] (2-4)

Sodium fluoroalkoxide solutions were prepared via addition of 2,2,2-trifluoroethanol, 2,2,3,3-tetrafluoropropanol or 2,2,3,3,4,4,5,5-octafluoropentanol (345 mmol) to a slurry of sodium hydride (60%) (13.4 g, 335 mmol) in THF (1.5 L) with cooling by an ice bath. Solutions of **1** (15.0 g, 129 mmol) dissolved in freshly distilled THF (1.5 L) were added dropwise to stirred solutions of the sodium fluoroalkoxide (335 mmol) in THF (1.5 L) at room temperature for 3-5 hours. The reaction mixtures were

concentrated by rotary evaporation and polymers **2-4** were purified by multiple precipitations into acidified water (pH~5) and hexanes followed by drying on a vac-line.

For **2**: White, semi-crystalline material. Yield = 27.3 g (87%). ^1H NMR (d_8 -THF): δ = 4.5 (q, J = 7.9 Hz, 4H, OCH_2CF_3). ^{31}P NMR (d_8 -THF): δ = -6.3 (s). ^{19}F NMR (d_8 -THF): -76.7 (s). Elemental analysis (calc, found): N = (10.37, 9.98), P = (22.92, 22.88), C = (35.55, 35.47), H = (7.47, 7.37), F = (46.91, 44.98).

For **3**: White, semi-crystalline material. Yield = 31.7 g (80%). ^1H NMR (d_8 -THF): δ = 6.1 (t, J = 52.5 Hz, 2H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$), 4.4 (t, J = 12.9 Hz, 4H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$). ^{31}P NMR (d_8 -THF): δ = -6.8 (s). ^{19}F NMR (d_8 -THF): -128.2 (s), -141.4 (s). Elemental analysis (calc, found): N = (10.37, 9.98), P = (22.92, 22.88), C = (35.55, 35.47), H = (7.47, 7.37), F = (49.49, 48.24).

For **4**: White, wax-like material. Yield = 31.7 g (80%). ^1H NMR (d_8 -THF): δ = 6.5 (t of t, J = 52.5, 25.2 Hz, 2H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.3 (t, J = 13.7 Hz, 4H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$). ^{31}P NMR (d_8 -THF): δ = -5.8 (s). ^{19}F NMR (d_8 -THF): -122.3 (s), -126.4 (s), -131.1 (s), -139.5 (s). Elemental analysis (calc, found): N = (10.37, 9.98), P = (22.92, 22.88), C = (35.55, 35.47), H = (7.47, 7.37), F = (59.96, 59.34).

4. Synthesis of Poly[bis(alkoxyphosphazenes)] (5-8)

Sodium alkoxide solutions were prepared via the addition of ethanol, 1-propanol, 2-propanol or 1-hexanol (345 mmol) to a slurry of NaH (60%) (13.4 g, 335 mmol) in THF (1.5 L) with stirring. Heat was applied to ensure conversion to the sodium salt. Solutions of **1** (15.0 g, 129 mmol) dissolved in freshly distilled THF (1.5 L) were added dropwise to stirred solutions of the sodium alkoxide (335 mmol) in THF (1.5 L) at ~50 °C and reactions were allowed to proceed until chlorine replacement had occurred, as

indicated by ^{31}P NMR (24-48 hrs.). The reaction mixtures were concentrated by rotary evaporation, and polymers **5-8** were purified by multiple precipitations into acidified water (pH~5) and methanol followed by drying on a vac-line.

For **5**: Tan, elastomeric polymer. Yield = 15.0 g (86%). ^1H NMR (d_8 -THF): δ = 4.0 (q, J = 6.6 Hz, 4H, OCH_2CH_3) 1.2 (t, J = 6.8 Hz, 6H, OCH_2CH_3). ^{31}P NMR (d_8 -THF): δ = -7.8 (s). Elemental analysis (calc, found): N = (10.37, 9.98), P= (22.92, 22.88), C = (35.55, 35.47), H = (7.47, 7.37).

For **6**: White, elastomeric polymer. Yield = 17.0 g (81%). ^1H NMR (d_8 -THF): δ = 3.9 (q, J = 6.4 Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 1.6 (sx, J = 7.1 Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 0.9 (t, J = 7.4 Hz, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_3$). ^{31}P NMR (d_8 -THF): δ = -7.5 (s). Elemental analysis (calc, found): N = (8.59, 8.31), P= (18.98, 19.04), C = (44.16, 44.52), H = (8.66, 8.93).

For **7**: White, semi-crystalline material. Yield = 16.1 g (77%). ^1H NMR (d_8 -THF): δ = 4.7 (2H, $\text{OCH}(\text{CH}_3)_2$), 1.3 (d, J = 6.1 Hz, 12H, $\text{OCH}(\text{CH}_3)_2$). ^{13}C NMR (d_8 -THF): δ = 22.2 (4C, $\text{OCH}(\text{CH}_3)_2$), 66.9 (2C, $\text{OCH}(\text{CH}_3)_2$). ^{31}P NMR (d_8 -THF): δ = -9.8 (s). Elemental analysis (calc, found): N = (8.59, 8.36), P= (18.98, 18.86), C = (44.16, 43.87), H = (8.66, 8.36).

For **8**: Tan, elastomeric polymer. Yield = 26.9 g (85%). ^1H NMR (d_8 -THF): δ = 4.0 (t, J = 6.2 Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.7 (mlt, J = 7.1 Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.4 (mlt, 12H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.9 (t, J = 6.2 Hz, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{31}P NMR (d_8 -THF): δ = -7.4 (s). Elemental analysis (calc, found): N = (5.66, 5.45), P= (12.52, 12.02), C = (58.26, 57.00), H = (10.62, 10.67).

5. Synthesis of Co-substituted Polyphosphazenes (9-32)

Sodium alkoxide solutions were prepared in distilled THF (75 mL) from ethanol, 1-propanol, 2-propanol and 1-hexanol (16.9 mmol for reactions with **2**, 13.4 mmol for reactions with **3**, and, 7.9 mmol for reactions with **4**) and sodium hydride (60%) (0.658 g, 16.5 mmol for reactions with **2**, 0.521 g, 13.0 mmol for reactions with **3**, and, 0.315 g, 8.1 mmol for reactions with **4**). These solutions were added to solutions of **2**, **3**, and **4** (2.0 g, 8.2 mmol, 2.0 g, 6.5 mmol, and, 2.0 g, 3.94 mmol respectively) in distilled THF (100 mL). Reactions were carried out at room temperature and at reflux in THF for each polymer/alkoxide reaction. The reaction mixtures were stirred for 48 hours, concentrated by rotary evaporation, and purified by multiple precipitations into triply deionized water (pH~5), followed by multiple precipitations into hexanes. The co-substituted polymers were then dried for 48 hours in a vacuum oven at 55 °C to remove residual solvents. Typical yields ranged from 65-75% based on NMR calculation of side group ratios.

For **9**: White, elastomeric polymer. ^1H NMR ($\text{d}_8\text{-THF}$): δ = 4.5 (m, 4H, OCH_2CF_3), 4.0 (m, 4H, OCH_2CH_3) 1.2 (m, 6H, OCH_2CH_3). ^{31}P NMR ($\text{d}_8\text{-THF}$): δ = -7.3, -5.8 (broad (br), overlapping (o)). ^{19}F NMR ($\text{d}_8\text{-THF}$): δ = -76.5 (br, m). Elemental analysis (calc, found): N = (7.05, 6.88), C = (24.17, 24.26), H = (3.28, 2.99), F = (33.83, 31.26).

For **10**: Tan, elastomeric polymer. ^1H NMR ($\text{d}_8\text{-THF}$): δ = 4.5 (m, 4H, OCH_2CF_3), 4.0 (m, 4H, OCH_2CH_3) 1.2 (m, 6H, OCH_2CH_3). ^{31}P NMR ($\text{d}_8\text{-THF}$): δ = -7.2, -7.0, -6.5 (br, o). ^{19}F NMR ($\text{d}_8\text{-THF}$): δ = -76.5 (br, m). Elemental analysis (calc, found): N = (7.81, 7.78), C = (26.78, 27.27), H = (4.25, 4.43), F = (26.05, 24.02).

For **11**: White gum. ^1H NMR (d_8 -THF): $\delta = 4.5$ (mlt, 4H, OCH_2CF_3), 3.9 (mlt, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 1.6 (mlt, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 0.9 (mlt, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_3$). ^{31}P NMR (d_8 -THF): $\delta = -8.0, -6.0$ (br, o). ^{19}F NMR (d_8 -THF): $\delta = -76.5$ (br, mlt). Elemental analysis (calc, found): N = (6.38, 6.09), C = (24.94, 24.51), H = (3.16, 2.91), F = (37.39, 35.10).

For **12**: White, adhesive polymer. ^1H NMR (d_8 -THF): $\delta = 4.5$ (mlt, 4H, OCH_2CF_3), 3.9 (mlt, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 1.6 (mlt, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 0.9 (mlt, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_3$). ^{31}P NMR (d_8 -THF): $\delta = -8.0, -6.0$ (br, o). ^{19}F NMR (d_8 -THF): $\delta = -76.2$ (br, mlt). Elemental analysis (calc, found): N = (6.45, 6.55), C = (25.57, 25.18), H = (3.30, 3.18), F = (36.24, 31.76).

For **13**: White, semi-crystalline material. ^1H NMR (d_8 -THF): $\delta = 4.5$ (mlt, 4H, OCH_2CF_3), 4.7 (s, br), 2H, $\text{OCH}(\text{CH}_3)_2$, 1.3 (mlt, 12H, $\text{OCH}(\text{CH}_3)_2$). ^{31}P NMR (d_8 -THF): $\delta = -7.7, -7.1$ (br, o). ^{19}F NMR (d_8 -THF): $\delta = -76.2$ (br, mlt). Elemental analysis (calc, found): N = (6.16, 6.19), C = (24.14, 23.97), H = (2.90, 2.60), F = (38.87, 36.72).

For **14**: Tan, semi-crystalline material. ^1H NMR (d_8 -THF): $\delta = 4.5$ (mlt, 4H, OCH_2CF_3), 4.7 (s, br, 2H, $\text{OCH}(\text{CH}_3)_2$), 1.3 (d, 12H, $\text{OCH}(\text{CH}_3)_2$). ^{31}P NMR (d_8 -THF): $\delta = -7.7, -7.1$ (br, o). ^{19}F NMR (d_8 -THF): $\delta = -76.2$ (br, mlt). Elemental analysis (calc, found): N = (6.66, 6.33), C = (27.30, 27.22), H = (3.79, 3.92), F = (33.07, 30.22).

For **15**: Off-white, elastomeric polymer. ^1H NMR (d_8 -THF): $\delta = 4.5$ (mlt, 4H, OCH_2CF_3), 4.0 (mlt, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.7 (mlt, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.4 (mlt, 12H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.9 (mlt, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{31}P NMR (d_8 -THF): $\delta = -8.0, -6.1$ (br, o). ^{19}F NMR (d_8 -

THF): $\delta = -76.1$ (br, mlt). Elemental analysis (calc, found): N = (6.16, 5.59), C = (33.38, 32.62), H = (4.61, 4.65), F = (35.59, 30.66).

For **16**: Tan, elastomeric polymer. ^1H NMR (d_8 -THF): $\delta = 4.5$ (mlt, 4H, OCH_2CF_3), 4.0 (mlt, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.7 (mlt, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.4 (mlt, 12H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.9 (mlt, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{31}P NMR (d_8 -THF): $\delta = -6.8$ (br, s). ^{19}F NMR (d_8 -THF): $\delta = -76.1$ (br, mlt). Elemental analysis (calc, found): N = (5.71, 5.44), C = (40.72, 41.07), H = (6.54, 6.63), F = (21.39, 19.84).

For **17**: White, semi-crystalline material. ^1H NMR (d_8 -THF): $\delta = 6.1$ (t, $J = 52.5$ Hz, 2H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$), 4.4 (mlt, 4H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$), 4.0 (mlt, 4H, OCH_2CH_3) 1.2 (mlt, 6H, OCH_2CH_3). ^{31}P NMR (d_8 -THF): $\delta = -7.0, -6.0$ (br, o). ^{19}F NMR (d_8 -THF): $\delta = -126.9$ (s, br), -139.6 (s, br). Elemental analysis (calc, found): N = (5.30, 5.27), C = (25.01, 25.29), H = (2.68, 2.59), F = (43.16, 41.93).

For **18**: Light brown, semi-crystalline material. ^1H NMR (d_8 -THF): $\delta = 6.1$ (t, $J = 52.5$ Hz, 2H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$), 4.4 (mlt, 4H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$), 4.0 (mlt, 4H, OCH_2CH_3) 1.2 (mlt, 6H, OCH_2CH_3). ^{31}P NMR (d_8 -THF): $\delta = -7.0, -6.0$ (br, o). ^{19}F NMR (d_8 -THF): $\delta = -126.9$ (s, br), -139.6 (s, br). Elemental analysis (calc, found): N = (5.59, 5.52), C = (25.61, 26.35), H = (2.95, 2.89), F = (40.68, 38.22).

For **19**: White gum. ^1H NMR (d_8 -THF): $\delta = 6.1$ (t, $J = 52.5$ Hz, 2H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$), 4.4 (mlt, 4H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$), 3.9 (mlt, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 1.6 (mlt, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 0.9 (mlt, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_3$). ^{31}P NMR (d_8 -THF): $\delta = -7.1, -5.9$ (br,

o). ^{19}F NMR (d_8 -THF): $\delta = -128.3$ (s, br), -141.5 (s, br). Elemental analysis (calc, found): N = (5.00, 4.88), C = (25.76, 24.82), H = (2.71, 2.49), F = (43.46, 40.71).

For **20**: Tan, crystalline material. ^1H NMR (d_8 -THF): $\delta = 6.1$ (t, $J = 52.5$ Hz, 2H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$), 4.4 (m, 4H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$), 3.9 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 1.6 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 0.9 (m, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_3$). ^{31}P NMR (d_8 -THF): $\delta = -7.1$, -5.9 (br, o). ^{19}F NMR (d_8 -THF): $\delta = -126.5$ (s, br), -139.6 (s, br). Elemental analysis (calc, found): N = (5.11, 5.01), C = (26.29, 25.97), H = (2.89, 2.68), F = (42.71, 39.87).

For **21**: Dark brown powder. ^1H NMR (d_8 -THF): $\delta = 6.1$ (t, $J = 52.5$ Hz, 2H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$), 4.4 (m, 4H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$), 4.7 (2H, $\text{OCH}(\text{CH}_3)_2$), 1.3 (m, 12H, $\text{OCH}(\text{CH}_3)_2$). ^{31}P NMR (d_8 -THF): $\delta = -7.0$ (br, s). ^{19}F NMR (d_8 -THF): -126.9 (s, br), -139.6 (s, br). Elemental analysis (calc, found): N = (4.88, 4.98), C = (25.11, 25.43), H = (2.51, 2.36), F = (45.55, 43.09).

For **22**: Dark brown powder. ^1H NMR (d_8 -THF): $\delta = 6.1$ (t, $J = 52.5$ Hz, 2H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$), 4.4 (m, 4H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$), 4.7 (2H, $\text{OCH}(\text{CH}_3)_2$), 1.3 (m, 12H, $\text{OCH}(\text{CH}_3)_2$). ^{31}P NMR (d_8 -THF): $\delta = -7.0$ (br, s). ^{19}F NMR (d_8 -THF): $\delta = -126.9$ (s, br), -139.6 (s, br). Elemental analysis (calc, found): N = (5.00, 4.98), C = (25.76, 25.91), H = (2.71, 2.36), F = (43.46, 43.09).

For **23**: Light brown gum. ^1H NMR (d_8 -THF): $\delta = 6.1$ (t, $J = 52.5$ Hz, 2H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$), 4.4 (m, 4H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$), 4.0 (t, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.7 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.4 (m, 12H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.9 (m, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{31}P NMR (d_8 -THF): $\delta = -7.0$, -6.2 (br, o). ^{19}F

NMR (d_8 -THF): δ = -128.1 (s, br), -141.5 (s, br). Elemental analysis (calc, found): N = (4.75, 4.72), C = (29.30, 28.96), H = (3.42, 3.17), F = (41.19, 37.90).

For **24**: Dark brown gum. ^1H NMR (d_8 -THF): δ = 6.1 (t, J = 52.5 Hz, 2H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$), 4.4 (m, 4H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$), 4.0 (t, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.7 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.4 (m, 12H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.9 (m, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{31}P NMR (d_8 -THF): δ = -7.0, -6.2 (br, o). ^{19}F NMR (d_8 -THF): δ = -128.1 (s, br), -141.5 (s, br). Elemental analysis (calc, found): N = (4.84, 4.77), C = (32.39, 31.57), H = (4.19, 3.82), F = (36.79, 34.14).

For **25**: Tan gum. ^1H NMR (d_8 -THF): δ = 6.5 (t, J = 52.5 Hz, 2H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.3 (m, 4H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.0 (m, 4H, OCH_2CH_3), 1.2 (m, 6H, OCH_2CH_3). ^{31}P NMR (d_8 -THF): δ = -7.0, -6.0 (br, o). ^{19}F NMR (d_8 -THF): δ = -122.2 (s, br), -126.3 (s, br), -131.1 (s, br), -139.5 (s, br). Elemental analysis (calc, found): N = (3.20, 3.17), C = (24.37, 24.51), H = (1.56, 1.54), F = (56.42, 54.50).

For **26**: Tan gum. ^1H NMR (d_8 -THF): δ = 6.5 (t, J = 52.5 Hz, 2H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.3 (m, 4H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.0 (m, 4H, OCH_2CH_3), 1.2 (m, 6H, OCH_2CH_3). ^{31}P NMR (d_8 -THF): δ = -7.0, -6.0 (br, o). ^{19}F NMR (d_8 -THF): δ = -122.2 (s, br), -126.3 (s, br), -131.1 (s, br), -139.5 (s, br). Elemental analysis (calc, found): N = (3.32, 3.48), C = (24.55, 24.13), H = (1.78, 1.31), F = (55.52, 53.93).

For **27**: Tan, adhesive polymer. ^1H NMR (d_8 -THF): δ = 6.5 (t, J = 52.5 Hz, 2H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.3 (m, 4H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 3.9 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 1.6 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 0.9 (m, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_3$). ^{31}P NMR (d_8 -THF): δ = -6.7, -5.9 (br, o). ^{19}F NMR (d_8 -THF): δ = -122.2 (s, br), -126.3 (s, br), -

131.1 (s, br), -139.5 (s, br). Elemental analysis (calc, found): N = (3.22, 3.14), C = (25.32, 25.15), H = (1.78, 1.52), F = (55.22, 52.99).

For **28**: Tan gum. ^1H NMR (d_8 -THF): δ = 6.5 (mlt, J = 52.5, 2H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.3 (mlt, 4H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 3.9 (mlt, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 1.6 (mlt, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 0.9 (mlt, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_3$). ^{31}P NMR (d_8 -THF): δ = -6.7, -5.9 (br, o). ^{19}F NMR (d_8 -THF): δ = -122.2 (s, br), -126.3 (s, br), -131.1 (s, br), -139.5 (s, br). Elemental analysis (calc, found): N = (3.30, 3.39), C = (25.57, 25.37), H = (1.88, 1.61), F = (54.41, 53.97).

For **29**: Light brown gum. ^1H NMR (d_8 -THF): δ = 6.5 (t, J = 52.5 Hz, 2H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.3 (mlt, 4H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.7 (2H, $\text{OCH}(\text{CH}_3)_2$), 1.3 (mlt, 12H, $\text{OCH}(\text{CH}_3)_2$). ^{31}P NMR (d_8 -THF): δ = -7.0 (br, s). ^{19}F NMR (d_8 -THF): δ = -122.2 (s, br), -126.3 (s, br), -131.1 (s, br), -139.5 (s, br). Elemental analysis (calc, found): N = (3.12, 3.28), C = (24.95, 25.20), H = (1.66, 1.35), F = (56.24, 54.08).

For **30**: Light brown gum. ^1H NMR (d_8 -THF): δ = 6.5 (t, J = 52.5 Hz, 2H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.3 (mlt, 4H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.7 (2H, $\text{OCH}(\text{CH}_3)_2$), 1.3 (mlt, 12H, $\text{OCH}(\text{CH}_3)_2$). ^{31}P NMR (d_8 -THF): δ = -7.0 (br, s). ^{19}F NMR (d_8 -THF): δ = -122.2 (s, br), -126.3 (s, br), -131.1 (s, br), -139.5 (s, br). Elemental analysis (calc, found): N = (3.19, 3.28), C = (25.21, 24.61), H = (1.75, 1.70), F = (55.48, 53.27).

For **31**: Tan gum. ^1H NMR (d_8 -THF): δ = 6.5 (t of t, J = 52.5 Hz, 2H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.3 (mlt, 4H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.0 (mlt, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.7 (mlt, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.4 (mlt, 12H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.9 (mlt, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{31}P NMR (d_8 -

THF): $\delta = -6.6, -5.8$ (br, o). ^{19}F NMR (d_8 -THF): $\delta = -122.2$ (s, br), -126.3 (s, br), -131.1 (s, br), -139.5 (s, br). Elemental analysis (calc, found): N = (2.99, 2.97), C = (26.42, 26.92), H = (1.94, 1.93), F = (55.19, 52.56).

For **32**: Tan adhesive. ^1H NMR (d_8 -THF): $\delta = 6.5$ (t of t, $J = 52.5$ Hz, 2H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.3 (m, 4H, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.0 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.7 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.4 (m, 12H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.9 (m, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{31}P NMR (d_8 -THF): $\delta = -6.6, -5.8$ (br, o). ^{19}F NMR (d_8 -THF): $\delta = -122.2$ (s, br), -126.3 (s, br), -131.1 (s, br), -139.5 (s, br). Elemental analysis (calc, found): N = (3.03, 2.97), C = (26.82, 27.22), H = (2.05, 1.93), F = (54.49, 51.78).

6. Addition of 2,2,2-trifluoroethoxide to Polymers **9**, **10**, **15**, and **16**

Sodium 2,2,2-trifluoroethoxide solutions in THF (75 mL) (2 equivalents per repeat unit) were added to solutions of **9**, **10**, **15**, and **16** (1.0 g) in distilled THF (100 mL). The reaction mixtures were stirred for 48 hours, concentrated by rotary evaporation, and purified by multiple precipitations into acidified water (pH~5) and hexanes. The polymer composition remained the same as determined by ^1H NMR spectroscopy.

E. References

- 1) Allcock, H.R. *Chemistry and Applications of Polyphosphazenes*; Wiley-Interscience: Hoboken, N.J., **2003**.
- 2) Ibim, S. E. M.; Ambrosia, A. M. A.; Kwon, M. S.; El-Amin, S.F.; Allcock, H. R.; Laurencin, C. T. *Biomaterials*, **1997**, *18*, 1565-1569.
- 3) Schacht, E.; Vandorpe, J.; Dejardin, S.; Lemmouchi, Y.; Seymour, L. *Biotechnol. Bioeng.*, **1996**, *52*, 102-108.
- 4) Reed, C. S.; Taylor, J. P.; Guigley, K. S.; Coleman, M. M.; Allcock, H. R. *Poly. Eng. Sci.*, **2000**, *40*, 465-472.
- 5) Taylor, J. P.; Allcock, H. R. *Poly. Eng. Sci.*, **2000**, *40*, 1177-1189.
- 6) Allcock, H. R. *Adv. Mater.*, **1994**, *6*, 106-115.
- 7) Guo, Q. H.; Pintauro, P. N.; Tang, H; O'Connor, S. *J. Memb. Sci.*, **1999**, *154*, 175-181.
- 8) Allcock, H. R.; Kellam, E. C.; Morford, R. V. *Solid State Ionics*, **2001**, *143*, 297-308.
- 9) Allcock, H. R. In *Functional Polymers*; Patil, A.O.; Schulz, D.N.; Novak, B.M., Eds; American Chemical Society: Washington, D.C., **1998**, ACS Symposium Series 704, p 261-275.
- 10) Allcock, H. R.; Nelson, J.M.; deDenus, C.R.; Manners, I. In *Tailored Polymers & Applications*; Yagci, Y.; Mishra, M.K.; Nuyken, O.; Ito, K.; Wnek, G.; Eds; VSP: Boston, **2000**, p 165-173.
- 11) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.*, **1966**, *5*, 1709-1715.
- 12) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.*, **1966**, *5*, 1716-1718.

- 13) D'Halluin, G.; De Jaeger, R.; Chambrette, J. P.; Potin, P. *Bull. Soc. Chim. Belg.*, **1989**, 98, 653-665.
- 14) D'Halluin, G.; De Jaeger, R.; Potin, P. *Macromolecules*, **1992**, 25, 1254-1258.
- 15) Allcock, H. R.; Crane, C. A.; Morrissey, C. T.; Nelson, J. M.; Reeves, S. D.; Honeyman, C. H.; Manners, I. *Macromolecules*, **1996**, 29, 7740-7747.
- 16) Allcock, H. R.; Nelson, J. M.; Reeves, S. D.; Honeyman, C. H.; Manners, I. *Macromolecules*, **1997**, 30, 50-56.
- 17) Allcock, H. R.; Fitzpatrick, R. J.; Salvati, L. *Chem. Mater.*, **1991**, 3, 1120-1132.
- 18) Allcock, H. R.; Fuller, T. J.; Evans, T. L. *Macromolecules*, **1980**, 13, 1325-1332.
- 19) Allcock, H. R.; Rutt, J.S.; Fitzpatrick, R.J. *Chem. Mater.*, **1991**, 3, 442-449.
- 20) Allcock, H. R.; Kim, Y.B. *Macromolecules* **1994**, 27, 3933-3942.
- 21) Allcock, H. R.; Kugel, R.L. ; Walsh, E.J. *Chem. Comm.*, **1970**, 20, 1283-1284.
- 22) Allcock, H. R.; Smeltz., L.A. *J. Am. Chem. Soc.*, **1976**, 98, 4143-4149.
- 23) Smeltz, L. A. Doctoral Thesis, The Pennsylvania State University, **1975**, 119-122.
- 24) Allcock, H. R.; Moore, G.Y. *Macromolecules*, **1972**, 5, 231-232.
- 25) Allcock, H. R.; Fitzpatrick, R.J.; Salvati, L. *Chem. Mater.*, **1991**, 3, 450-454.
- 26) It is necessary to assume that the rate of substitution is independent of the polymer chain length. This allows for quantitative determination of the average composition for a given system.
- 27) Mooney, E. F. *An Introduction to ¹⁹F NMR Spectroscopy*; Heyden & Son Ltd.: Philadelphia, 1970, 9-10.
- 28) Information obtained from QTI, PO Box 470, Rt. 22 East, Salem Industrial Park – Building #5, Whitehouse, NJ 08888-0470. (908) 534-4445

29) Cowie, J. M. G. *Polymers: Chemistry & Physics of Modern Materials*; 2nd ed.;

Blackie Academic & Professional: New York, 1997, 211.

Chapter 3

Side Group Exchange in Poly(organophosphazenes) with Fluoroalkoxy Substituents, Part II: Fluoroalkoxide Nucleophiles

A. Introduction

The previous chapter dealt with reactions of fluoroalkoxide substituted polyphosphazenes with alkoxide nucleophiles to give co-substituted polyphosphazenes. In those reactions, the extent of side group exchange was affected by both steric and electronic considerations. The reactions were also demonstrated to be irreversible substitution reactions. This chapter deals with side group exchange between polyphosphazenes with fluoroalkoxide substituents and fluoroalkoxide nucleophiles. Comparison with the non-fluorinated alkoxide nucleophiles reveals quite different results both in terms of the extent and reversibility of the exchange reactions.

B. Results and Discussion

1. Synthesis of Co-substituted Poly(fluoroalkoxyphosphazenes)

Poly[bis(2,2,2-trifluoroethoxy)phosphazene] (**2**), poly[bis(2,2,3,3-tetrafluoropropoxy)phosphazene] (**3**) and poly[bis(2,2,3,3,4,4,5,5-octafluoropentoxy)phosphazene] (**4**) were synthesized via previously described methods.¹ Co-substituted polymers **5-22** were then prepared from polymers **2-4** via side group exchange. Samples of polymer **2** were dissolved in THF and were reacted with solutions of one equivalent per side group sodium tetrafluoropropoxide, sodium octafluoropentoxide and sodium pentafluoropropoxide in THF. Samples of polymer **3**

were dissolved in THF and were reacted with solutions of one equivalent per side group sodium trifluoroethoxide, sodium octafluoropentoxide and sodium pentafluoropropoxide in THF. Samples of polymer **4** were dissolved in THF and were reacted with solutions of one equivalent per side group sodium trifluoroethoxide, sodium tetrafluoropropoxide and sodium pentafluoropropoxide in THF. For each nucleophile, reactions were carried out for 48 hours at ambient temperature (25 °C) and at reflux in THF (67 °C). Typical work-up of these polymers involved multiple precipitations into water (pH~4) and hexanes followed by drying in a vacuum oven at 40 °C for 48 hours. The polymers were then stored under argon prior to characterization.

Side group exchange of **2-4** with alkoxide nucleophiles could easily be followed by ^{31}P NMR spectroscopy, but changes in the ^{31}P NMR spectra during side group exchange with fluoroalkoxide nucleophiles were negligible. Although the fluoroalkoxide exchange reactions could not be monitored by NMR, they were stopped at 48 hours because the alkoxide substitution reactions all took less than 48 hours to reach completion. ^1H NMR spectroscopy was used to quantify most of the ratios of the side groups after the exchange reactions and ^{19}F NMR spectroscopy was used to confirm the side group ratios obtained from ^1H NMR. In the case of polymers with overlapping hydrogen signals (i.e. with both trifluoroethoxy and pentafluoropropoxy substituents), ^{19}F NMR spectroscopy had to be used to quantify the side group ratios (Figure 3-1).

In addition to the polymer hydrogen signals in the ^1H NMR spectra, there were also several unidentified peaks in the spectra for all of the co-substituted polymers. These peaks did not interfere with integration of the polyphosphazene peaks and the side group ratios were still obtainable. Several attempts were made to remove the impurity.

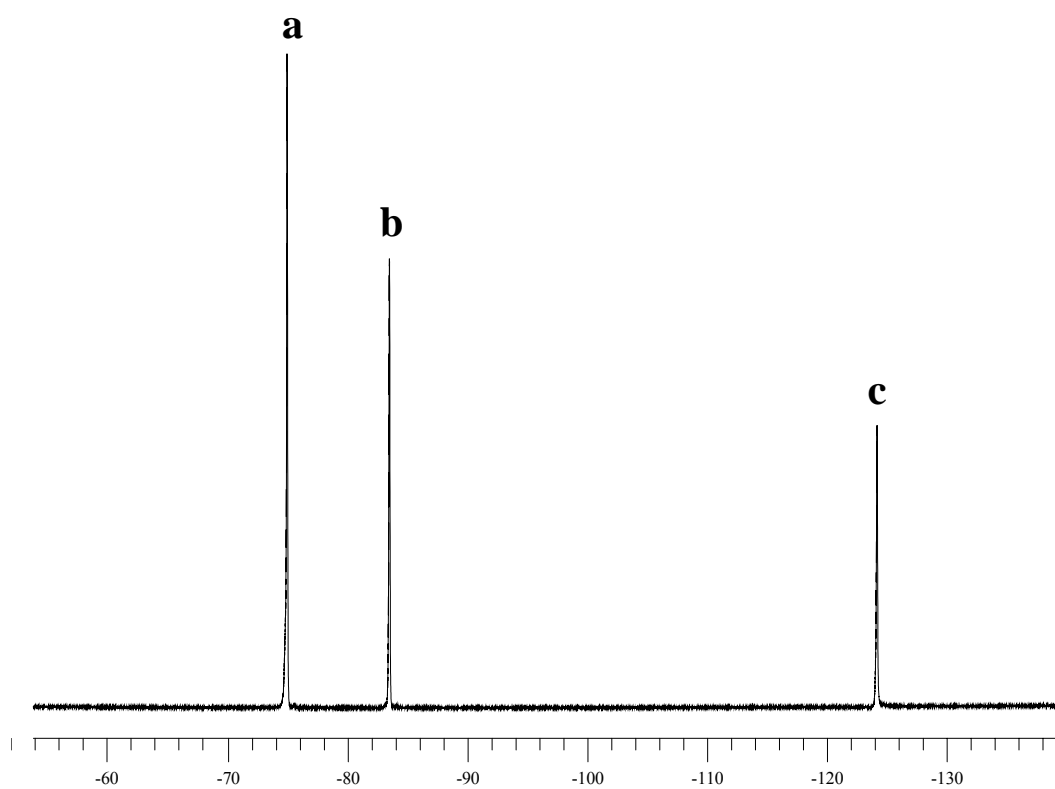


Figure 3-1: ^{19}F Spectrum of Polymer 8. a) CF_3 group of the trifluoroethoxy substituent; b) CF_3 group on the pentafluoropropoxy substituent; c) CF_2 group on the pentafluoropropoxy substituent.

Dialysis of polymer **5** versus THF for 3 days in 12-14000 MWCO tubing was unsuccessful. The fact that dialysis did not remove the impurity suggest that it is polymeric in nature or attached to the polyphosphazene backbone. However, if there is attachment to the polyphosphazene it is not enough to cause significant changes in the ^{31}P NMR spectra. A small amount of attachment of a polymeric impurity to the polyphosphazene backbone would not substantially affect the amounts of side group exchange obtained. Additional precipitations into water, hexanes, pentane and dichloromethane did not decrease the size of the impurity peaks in the ^1H NMR. Attempts were also made to discern the identity of the impurity. Polymer **5** was examined by HMQC and HMBC NMR spectroscopy. These techniques revealed that the impurity is non-fluorinated and has an alcohol or amine group present.

The molecular weights of the resultant polymers **5-22** show a large decrease for most of the polymers (table 3-1). For example, polymer **5** (made from reaction of polymer **2** with tetrafluoropropoxide) has a M_w of 352,000 while polymer **2** has an M_w of about 1,500,000. Some of this is likely due to side group mass and hydrodynamic radii differences but mostly to polymer chain cleavage. To remove the influence of side group mass and hydrodynamic radius, samples of poly[bis(trifluoroethoxy)phosphazene] (**23**) were reacted with solutions of sodium trifluoroethoxide (1 eq / side group) at 25 °C and at 67 °C in THF for 48 hours to give polymer **24** and **25** respectively. The molecular weight decline is greater for the reaction at reflux but it is clear that molecular weight decline has occurred in both samples (table 3-1). Therefore, chain cleavage is certain to accompany

Table 3-1: GPC Results

Polymer	M_w	M_n	Polymer	M_w	M_n
2	1530000	148000	13	420000	77000
3	409000	132000	14	367000	83000
4	677000	357000	15	471000	90000
5	352000	106000	16	421000	82000
6	266000	126000	17	401000	114000
7	259000	127000	18	528000	85000
8	286000	149000	19	580000	117000
9	636000	181000	20	303000	88000
10	525000	145000	21	541000	173000
11	373000	134000	22	319000	115000
12	374000	134000	23	422000	152000
13	420000	77000	24	311000	118000
14	367000	83000	25	156000	107000

side group exchange with fluoroalkoxy nucleophiles and is likely more pronounced at elevated temperatures.

2. Reactions of Fluoroalkoxide Nucleophiles with Polymer 2

Poly[bis(trifluoroethoxy)phosphazene (**2**) was reacted with tetrafluoropropoxide, pentafluoropropoxide and octafluoropentoxide nucleophiles under ambient temperatures and reflux conditions for 48 hours to yield polymers **5-10** (table 3-2). Significant amounts of substituents were exchanged in each of the reactions but temperature did not appear to affect the end polymer composition. The highest quantity of replacement (~63-66 %) occurred when the nucleophile was tetrafluoropropoxide (Polymers **5** and **6**, Table 2). The pentafluoropropoxide only displaced about 40 % of the trifluoroethoxy groups by comparison (Polymers **7** and **8**, table 3-2). Clearly the presence of the fluorine atom in place of the terminal hydrogen makes the pentafluoropropoxide more electron-withdrawing and a better leaving group than the tetrafluoropropoxy group. Lastly, the octafluoropentoxide nucleophile resulted in ~43-46 % exchange. The trifluoroethoxy group is an electron-withdrawing group and a good leaving group. The fact that temperature played little role in the replacement indicates that the replacement is controlled by an equilibrium exchange of the polymer side group and the nucleophile.

3. Reactions of Fluoroalkoxide Nucleophiles with Polymer 3

Reactions of fluoroalkoxide nucleophiles with poly[bis(tetrafluoropropoxy)phosphazene] (**3**) did show some dependence on temperature (Table 3-2). At 25 °C the amount of exchange ranged from 17 % for the reaction with the

Table 3-2: Side Group Exchange Results

<i>Starting Polymer</i>	<i>Nucleophile</i>	<i>% Exchange RT/(Resultant Polymer)</i>	<i>% Exchange Reflux/(Resultant Polymer)</i>
2	-OCH ₂ CF ₂ CF ₂ H	66 / (5)	63 / (6)
2	-OCH ₂ CF ₂ CF ₃	40 / (7)	40 / (8)
2	-OCH ₂ (CF ₂) ₄ H	43 / (9)	46 / (10)
3	-OCH ₂ CF ₃	27 / (11)	34 / (12)
3	-OCH ₂ CF ₂ CF ₃	17 / (13)	25 / (14)
3	-OCH ₂ (CF ₂) ₄ H	20 / (15)	33 / (16)
4	-OCH ₂ CF ₃	62 / (17)	62 / (18)
4	-OCH ₂ CF ₂ CF ₂ H	63 / (19)	64 / (20)
4	-OCH ₂ CF ₂ CF ₃	50 / (21)	50 / (22)

pentafluoropropoxide to 27 % for the trifluoroethoxide nucleophile (Polymers **11**, **13** and **15**). At reflux conditions, 25 % of the side groups were exchanged by the pentafluoropropoxide and both the octafluoropentoxide and trifluoroethoxide replaced about 34 % (Polymers **12**, **14** and **16**). There are two explanations that seem likely for the temperature dependence. First, it may be more difficult to displace the tetrafluoropropoxy side group because it is not as electron-withdrawing as the octafluoropentoxy and pentafluoropropoxy side groups in the equilibrium reactions. Second, the tetrafluoropropoxy substituent provides more backbone protection than the trifluoroethoxy side group. Thus the final composition of polymer **11** obtained at ambient temperature equilibrium is significantly different than polymers **7**, **8** and **12**.

4. Reactions of Fluoroalkoxide Nucleophiles with Polymer **4**

Reactions of poly[bis(octafluoropentoxy)phosphazene] (**4**) with the trifluoroethoxide nucleophile yielded polymers **18** and **19**. These polymers were similar in composition to polymers made from reactions of polymer **2** with sodium octafluoropentoxide (**9** and **10**). The amount of side group exchange (~62 %) did not change with temperature, but depended on the ratio of the two possible substituents (side group and nucleophile) in the reaction. Polymers **16**, **20** and **21** also had approximately the same side group ratios and showed equilibrium exchange independent of temperature. In addition, trifluoroethoxide and tetrafluoropropoxide nucleophiles each replaced 62-64 % of the octafluoropentoxide side group. Lastly, reactions of polymer **4** with pentafluoropropoxide nucleophiles gave the least amount of exchange (~50 %) and the amount of substitution was temperature independent (polymers **22** and **23**, Table 2).

5. Equilibrium Exchange Reactions

The overall side group preferences in each polymer system followed the order tetrafluoropropoxy > trifluoroethoxy > octafluoropentoxy > pentafluoropropoxy. In each of the polymer systems, the amount of side group replacement depended primarily on the identity and equilibrium exchange with the fluoroalkoxide nucleophile, although some temperature dependence did accompany substituent exchange of polymer **3** as discussed above.

In reactions with the non-fluorinated alkoxides, size of the fluoroalkoxy side group and temperature played a significant role in the extent of exchange that occurred. However, side group exchange reactions of fluoroalkoxides with polymers **2**, **3** and **4** differed markedly from reactions of those polymers with non-fluorinated alkoxides.² In the fluoroalkoxide reactions, two related differences between the systems are observed. First, in side group exchange with fluoroalkoxides, the reactions are reversible. This is deduced from the fact that each fluoroalkoxide nucleophile can displace each fluoroalkoxy side group. Second, nucleophilic susceptibility of the phosphorus atoms in the polyphosphazene backbone does not vary much with the amount of side group exchange. All of the nucleophiles are very electron-withdrawing, and substitution of a phosphorus atom does not decrease the nucleophilicity of the phosphorus atoms to a significant degree. In the non-fluorinated alkoxide system, however, the substituent replacement is irreversible. The alkoxy side groups are less electron-withdrawing than the fluoroalkoxy side groups and substituent exchange decreases the overall nucleophilicity of the backbone phosphorus atoms. Therefore, the difference in the extent and reversibility of side group exchange in each of these systems is not surprising.

C. Conclusions

Polyphosphazenes with fluoroalkoxide substituents readily undergo side group exchange reactions with fluoroalkoxide nucleophiles to yield cosubstituted polymers. Most of the reactions showed little dependence on the temperature in terms of amount of side groups replaced but depended on the concentration and amounts of the substituents. Ease of displacement followed the trend pentafluoropropoxy > octafluoropentoxo > trifluoroethoxy > tetrafluoropropoxy.

Unlike side group exchange with alkoxide nucleophiles, replacement reactions with fluoroalkoxide nucleophiles were reversible reactions. The amounts of fluoroalkoxy side groups displaced were generally greater for the fluoroalkoxide system and did not appear dependent on the size of the side group, but on its electron-withdrawing ability. These reactions provide an alternative synthetic approach to the preparation of cosubstituted poly(fluoroalkoxy)phosphazenes.

D. Experimental Section

1. Materials

2,2,2-trifluoroethanol, 2,2,3,3-tetrafluoropropanol, 2,2,3,3,3-pentafluoropropanol, and 2,2,3,3,4,4,5,5-octafluoropentanol from Aldrich were used as received. Sodium, and sodium hydride (95% in mineral oil) was obtained from Aldrich and was weighed into Schlenk flasks in an argon filled glove box. Poly(dichlorophosphazene) (**1**) was prepared

via thermal ring-opened polymerization as reported previously.¹ Tetrahydrofuran was distilled from sodium benzophenone ketyl under a dry argon atmosphere.

2. Equipment

¹H and ³¹P spectra were recorded on a Bruker AMX-360 NMR spectrometer operated at 360 and 90.27 MHz, respectively. ¹H NMR spectra were referenced to external tetramethylsilane. ³¹P and ¹⁹F NMR (Bruker DPX-300, 282 MHz) proton decoupled chemical shifts were relative to external 85% phosphoric acid standard and trichlorofluoromethane, respectively. Molecular weights and polydispersities were estimated using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector, Phenomenex Phenogel 10 μm linear columns, and calibrated versus polystyrene standards. Sample elution was carried out at 40 °C with a 0.1 wt % solution of tetra-n-butylammonium nitrate (Aldrich) in THF (OmniSolv).

3. Synthesis of Polyphosphazenes (2-22)

Polymers **2-4** were synthesized as described previously.² Polymers **5-22** were synthesized from polymers **2-4** as follows. Solutions of sodium fluoroalkoxides were prepared in distilled THF (75 mL) from 2,2,2-trifluoroethanol, 2,2,3,3-tetrafluoropropanol, 2,2,3,3,3-pentafluoropropanol, and 2,2,3,3,4,4,5,5-octafluoropentanol (16.9 mmol for reactions with **2**, 13.4 mmol for reactions with **3**, and, 7.9 mmol for reactions with **4**) and sodium hydride (95%) (0.658 g, 16.5 mmol for

reactions with **2**, 0.521 g, 13.0 mmol for reactions with **3**, and, 0.315 g, 8.1 mmol for reactions with **4**). These solutions were added to solutions of **2**, **3**, and **4** (1.0 g, 4.1 mmol, 1.0 g, 3.2 mmol, and, 1.0 g, 1.97 mmol respectively) in distilled THF (100 mL). Reactions were carried out at room temperature and at reflux in THF for each polymer/alkoxide reaction. The reaction mixtures were stirred for 48 hours, concentrated by rotary evaporation, and purified by multiple precipitations into triply deionized water (pH~5), followed by multiple precipitations into hexanes. The co-substituted polymers were then dried for 48 hours in a vacuum oven at 55 °C to remove residual solvents. Typical yields ranged from 60-85% based on NMR calculation of side group ratios.

Representative NMR spectroscopy data are given for polymers **5**, **7**, and **9**.

For polymer **5**: ^1H NMR (d_8 -acetone): δ = 6.5 (t), 4.4 (m, overlapping(o)) 4.3 (m, o). ^{31}P NMR (d_8 -acetone): δ = -6.1 (s, br). ^{19}F NMR (d_8 -acetone): δ = -75.0 (s), -125.5 (s, br, o), -126.9 (s, br, o), -138.7 (s, br, o), -140.4 (s, br, o).

For polymer **7**: ^1H NMR (d_8 -acetone): δ = 4.4 (m). ^{31}P NMR (d_8 -acetone): δ = -6.2 (s, br). ^{19}F NMR (d_8 -acetone): δ = -75.0 (s), -83.4 (s), -124.2 (s).

For polymer **9**: ^1H NMR (d_8 -acetone): δ = 6.5 (t), 4.5 (m, o) 4.4 (m, o). ^{31}P NMR (d_8 -acetone): δ = -6.1 (s, br). ^{19}F NMR (d_8 -acetone): δ = -75.0 (s), -120.6 (s), -124.7 (s,br), -129.6 (s, br), -138.1 (s).

E. References

- 1) Allcock, H.R.; *Chemistry and Applications of Polyphosphazenes*; Wiley-Interscience: Hoboken, N.J., **2003**.
- 2) Allcock, H.R.; Maher, A.E.; Ambler, C.M. *Macromol.* **2003**, 35, 5566-5572.

Chapter 4

Dependence of Thermal and Mechanical Properties on the Composition of Mixed-Substituent Poly(fluoroalkoxyphosphazenes)

A. Introduction

Few materials have impacted modern technology more than elastomers. An elastomer is defined as a polymer that returns substantially to its original shape and size following removal of the force responsible for its deformation.¹ In 1839, Goodyear's discovery of the vulcanization of natural rubber revolutionized technology.² About 60 years later, synthetic materials were developed with similar properties to vulcanized natural rubber. Over the years many technologies from automobiles to aerospace vehicles have taken advantage of the unique physical and chemical properties characteristic of both natural and synthetic elastomers.^{3,4}

Most commodity elastomers have serious limitations, such as poor chemical resistance and a limited temperature range of operation due to poor flexibility at low temperatures and limited thermal stability.^{5,6} Fluoroelastomers overcome many of these disadvantages.⁵⁻⁸ The synthesis, properties, and fabrication of fluoroelastomers is discussed in detail in a recent review article.⁸ Most fluoroelastomers are either fluorocarbon polymers (based on co-polymers with vinylidene fluoride or tetrafluoroethylene) or fluorosilicone elastomers (figure 4-1). Fluorocarbon elastomers possess good chemical resistance and high thermal stability due to the nature of the carbon-fluorine bonds.⁸⁻¹¹ Fluorosilicone elastomers are polymers with a silicon-oxygen

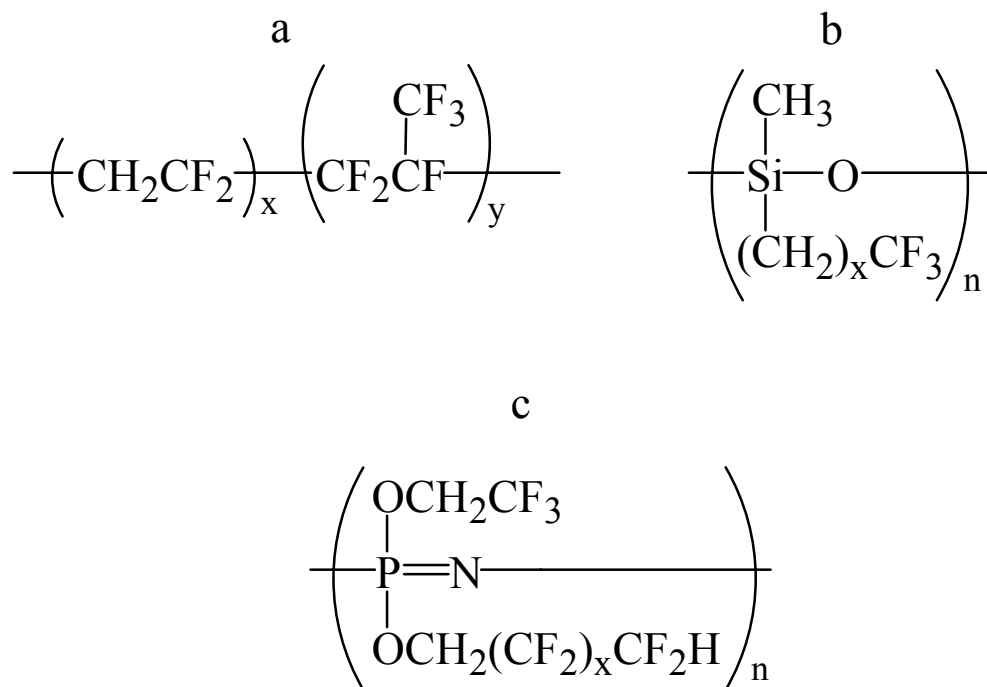


Figure 4-1: Examples of fluoroelastomers: a) vinylidene fluoride-hexafluoropropylene (VDF-HFP) fluorocarbon elastomer, b) fluorosilicone elastomer, c) poly(fluoroalkoxyphosphazene) elastomer

backbone and with fluoroalkyl side groups. These polymers generally have poorer thermal stability and mechanical properties than fluorocarbon elastomers, but have better low temperature flexibility.¹⁰

Mixed-substituent poly(fluoroalkoxyphosphazenes) are an alternative type of fluoroelastomer (Figure 4-1). These polymers have a backbone of alternating phosphorus and nitrogen atoms, with two fluoroalkoxy side groups linked to each phosphorus atom. Typically, each polymer chain bears two different types of side group, such as trifluoroethoxy and octafluoropentoxy, to prevent crystallization. These materials have better low temperature mechanical properties and lower glass transition temperatures than fluorosilicone elastomers¹², and also possess good thermal and oxidative stability.¹³ Initial development of poly(fluoroalkoxyphosphazene) elastomers was carried out by Horizons, Inc.¹⁴⁻¹⁶ and by the U.S. Army Laboratories.^{17,18} Commercially, PN-F (Firestone)^{19,20} and EypelTM-F (Ethyl Corporation)^{21,22} are examples of fluoroalkoxy phosphazene elastomers that have been used as materials for O-ring seals^{12,13,23}, air plenum seals²³ and in dental applications.^{13,24-26} As with most polymeric elastomers, the mechanical properties can be improved through cross-linking and compounding of the raw polymer gum with materials such as fumed silica or various types of carbon black.^{8,12,27} The aim of the current work was to examine the influence of different ratios of two different fluoroalkoxy side groups on the polymer properties. Polyphosphazenes with varying ratios of 2,2,3,3,4,4,5,5-octafluoropentoxy and 2,2,2-trifluoroethoxy side groups were utilized for this purpose.

B. Results and Discussion

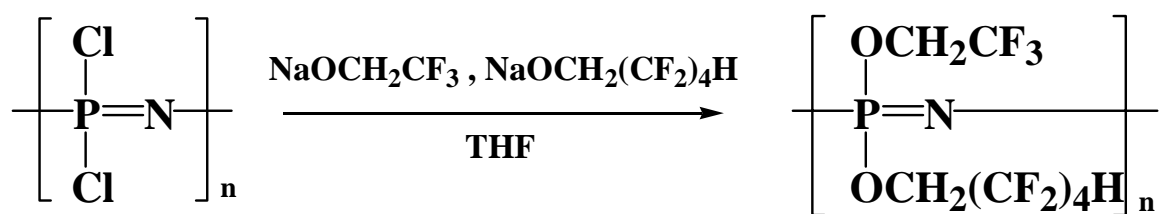
1. Synthesis and Structural Characterization of Polymers

Poly(dichlorophosphazene) (**1**) was prepared via the thermal ring opening polymerization of hexachlorocyclotriphosphazene. Polymer **1** readily underwent replacement of the labile chlorine atoms, by the fluoroalkoxide nucleophiles, sodium 2,2,3,3,4,4,5,5-octafluoropentoxide and 2,2,2-trifluoroethoxide in tetrahydrofuran (THF), to yield poly(fluoroalkoxyphosphazenes) as shown in table 4-1. Thus, the mixed-substituent polymers **3** through **8** were synthesized by the simultaneous addition of the sodium fluoroalkoxide solutions to **1** to yield polymers with 25% to 94% trifluoroethoxy substituents (scheme 4-1). Simultaneous addition of the nucleophiles was utilized due to the higher reactivity of the sodium trifluoroethoxide and the ability of the nucleophiles to undergo side group exchange reactions with each other. ^{31}P NMR spectroscopy was utilized to monitor the reactions to ensure complete replacement of the chlorine atoms. The single-substituent control polymers poly[bis(octafluoropentoxyphosphazene)] and poly[bis(trifluoroethoxyphosphazene)] (**2** and **9**) were synthesized by the addition of a slight excess of the sodium 2,2,3,3,4,4,5,5-octafluoropentoxide or sodium 2,2,2-trifluoroethoxide in THF to a solution of **1** in THF.

Polymers **2-9** were characterized using ^1H , ^{31}P , ^{13}C , and ^{19}F NMR spectroscopy. Quantitative information about the ratios of side groups was obtained from the ^1H NMR spectra. Although the peaks of the CH_2 protons of trifluoroethoxy and octafluoropentoxy groups overlap at 4.6 ppm, the ratios of side groups could still be determined integration

Table 4-1: Side Group Ratios and Molecular Weight Characterization

$[\text{NP}(\text{OCH}_2(\text{CF}_2)_4\text{H})_x(\text{OCH}_2\text{CF}_3)_y]_n$	x	y	%	M_n	M_w	<i>PDI</i>
			<i>Yeild</i>	$(\times 10^5)$	$(\times 10^5)$	
2	100	0	70	1.78	15.09	8.5
3	75	25	67	2.38	7.06	3.0
4	58	42	71	4.43	20.75	4.7
5	42	58	57	5.20	14.80	2.8
6	23	77	65	4.17	12.71	3.0
7	13	87	67	5.55	18.25	3.3
8	6	94	66	4.40	14.58	3.3
9	0	100	75	1.29	4.53	3.5



Scheme 4-1: Synthesis of Poly(fluoroalkoxyphosphazenes)

of the terminal proton in the octafluoropentoxy group at 6.6 ppm (figure 4-2). Twice the integration of the octafluoropentoxy terminal hydrogen is the amount of octafluoropentoxy CH₂ proton contribution to the overlapping peak at 4.6 ppm. ³¹P NMR spectra of the mixed-substituent polymers gave overlapping peaks from phosphorus atoms that bear two trifluoroethoxy groups, two octafluoropentoxy groups or one of each fluoroalkoxy group, and they appeared as a singlet at -6.1 ppm and could only be used for qualitative characterization. Fluorine-fluorine coupling was not detectable in the ¹⁹F NMR spectra due to the small coupling constants (<1 ppm) within the fluoroalkyl chains of the octafluoropentoxy side groups. This usually occurs only in symmetrically substituted fluoroalkanes.^{28,29}

The molecular weights of the poly(fluoroalkoxyphosphazenes) **2-9**, as determined by gel permeation chromatography (GPC) versus polystyrene standards, are shown in table 4-1. The broad polydispersities obtained (2.8-8.5) are typical of polymers prepared via the thermal ring opening polymerization route to polymer **1**.¹³ As a consequence the molecular weights of the fluoroalkoxy-substituted polymers also varied considerably and ranged from 1.29x10⁵-5.55x10⁵ for M_n. The range of the M_w values obtained (4.53x10⁵-2.075x10⁶) was considerably larger. In addition, factors such as hydrodynamic radius and molecular weight differences in the substituents probably influence the apparent molecular weight distributions.

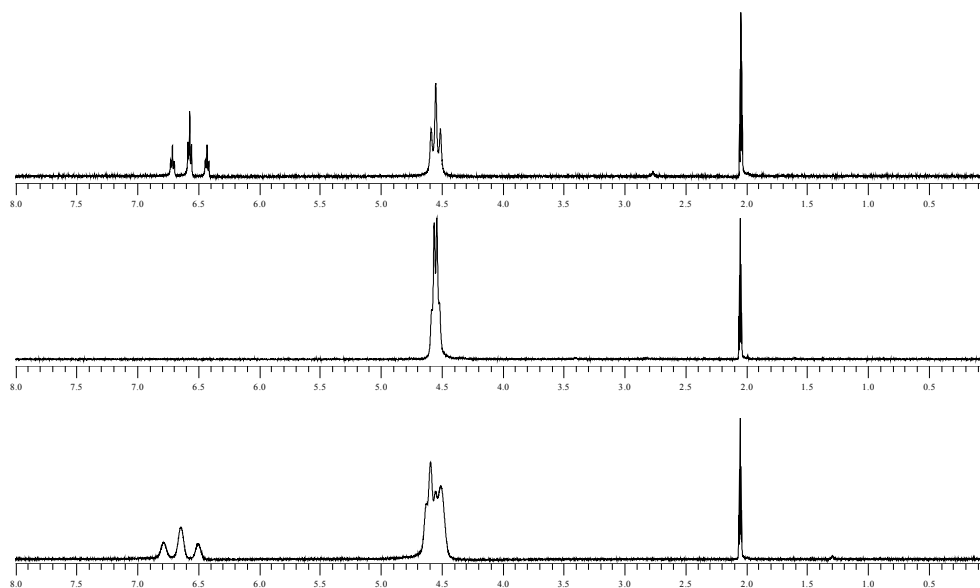


Figure 4-2: Substituent Ratio Determination by ^1H NMR in d_6 -acetone; Top spectrum) poly[bis(octafluoropentoxyphosphazene)] (2), middle spectrum) poly[bis(trifluoroethoxyphosphazene)] (9), bottom spectrum) mixed-substituent poly(fluoroalkoxyphosphazene) (5)

2. Fire Resistance and Thermal Stability

Limiting oxygen index tests and thermogravimetric analyses were performed on each of the polymers (table 4-2). Overall, the poly(fluoroalkoxyphosphazenes) possess excellent fire resistance and thermal stability. Incorporation of only 6% of octafluoropentoxy substituents was sufficient to increase the oxygen index (OI) values from a value of 26 for poly[bis(trifluoroethoxyphosphazene)] (**9**) to more than 40 for polymers **2-8**.³⁰ Incorporation of the octafluoropentoxy group increases the ratio of carbon to hydrogen, which generally results in better fire resistance (higher OI values).³¹ However, this alone is not enough to account for the magnitude of the observed increase. Other contributing factors include the increased fluorine content³² of the polymers that contain octafluoropentoxy substituents and possible thermal crosslinking reactions through the terminal hydrogen of the octafluoropentoxy side group. In addition, different pyrolysis residues were obtained from the trifluoroethoxy single substituent polymer (**9**) than for the other polymers. Polymer **9** gave only a small amount of black char after the polymer melted and self-extinguished. Polymers **2-8** also melted and self-extinguished, but left a small amount of adhesive gum that could not be ignited.

Fire resistance was dominated by the presence of the octafluoropentoxy side group but the thermal decomposition was controlled by the trifluoroethoxy side groups, as can be seen from the TGA results (table 4-2 and figure 4-3). The onset temperatures of decomposition for the polymers with trifluoroethoxy substituents were all near 380 °C and T_{50} s ranged from 575-595 °C. By contrast, the octafluoropentoxy single-substituent polymer showed no weight loss until 520 °C and had a faster rate of decomposition (T_{50}

Table 4-2. Thermal Analysis of Polymers 2-9 by LOI, TGA and DSC

Polymer	Trifluoroethoxy substituent (%)	Oxygen Index	Onset T °C	T₅₀ °C	T_g °C	Mesophase °C	T_m °C
2	0	>40	520	630	-72	-	-
3	25	>40	380	580	-69	-	-
4	42	>40	380	595	-72	-	-
5	58	>40	380	575	-73	-	-
6	77	>40	380	575	-73	-	-
7	87	>40	380	577	-73	-	-
8	94	>40	380	580	-73	16	139
9	100	26	380	580	-73	66	234

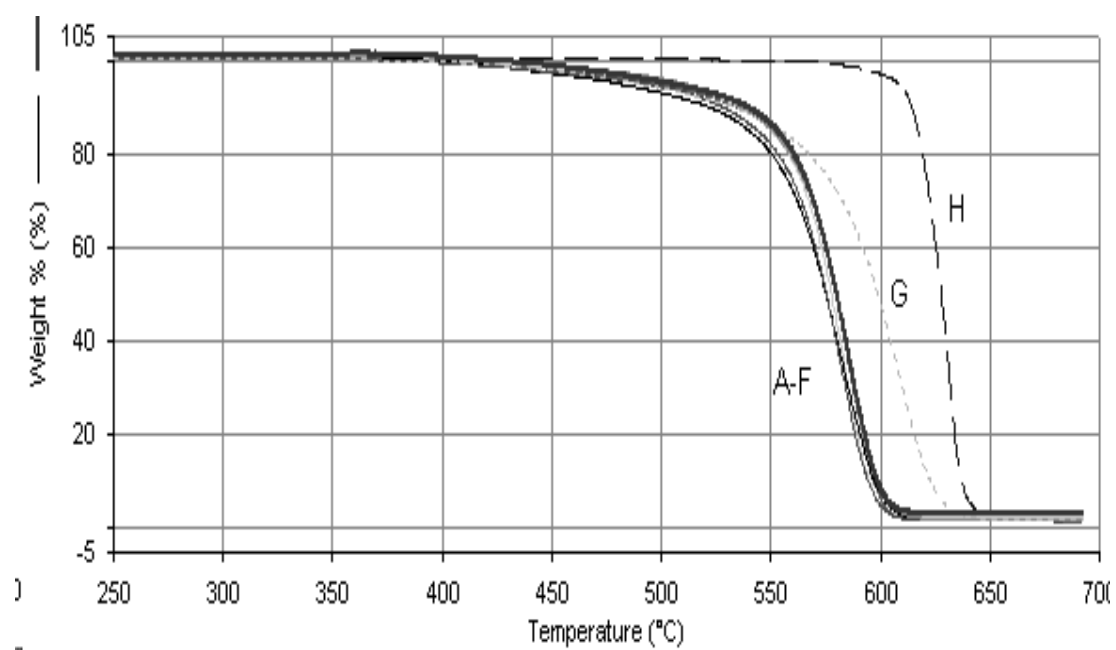


Figure 4-3: TGA Traces of Polymers 2-9; A-F) polymers 3 and 5-9, G) polymer 4, H) polymer 2

of ~ 620 °C) than polymers **3-9**. The thermal stability is also influenced by depolymerization reactions of the polymers probably to small-molecule cyclic species. It should be noted that depolymerization of some poly(fluoroalkoxyphosphazenes), over long periods of time at temperatures above 150 °C, can occur below the onset temperatures observed in the TGA experiments.³³

3. Glass Transition Temperatures

The glass transition temperatures of polymers **2-9** were found to be between -69 and -73 °C (-92 °F to -99 °F) by DSC (Table 4-2). This indicates excellent low temperature flexibility, a property that is important for elastomers to be used in low temperature environments such as high altitude aerospace applications. Polymers that contain up to 87% trifluoroethoxy substituents (**2-7**) are amorphous polymers with no additional transitions detected above the T_g . However, polymers **8** and **9**, with 94% and 100% trifluoroethoxy substituents respectively, were semicrystalline materials. Mesophase transitions¹² at 16 °C and 66 °C and crystalline melting transitions of 139 °C and 234 °C respectively were detected for **8** and **9**, as shown in figure 4-4. With just 6% incorporation of the octafluoropentoxy substituent, polymer **8** showed significantly decreased crystallinity and lower temperature transitions (mesophase and T_m) than the trifluoroethoxy single-substituent polymer (**9**). Thus, incorporation of the octafluoropentoxy side group disrupts crystalline domains in the poly(fluoroalkoxyphosphazenes) due to the size, flexibility and mobility of the longer fluoroalkoxy side group. Figure 4-4 illustrates the absence of mesophase and crystalline

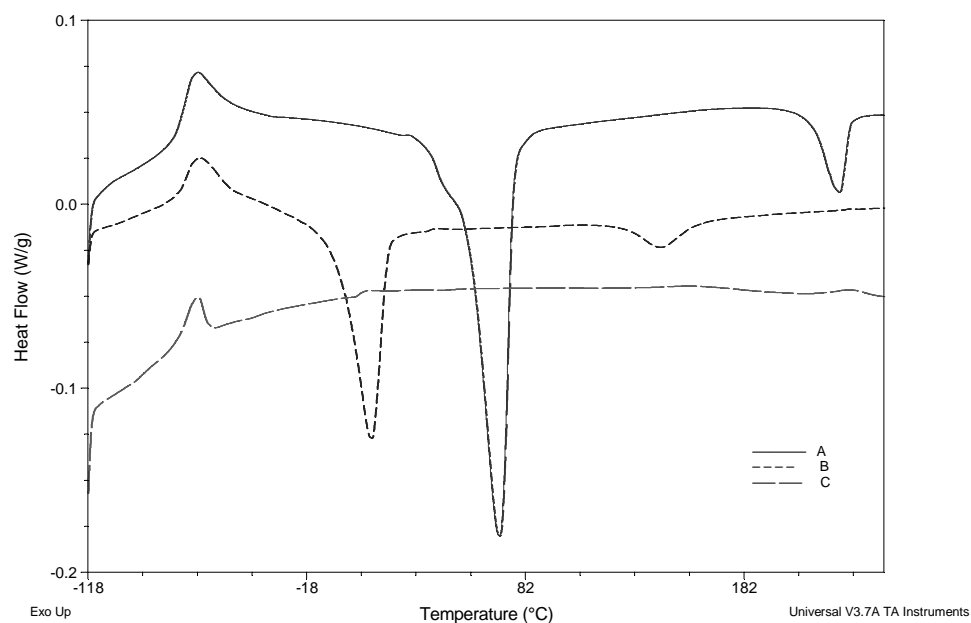


Figure 4-4: DSC Traces Showing Loss of Crystallinity; A) poly[bis(trifluoroethoxyphosphazene)] (9), B) mixed-substituent poly(fluoroalkoxyphosphazene) (8) with 94 % trifluoroethoxy substituents, C) mixed-substituent poly(fluoroalkoxyphosphazene) (6) with 77% trifluoroethoxy substituents

melting transitions in the polymers that have more than 6% octafluoropentoxy substituents (**2-7**).

4. Mechanical Properties

Qualitatively, the polymers can be divided into three groups. The mixed substituent poly(fluoroalkoxyphosphazenes) **4-7** (25-87% trifluoroethoxy substituent) were elastomeric gums which, when crosslinked, are applicable elastomers. Only polymer **4** had a tendency to undergo viscous flow over a period of several weeks. Poly[bis(octafluoropentoxyphosphazene)] (**2**) and the mixed-substituent polymers with 25% and 94% trifluoroethoxy substituents (**3** and **8**) had tough wax-like properties, while poly[bis(trifluoroethoxyphosphazene)] (**9**) is a tough, fibrous, microcrystalline material. The properties of polymers **8** and **9** are attributed to the crystallinity present in the samples, but an explanation for the similar properties seen in polymers **2** and **3** is less clear. The non-elastomeric character of polymers with 75% or more octafluoropentoxy substituents might be a consequence of the ability of the terminal hydrogen of the octafluoropentoxy side group to participate in dipole-dipole hydrogen bonding like interactions. These types of interactions have been used to explain for the higher boiling points of molecules with the CF_2H unit compared to similar molecules with the CF_3 moiety.³⁴⁻³⁶ In addition, Künzler and Ozark noticed that copolymers of dimethylacrylamide with methacrylate end-capped polydimethylsiloxanes that had octafluoropentoxy side chains did not phase separate.³⁷ They attributed this to hydrogen bond interactions between the terminal hydrogen and the amide linkage.³⁷ Thus, it is possible that the high octafluoropentoxy content of polymers **2** and **3** could induce

sufficient inter- and intra-chain bond-dipole interactions to account for the tough, wax-like properties that are characteristic of these polymers.

Variations in the ratios of side groups had a marked effect on the mechanical properties, as summarized in table 4-3. The stress at yield was greater than 1.8 MPa for polymers **2** and **3** (0-25% trifluoroethoxy side group) but decreased with higher incorporation of the trifluoroethoxy substituent to ~0.2 MPa for polymers **4** through **7** (42-87% trifluoroethoxy content) (figure 4-5) until it reached more than 4.5 MPa for polymers **8** and **9** (94%-100% trifluoroethoxy substituent). This behavior can be explained in terms of the bond-dipole interactions proposed for the octafluoropentoxy side group and the crystalline properties of polymers **8** and **9**. The bond-dipole interactions decrease in number with increased incorporation of the trifluoroethoxy group. These interactions can also account for decreased elongation-to-break of the octafluoropentoxy single- substituent polymer (**2**) (9.6%) and polymer **3** (90.6%) relative to mixed-substituent polymers **4** through **7** that had elongation to break values greater than 600% (figure 4-5). At very high incorporations of the trifluoroethoxy side group, crystallinity becomes an important factor as seen in the stress increases for polymers **8** and **9** compared to the polymers with lower trifluoroethoxy incorporation. Intermolecular interactions through crystalline “cross-links” have this effect in other polymer systems. Increases in intermolecular forces decreased the elongation-to-break substantially, but increased the stress at yield (figure 4-5). However, while only a small amount of the octafluoropentoxy side group was needed to reduce the crystallinity of the trifluoroethoxy single-substituent polymer, more than 25 % of the trifluoroethoxy side groups were

Table 4-3: Mechanical Properties of Polymers 2-9; *Polymer did not yield

Polymer	Trifluoroethoxy Substituent (%)	Stress at Yield (MPa)	Stress Std. Dev.	% Strain	Strain Std. Dev.	Young's Modulus (MPa)	Modulus Std. Dev.
2	0	3.06	0.61	26	9.6	36.0	3.34
3	25	1.86	0.71	90	30.4	17.8	2.10
4	42	0.21	0.01	1217	251	0.46	0.05
5	58	0.24	0.04	1258	49.9	0.64	0.08
6	77	0.24	0.02	1753	100	0.65	0.03
7	87	0.20	0.01	686	39.2	0.68	0.09
8	94	4.5	1.08	147	40.0	16.4	9.44
9	100	5.3 [*]	2.65 [*]	4.8	2.6	158	54.99

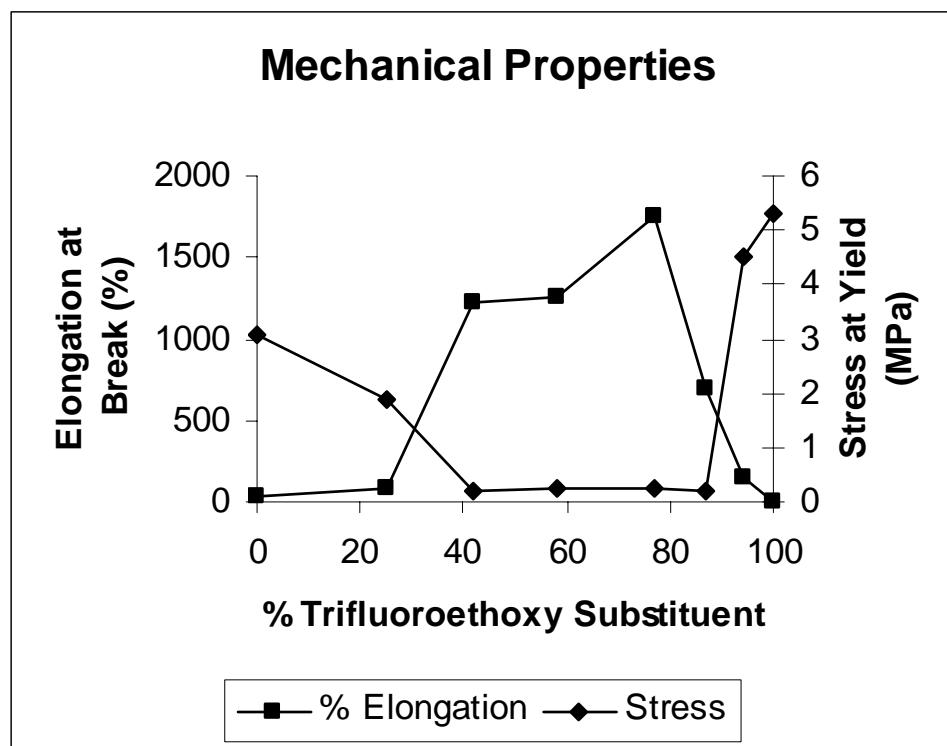


Figure 4-5: Mechanical Properties of Polymers 2-9

required to induce a similar effect on the mechanical properties of the octafluoropentoxy single-substituent polymer system.

The values of the Young's modulus followed the same trend as those found for the stress results (figure 4-6). The single-substituent polymers (**2** and **9**) and the mixed-substituent polymers closest in composition (**3** and **8**) showed higher modulus values than the other mixed-substituent polymers, probably due to the magnitude of molecular interactions which take place in the system. The largest increase in modulus came between polymers **8** and **9**, where the greater crystallinity of the single-substituent polymer caused an increase of over 100 MPa.

The influence of molecular weight on the mechanical properties was examined by a comparison of polymers **4-8**. GPC analysis of the mixed-substituent polymers **4** gave a polydispersity of 4.7 and an M_w of over 2×10^6 . Polymers **5-8** had similar molecular weights (M_n 4.17×10^5 – 5.55×10^5 , M_w 1.3 – 1.8×10^6) and similar polydispersities of 2.8–3.3. Despite these differences, polymer **4** showed mechanical properties very similar to polymers **5-7**. However, polymer **8** showed drastically different mechanical properties, such as strength at yield and elongation to break, than polymers **5-7**. This suggests that the mechanical properties of the polymers studied here depend primarily on polymer composition and not on molecular weight.

DSC experiments were used to examine all the polymers before and after fabrication into thin sheets to ensure that no increase in crystallinity had occurred. Semi-crystalline polymers (**8** and **9**) and waxy polymers (**2** and **3**) were also analyzed after microtensile testing. DSC traces showed no changes that would be indicative of increased crystallinity after fabrication as illustrated by figure 4-7, which shows the DSC

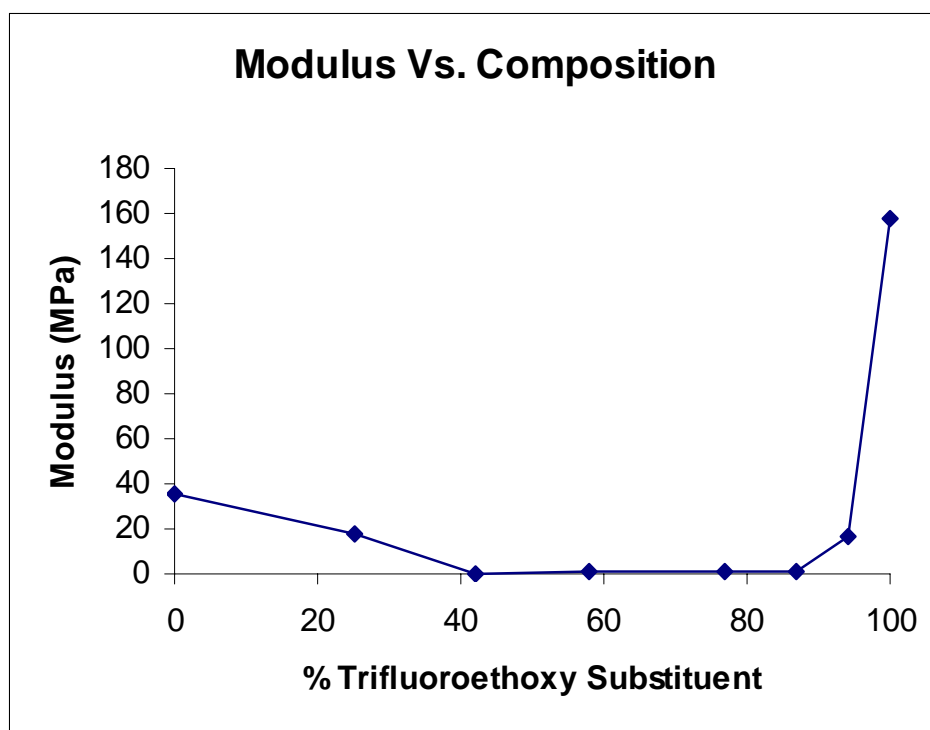


Figure 4-6 Young's Moduli of Polymers 2-9

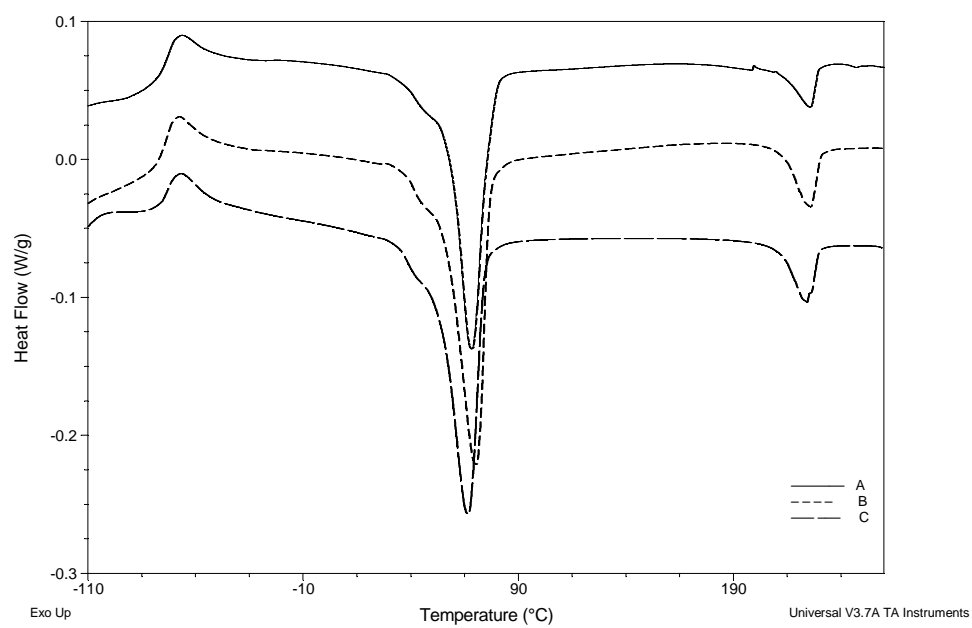


Figure 4-7: DSC Traces of Poly[bis(trifluoroethoxyphosphazene)] (9); A) prior to hot-press, B) after hot-press, C) after mechanical testing

traces for poly[bis(trifluoroethoxyphosphazene)] (**9**) before and after hot-press fabrication and also after microtensile testing.

C. Conclusions

The poly[bis(fluoroalkoxyphosphazenes)] examined showed good thermal stability, high OI values and large variations in mechanical properties. The T_g and T_d values of the co-substituted polymers differed very little from one another but the mechanical properties and molecular interactions were highly dependent on the ratios of the side groups. Polymers **2**, **3**, **8**, and **9** had the strongest intermolecular interactions and showed higher Young's modulus and stress at yield, but much lower elongation to break, than polymers **4-7**.

Polymers **4-7** have the properties needed for the fabrication of good elastomers. These polymers, which ranged in composition from 42% to 87% of the trifluoroethoxy side group, possess very similar thermal and mechanical behavior. Further improvements to these polymers through the incorporation of a cross-linking moiety and compounding with the proper materials can yield resilient low temperature elastomers.

D. Experimental Section

1. Materials

2,2,2-trifluoroethanol and 2,2,3,3,4,4,5,5-octafluoropentanol were used as received from Aldrich and VWR respectively. Sodium hydride (95% in mineral oil) was obtained from Aldrich and was weighed into Schlenk flasks in an argon filled glove box.

Tetrahydrofuran was distilled into the reaction flask from sodium benzophenone under a dry argon atmosphere.

All reactions were carried out using standard Schlenk techniques under an atmosphere of dry argon.

2. Equipment

^1H , ^{13}C , and ^{31}P spectra were recorded on a Bruker AMX-360 NMR spectrometer operated at 360, 90.56 and 90.27 MHz, respectively. ^1H and ^{13}C NMR were referenced to external tetramethylsilane. ^{31}P and ^{19}F NMR (Bruker DPX-300, 282 MHz) proton decoupled chemical shifts were relative to external 85% phosphoric acid and trichlorofluoromethane, respectively. Molecular weights and polydispersities were estimated using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector, Phenomenex Phenogel 10 μm linear and mixed-bed analytical columns, and calibrated versus polystyrene standards. Sample elution was carried out at 40 $^{\circ}\text{C}$ with a 0.1 wt % solution of tetra-*n*-butylammonium nitrate (Aldrich) in THF (OmniSolv). Thermal transitions such as T_g , T_m , and crystalline transitions were determined through analysis via a TA Q10 differential scanning calorimeter. Calibration was accomplished with indium, water and cyclohexane standards. All analyses were conducted over a temperature range of -120 $^{\circ}\text{C}$ to 320 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}$ per minute. The purge gas was nitrogen, flowing at 50 ml/min. Thermal decomposition traces were obtained from a Perkin-Elmer TGA 7 Thermogravimetric Analyzer, equipped with a standard oven and calibrated with nickel,

perkalloy, and alamel. Heating occurred at a rate of 10 °C/min from 50 °C to 800 °C under a nitrogen atmosphere and a flow rate of 20 ml/min. Limiting oxygen indices were determined through the use of a device constructed in accordance with ASTM-D-2863-91, and modified for testing bulk polymer samples as described previously.³⁸ The apparatus consists of a flame chamber and purge gas regulators; tests were run in an oxygen/nitrogen environment. LOI was taken as the oxygen concentration at which the material sustained burning for 30 seconds and self extinguished. A Carver Laboratory Press was operated for 2 hr at 85 °C followed by 16 hr at ambient temperature to fabricate thin sheets of the polymers. Thicknesses were controlled using stainless steel stops with a thickness of 0.8 mm as per ASTM method D 1708-96 specifications. A microtensile die also conforming to ASTM method D 1708-96 specifications was used to prepare samples for microtensile testing. Microtensile tests were performed on an Instron 4201 in accordance with ASTM method D 1708-96 with a 100 N static load cell and at a rate of 100 mm/min.

3. Synthesis of Poly[bis(fluoroalkoxyphosphazenes)] 2-9

Poly(dichlorophosphazene) (**1**) was prepared via thermal ring-opened polymerization of hexachlorocyclotriphosphazene at 250 °C in an evacuated sealed tube. Polymer **1** was dissolved in 1 L THF in a 3 L round bottom flask equipped with a mechanical stirrer. Sodium fluoroalkoxide solutions were prepared by the slow addition of varying ratios of 2,2,2-trifluoroethanol and 2,2,3,3,4,4,5,5-octafluoropentanol to slurries of NaH (95%) in 400 mL THF. The mixed sodium fluoroalkoxide solutions were

then added to the solution of **1**, and the reaction mixture was stirred for 18 hr at ambient temperature. The mixture was concentrated by removal of THF via a rotary evaporator and the solids were precipitated into acidic water (pH \sim 4). The polymers were rinsed with triply deionized water, air-dried overnight, dissolved in THF and again precipitated into triply deionized water. This was followed by two precipitations into hexane and one into dichloromethane from THF. The product was dried for two days in a vacuum oven at 65 °C.

The amounts of polymer **1** (15.0 g, 129 mmol) and 95% NaH (7.74 g, 305 mmol) used for the synthesis of polymers **2** through **9** was kept constant.

For polymer **2**, 72.02 g (310 mmol) 2,2,3,3,4,4,5,5-octafluoropentanol was used for the synthesis of the fluoroalkoxide solution. The product was isolated as a white fibrous/waxy material. Yield = 46.0 g (70%). ^1H NMR (d_6 -acetone): δ = 6.5 (t of t, J = 52.5, 25.2 Hz, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$) 4.3 (t, J = 13.7 Hz, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$). ^{13}C NMR (d_6 -acetone): δ = 108-120 (overlapping multiplets, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 64.5 (t, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$). ^{31}P NMR (d_6 -acetone): δ = -5.8 (s). ^{19}F NMR (d_6 -acetone): -120.6 (s), -124.7 (s), -129.5 (s), -138.0 (s) ($\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$).

For polymer **3**, 7.63 g (76 mmol) 2,2,2-trifluoroethanol and 54.31 g (234 mmol) 2,2,3,3,4,4,5,5-octafluoropentanol were used for the synthesis of the fluoroalkoxide solution. The product was isolated as a white fibrous/waxy material. Yield = 38.2 g (67%). ^1H NMR (d_6 -acetone): δ = 6.6 (t, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.6 (mlt, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.6 (mlt, OCH_2CF_3). ^{13}C NMR (d_6 -acetone): δ = 108-120 (overlapping multiplets, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 64.5 (t, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 124 (qt,

OCH₂CF₃), 65 (t, OCH₂CF₃). ³¹P NMR (d₆-acetone): δ = -6.1 (s). ¹⁹F NMR (d₆-acetone): δ = -120.6 (s), -124.7 (s), -129.5 (s), -138.0 (s) (OCH₂CF₂CF₂CF₂CF₂H), -74.7 (s, OCH₂ CF₃).

For polymer **4**, 11.90 g (119 mmol) 2,2,2-trifluoroethanol and 44.42 g (191 mmol) 2,2,3,3,4,4,5,5-octafluoropentanol were used for the synthesis of the fluoroalkoxide solution. The product was isolated as a tan gum. Yield = 36.0 g (71%). ¹H NMR (d₆-acetone): δ = 6.6 (t, OCH₂CF₂ CF₂ CF₂ CF₂H), 4.6 (mlt, OCH₂CF₂ CF₂ CF₂ CF₂H), 4.6 (mlt, 2H, OCH₂CF₃). ¹³C NMR (d₆-acetone): δ = 108-120 (overlapping multiplets, OCH₂CF₂ CF₂ CF₂ CF₂H), 64.5 (t, OCH₂CF₂ CF₂ CF₂ CF₂H), 124 (qt, OCH₂CF₃), 65 (t, OCH₂CF₃). ³¹P NMR (d₆-acetone): δ = -6.1 (s). ¹⁹F NMR (d₆-acetone): δ = -120.6 (s), -124.7 (s), -129.5 (s), -138.0 (s) (OCH₂CF₂CF₂CF₂CF₂H), -74.7 (s, OCH₂ CF₃).

For polymer **5**, 16.84 g (168 mmol) 2,2,2-trifluoroethanol and 32.97 g (142 mmol) 2,2,3,3,4,4,5,5-octafluoropentanol were used for the synthesis of the fluoroalkoxide solution. The product was isolated as a tan gum. Yield = 26.2 g (57%). ¹H NMR (d₆-acetone): δ = 6.6 (t, OCH₂CF₂ CF₂ CF₂ CF₂H), 4.6 (mlt, OCH₂CF₂ CF₂ CF₂ CF₂H), 4.6 (mlt, 2H, OCH₂CF₃). ¹³C NMR (d₆-acetone): δ = 108-120 (overlapping multiplets, OCH₂CF₂ CF₂ CF₂ CF₂H), 64.5 (t, OCH₂CF₂ CF₂ CF₂ CF₂H), 124 (qt, OCH₂CF₃), 65 (t, OCH₂CF₃). ³¹P NMR (d₆-acetone): δ = -6.1 (s). ¹⁹F NMR (d₆-acetone): δ = -120.6 (s), -124.7 (s), -129.5 (s), -138.0 (s) (OCH₂CF₂CF₂CF₂CF₂H), -74.7 (s, OCH₂ CF₃).

For polymer **6**, 22.76 g (228 mmol) 2,2,2-trifluoroethanol and 19.30 g (83 mmol) 2,2,3,3,4,4,5,5-octafluoropentanol were used for the synthesis of the fluoroalkoxide solution. The product was isolated as a tan gum. Yield = 25.9 g (65%). ^1H NMR (d_6 -acetone): δ = 6.6 (t, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.6 (m, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.6 (m, 2H, OCH_2CF_3). ^{13}C NMR (d_6 -acetone): δ = 108-120 (overlapping multiplets, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 64.5 (t, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 124 (qt, OCH_2CF_3), 65 (t, OCH_2CF_3). ^{31}P NMR (d_6 -acetone): δ = -6.1 (s). ^{19}F NMR (d_6 -acetone): δ = -120.6 (s), -124.7 (s), -129.5 (s), -138.0 (s) ($\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), -74.7 (s, OCH_2CF_3).

For polymer **7**, 24.85 g (248 mmol) 2,2,2-trifluoroethanol and 14.40 g (62 mmol) 2,2,3,3,4,4,5,5-octafluoropentanol were used for the synthesis of the fluoroalkoxide solution. The product was isolated as a tan gum. Yield = 24.1 g (67%). ^1H NMR (d_6 -acetone): δ = 6.6 (t, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.6 (m, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.6 (m, 2H, OCH_2CF_3). ^{13}C NMR (d_6 -acetone): δ = 108-120 (overlapping multiplets, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 64.5 (t, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 124 (qt, OCH_2CF_3), 65 (t, OCH_2CF_3). ^{31}P NMR (d_6 -acetone): δ = -6.1 (s). ^{19}F NMR (d_6 -acetone): δ = -120.6 (s), -124.7 (s), -129.5 (s), -138.0 (s) ($\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), -74.7 (s, OCH_2CF_3).

For polymer **8**, 28.60 g (286 mmol) 2,2,2-trifluoroethanol and 6.00 g (26 mmol) 2,2,3,3,4,4,5,5-octafluoropentanol were used for the synthesis of the fluoroalkoxide solution. The product was isolated as a white semi-crystalline material. Yield = 22.0 g (66%). ^1H NMR (d_6 -acetone): δ = 6.6 (t, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.6 (m, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 4.6 (m, 2H, OCH_2CF_3). ^{13}C NMR (d_6 -acetone): δ = 108-120 (overlapping multiplets, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), 64.5 (t, $\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$),

124 (qt, OCH_2CF_3), 65 (t, OCH_2CF_3). ^{31}P NMR (d_6 -acetone): $\delta = -6.1$ (s). ^{19}F NMR (d_6 -acetone): $\delta = -120.6$ (s), -124.7 (s), -129.5 (s), -138.0 (s) ($\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$), -74.7 (s, OCH_2CF_3).

For polymer **9**, 31.04 g (310 mmol) 2,2,2-trifluoroethanol was used for the synthesis of the fluoroalkoxide solution. The product was isolated as a white semi-crystalline material. Yield = 23.5 g (75%). ^1H NMR (d_6 -acetone): $\delta = 4.6$ (q, $J = 7.9$ Hz, 4H, OCH_2CF_3). ^{13}C NMR (d_6 -acetone): $\delta = 124$ (qt, OCH_2CF_3), 65 (t, OCH_2CF_3). ^{31}P NMR (d_6 -acetone): $\delta = -6.3$ (s). ^{19}F NMR (d_6 -acetone): -74.7 (s).

E. References

- 1) Blackley, D.C. *Synthetic Rubbers: Their Chemistry and Technology*; Applied Science Publishers: New York, 1983; p 1.
- 2) Fried, J.R. *Polymer Science and Technology*; Prentice Hall: Englewood Cliffs, 1995; p 2.
- 3) *Science and Technology of Rubber* 2nd ed.; Mark, J.E.; Erman, B.; Elrich, F.R., Ed.; Academic Press: New York, 1994.
- 4) *Handbook of Elastomers* 2nd ed.; Bhowmick, A.K.; Stephens, H.L., Ed.; Marcel Dekker: New York, 2001.
- 5) Logothetis, A.L. In *Organofluorine Chemistry*, Banks, R.E.; Smart, B.E.; Tetlow, J.C., Ed.; Plenum Press: New York, 1994; Chapter 16.
- 6) Schmiegel, W.W. In *Chemistry of Fluorine Compounds II: A Critical Review*; Hudlicky, M.; Pavlath, A.E., Ed.; ACS Monograph 187, American Chemical Society: Washington, 1995; p 1116.
- 7) Tullo, A.H.; *Chem. Eng. News*, **2002**, 80, 15-16.
- 8) Ameduri, B.; Boutevin, B.; Kostov, G. *Prog. Polym. Sc.* **2001**, 26, 105-188.
- 9) Saint-Loup, R.; Manseri, A.; Ameduri, B.; Lebrete, B.; Vignane, P. *Macromol.* **2002**, 35, 1524-1536.
- 10) Thomas, R.R. In *Fluoropolymers 2: Properties*, Hougham, G.; Cassidy, P.E.; Johns, K.; Davidson, T., Ed.; Kluwer Academic/Plenum Publishers: New York, 1999; Chapter 4.
- 11) Drobny, J.G. *Technology of Fluoropolymers*, CRC Press: New York, 2001; Ch 5.

- 12) Lohr, D.F.; Penton, H.R. In *Handbook of Elastomers*, 2nd ed.; Bhowmick, A.K.; Stephens, H.L., Ed.; Marcel Dekker: New York, 2001; Chapter 23.
- 13) Allcock, H.R. *Chemistry and Applications of Polyphosphazenes*, Wiley-Interscience: Hoboken, N.J., 2003.
- 14) Rose, S.H. *J. Polym. Sci., Ser. B*, **1968**, 6, 837-839.
- 15) Rose, S.H. *US Patent* 3,515,688 **1970**.
- 16) Reynard, K.A.; Rose, S.H. *US Patent* 3,700,629, **1972**.
- 17) Singler, R.E.; Schneider, N.S.; Hagnauer, G.L. *Polym. Eng. Sci.* **1975**, 15, 321-338.
- 18) Singler, R.E.; Hagnauer, G.L.; Sicka, R.W. *ACS Symp. Ser.* **1982**, 193, 229-242.
- 19) Tate, D.P. *J. Polym. Sci., Polym. Symp.* **1974**, 48, 33-45.
- 20) Tate, D.P. *Rubber World* **1975**, 172, 41-43.
- 21) Kolich, C.H.; Klobucar, W.D.; Books, J.T. *US Patent* 4,945,193, **1990**.
- 22) Penton, H.R. *ACS Symp. Ser.* **1988**, 360, 277-282.
- 23) *EypelTM-F Performance Elastomers*; Sales Brochure, Ethyl Corporation, 1986.
- 24) Gettleman, L. *Phosphorus, Sulfur and Silicon*, **1999**, 144-146, 205-208.
- 25) Gettleman, L.; Vargo, J.M.; Gebert, P.H.; Farris, C.L.; LeBouef, R.J.; Rawls, H.R. *Polym. Sci. Technol.*, **1987**, 35, 55-61.
- 26) Gettleman, L.; Gebert, P.H. *US Patent* 04,661,065, **1987**.
- 27) Lohr, D.F.; Beckman, J.A. *Rubber & Plastics*, June 21, 1982; pp 16-17.
- 28) Mooney, E.F. *An Introduction to ¹⁹F NMR Spectroscopy*; Heyden & Son: New York, 1970; pp 9-10.
- 29) Berger, S.; Braun, S.; Kalinowski, H. *NMR Spectroscopy of the Non-metallic Elements*, Beconsall, J., trans.; John Wiley & Sons: New York, 1997; pp 636-643.

- 30) The apparatus employed in our laboratory is limited to measurements of OIs up to 40 with accuracy.
- 31) Coad, E.C.; Rasmussen, P.G. In *Fire and Polymers II: Materials and Tests for Hazard Prevention*, Nelson, G.L., Ed.; ACS Symposium Series 599; American Chemical Society: Washington, DC, 1995; pp 256-257.
- 32) Lewin, M. In *Fire Retardancy of Polymers: The Use of Intumescence*, Le Bras, M.; Camino, G.; Bourbigot, S.; Delobel, R., Ed.; The Royal Society of Chemistry: Cambridge, UK, 1998; p 7.
- 33) Connelly, T.M.; Gillham, J.K. *J. Appl. Polym. Sci.* **1976**, 20, 473-488.
- 34) Smart, B.E. In *Chemistry of Fluorine Compounds II: A Critical Review*; Hudlicky, M.; Pavlath, A.E., Ed.; ACS Monograph 187, American Chemical Society: Washington, 1995; p 982.
- 35) Woolf, A.A. *J. Fluor. Chem.* **1990**, 50, 89-99.
- 36) Hudlicky, M. *Chemistry of Organic Fluorine Compounds*, The Macmillan Company: New York, 1962.
- 37) Künzler, J.; Ozark, R. *J. Appl. Polym. Sci.* **1997**, 65, 1081-1089.
- 38) Hindersinn, R.R. In *Fire and Polymers: Hazards Identification and Prevention*, Nelson, G.L., Ed.; ACS Symposium Series 425; American Chemical Society: Washington, DC, 1990; pp 91-92.

Chapter 5

Synthesis and Conductive Properties of Polyphosphazenes Bearing Sulfonimide Functional Groups: Evaluation as Single Ion Conductors

A. Introduction

Secondary or rechargeable lithium batteries are lightweight systems that have high power densities when compared to lead-acid or nickel based materials and offer a solution to numerous energy storage problems.^{1,2} Traditional lithium ion battery systems contain liquid electrolytes that give high conductivities due to high ion mobility in the electrolyte.¹ However, these systems have inherent disadvantages such as the high flammability, electrolyte containment, and possible reactions of the liquid electrolytes with the anode.¹ For these reasons, solid-state lithium battery systems are the subject of intense research.^{1,3} Solid polymer electrolytes (SPEs) are polymeric materials that can transport ions without the aid of a liquid electrolyte. However, such systems are not yet able to achieve the high conductivities needed to compete with most commercially available batteries.⁴ Many commercial lithium ion battery cells use LiPF_6 mixed with a polymer electrolyte to increase the concentration of charge carriers and the overall lithium ion transport.⁵ However, PF_6^- binds to the lithium cation, decreasing ionic conductivity. Moreover, LiPF_6 is susceptible to thermal decomposition.¹ The use of a large delocalized anion in place of PF_6^- can weaken the ionic bonding and the lithium ion transport can thereby be increased.⁶

Several research groups have attempted to increase cation mobility in SPEs through immobilization of an anion by linkage to a polymer to make single ion

conductors.⁷⁻¹⁰ To be effective, these materials must achieve high ionic dissociation. Ideally, the anion bound to the polymer electrolyte should have a highly delocalized charge and be the conjugate base for very strong acids.⁶ Recently, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) has been found to be one of the most weakly coordinating salts yet discovered.⁸ Weak coordination between lithium and the anion provides access to a high concentration of charge carriers and increased ion transport. Watanabe and co-workers used a polymeric analogue (poly(2-oxo-1-difluoroethylene sulfonylimide)) of LiTFSI salt as a single ion conductive material and achieved ambient temperature conductivities of 10^{-7} S/cm.¹¹ Shriver and coworkers synthesized siloxane polymers with ethyleneoxy and trifluoromethylsulfonamide functionalized side chains and obtained maximum ambient temperature conductivities in the range of 10^{-6} S/cm.⁵

A small molecule analog of TFSI, is the sulfonylimide derivative with the structure $\text{HOC}_6\text{H}_4\text{SO}_2\text{N}(\text{Na})\text{SO}_2\text{CF}_3$. This was developed in our laboratories for use in proton conducting fuel cell membranes.^{12,13} The work described here incorporates a lithiated derivative of this molecule into mixed-substituent polyphosphazenes that bear both sulfonimide and 2-(2-methoxyethoxy)ethoxy pendent groups for use as a single ion conductor. The methoxyethoxyethoxy side group has already been shown to possess good properties for lithium ion transport.¹⁴⁻¹⁷ The lone pair electrons on each oxygen atom function as weak lithium ion coordination sites, and this increases the overall ion transport. Lithium ion transport is also increased by a large free volume due to the flexibility of the methoxyethoxyethoxy side group. Polymers with oligoethyleneoxy side groups usually have low T_g s and significant macromolecular motion. In this work, the

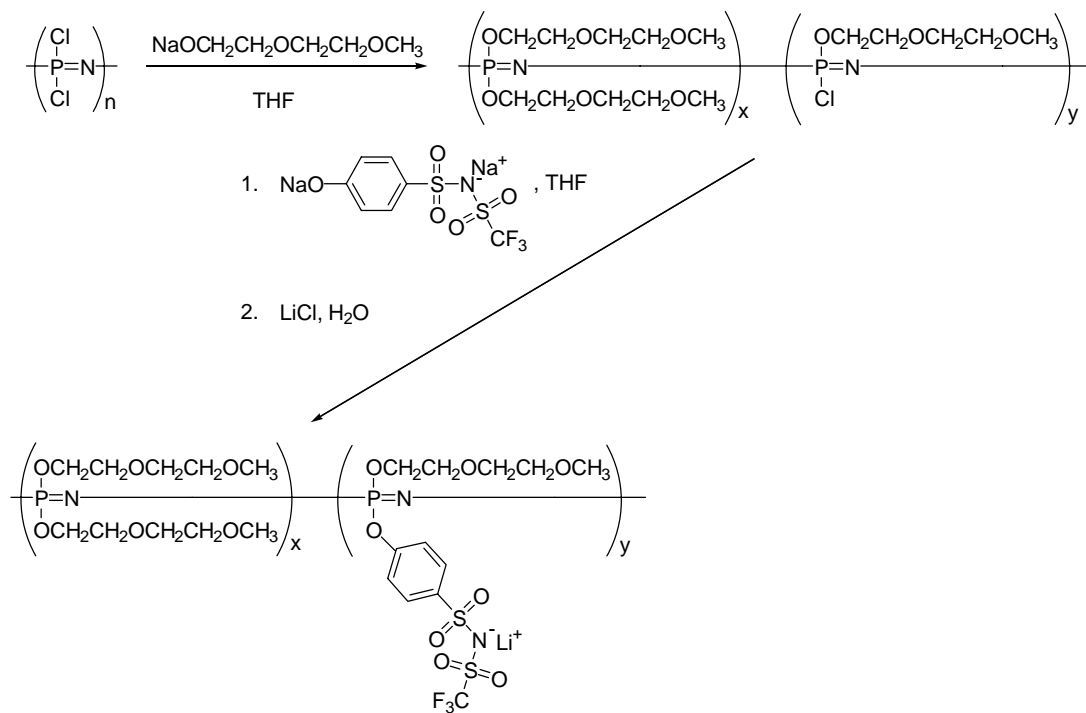
percentage of side groups functionalized with sulfonimide groups was varied from 5% to 22% incorporation in order to study the effect of the side group ratios on the conductive properties of the polymer electrolytes.

B. Results and Discussion

1. Synthesis of $[\text{NP}(\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)_x(\text{OC}_6\text{H}_4\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{CF}_3)_{2-x}]_n$

Sequential addition of solutions of sodium 2-(2-methoxyethoxy)ethoxide and the disodium salt of the sulfonylimide derivative allowed control in the side group ratios of the resultant polymers (scheme 5-1). Because of the possibility for displacement of the sulfonimide-containing pendent groups by sodium 2-(2-methoxyethoxy)ethoxide, the oligoethyleneoxy nucleophile was linked to the polyphosphazene backbone first.^{18,19} Replacement of the chlorine atoms in poly(dichlorophosphazene) (**1**) was monitored by ³¹P NMR spectroscopy. When the desired amount of the oligoethyleneoxy substituent had been linked to the polyphosphazene, a solution of the disodium salt of the sulfonimide-functionalized nucleophile was added. After reaction with the sulfonimide-containing side group, the polymers slowly precipitated out of solution due to the poor solubility of the fully substituted polymers in tetrahydrofuran (THF). Each polymer was then dissolved in acidic water (pH ~ 4) and dialyzed for two days versus deionized water to remove unreacted sodium salts and sodium chloride.

Initially, lithium carbonate was investigated to prepare the lithium salt of the polymer, but several new broad peaks near 0 ppm in the ³¹P NMR spectra suggested polymer decomposition, probably as a consequence of the basicity of the medium.



Scheme 5-1: Synthetic Route for the Synthesis of Polymers 2-5

Therefore, lithiation of the sulfonimide moiety was accomplished by dialysis with 0.1 M solutions of lithium chloride in deionized water for three days. These solutions were less basic than the lithium carbonate solutions and the sulfonimide unit was lithiated without decomposition or of the polyphosphazene. The polymers were then dialyzed for five days with deionized water to remove excess lithium chloride and were dried in a vacuum oven at 40 °C to remove excess solvent.

2. Polymer Characterization

Polymers **2-5** (table 5-1) were characterized by ^{31}P , ^{13}C and ^1H NMR spectroscopy to determine ratios of the side groups and purity of the materials. Two broad peaks were detected in the ^{31}P NMR spectra of polymers **2-5** at -6.4 ppm and -12.4 ppm. These peaks correspond to di-oligoethyleneoxy-substituted phosphorus and the mono-oligoethyleneoxy/mono-sulfonimide substituted phosphorus respectively (figure 5-1). Integration of these peaks allowed the ratios of the two side groups to be estimated. The side group ratios were also confirmed by integration of the aromatic protons of the sulfonimide-functionalized pendent group and by the broad peaks characteristic of the oligoethyleneoxy substituent in the ^1H NMR spectra.

Sodium flame atomic absorption spectroscopy was performed on each polymer to confirm complete lithiation. In all cases, the amount of sodium present was below the limit of detection (0.2 ng/mL) of the instrument. Elemental analyses for carbon, hydrogen, nitrogen and lithium, [(calcd, found): H (5.21, 5.20), C (35.66, 35.76), N

Table 5-1: Composition and Conductivity Results of Polymers 2-5

<i>Polymer</i>	<i>% Sulfonimide</i>	<i>Conductivity</i>	<i>Conductivity</i>	<i>T_g</i>
	<i>Functionalized</i>	<i>at 25 °C</i>	<i>at 80 °C</i>	<i>(°C)</i>
	<i>Substituent</i>	<i>(S/cm)</i>	<i>(S/cm)</i>	
2	5	2.45×10^{-6}	2.75×10^{-5}	-64
3	9	1.05×10^{-6}	3.47×10^{-5}	-45
4	19	7.52×10^{-7}	4.99×10^{-5}	-31
5	22	1.05×10^{-7}	2.24×10^{-5}	-16

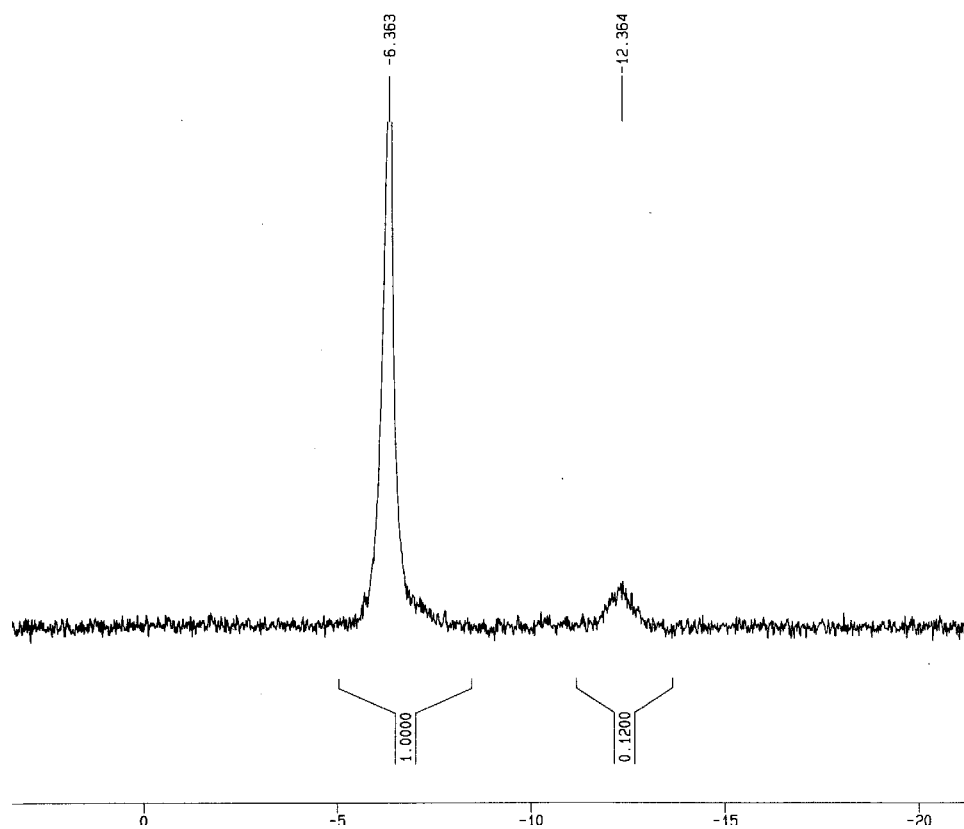


Figure 5-1: ^{31}P NMR of Polymer 2

(5.82, 5.62), Li (0.79, 0.72)], were performed on polymer **4** to further demonstrate lithiation of the polymer and to confirm the polymer structure.

As mentioned previously, polymers **2** through **5** were insoluble in THF and therefore gel permeation chromatography could not be used directly to obtain molecular weight data. Instead, 2.00 g of polymer **1** was used to synthesize poly[bis(trifluoroethoxyphosphazene)] (**6**), and molecular weight data were obtained for this polymer. Polymer **6** had a number average molecular weight of 1.52×10^5 g/mol and a weight average molecular weight of 4.22×10^5 g/mol, giving a polydispersity index value of 2.78.

3. Conductivity Results

The ionic conductivities of each of polymers **2-5** were measured via impedance analysis at temperatures from 20 °C to 80 °C. Conductivities in the range of 10^{-6} S/cm at 25 °C and 10^{-5} S/cm at 80 °C were obtained (table 5-1). These results are comparable to many other single ion lithium conducting polymers.^{5,20-23} In addition, the ambient temperature and high temperature (80 °C) ionic conductivities of polymers **2-5** were an order of magnitude higher than the ionic conductivities obtained for a polymer system with a sulfonimide moiety incorporated into the backbone of the polymer. This is probably due to the higher level of macromolecular motion in the polyphosphazene polymers compared to more restricted motion in the ionic backbone polymer that had a glass transition temperature (T_g) of 140 °C.¹¹

The conductivity of polymers **2-5** depends on several factors that can be related directly to the amount of sulfonimide functionalized substituent present. DSC analysis was performed on polymers **2-5** and on a sample of poly[bis(2-(2-methoxyethoxy)ethoxyphosphazene)] (**7**) to compare their T_g s and gain information about the macromolecular motion occurring in each sample. The T_g increased significantly from $-84\text{ }^{\circ}\text{C}$ for the homopolymer (**7**) to a maximum of $-16\text{ }^{\circ}\text{C}$ when 22% of the sulfonimide containing side group was present in polymer **4** (figure 5-2). This suggested that the T_g s of polymers **1-4** (table 5-2) were directly dependent on the amount of the sulfonimide functionalized substituent present in the system. The bulky structure of the sulfonimide functionality probably restricts motion of polymer chains. The ambient temperature impedance analysis results support this argument by showing that the conductivity decreases with the increase in the T_g and with sulfonimide content. These conductivities range from $2.45 \times 10^{-6}\text{ S/cm}$ for polymer **2** to $1.05 \times 10^{-7}\text{ S/cm}$ for polymer **5** with 5% and 22% sulfonimide containing side groups respectively. Higher incorporations of the sulfonimide functionality yielded brittle materials that could not be fabricated into samples for impedance analysis.

At elevated temperatures, the amount of salt plays a more important role. Increases in temperature resulted in increases in conductivity for all the polymers studied (figure 5-3). The higher sulfonimide content of the polymer, the greater the magnitude of the increase in conductivity with temperature. As the temperature is raised above the T_g , the increased macromolecular motion allows the polymers with higher salt content to conduct more freely, so that at $80\text{ }^{\circ}\text{C}$ all the polymers conduct in the range of 10^{-5} S/cm .

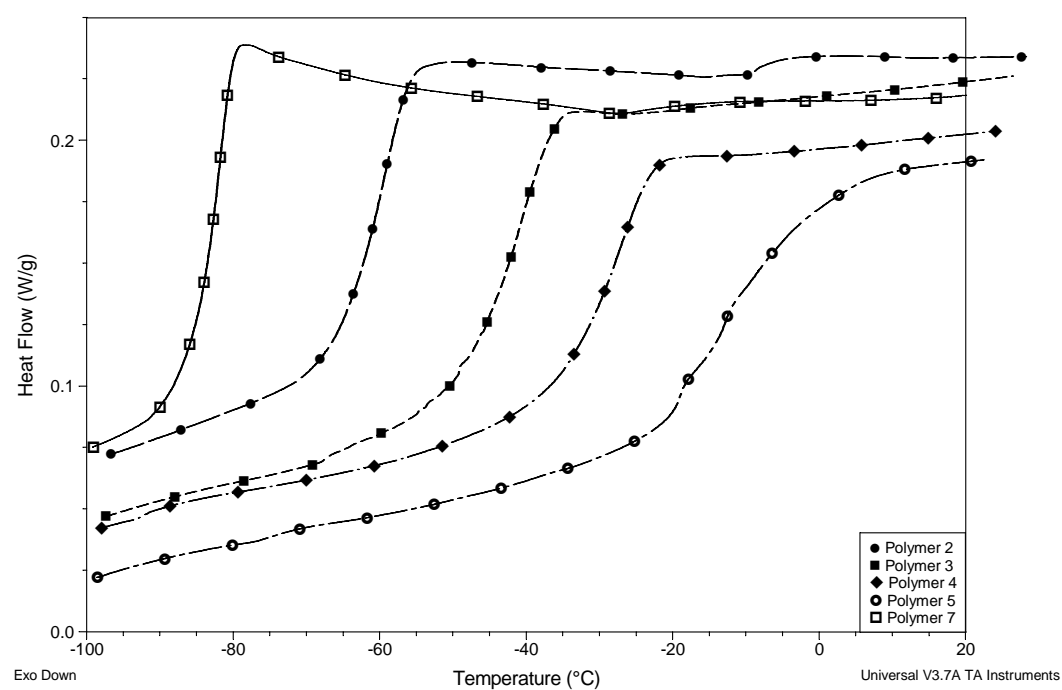


Figure 5-2: DSC Results for Polymers 2-5 and 7

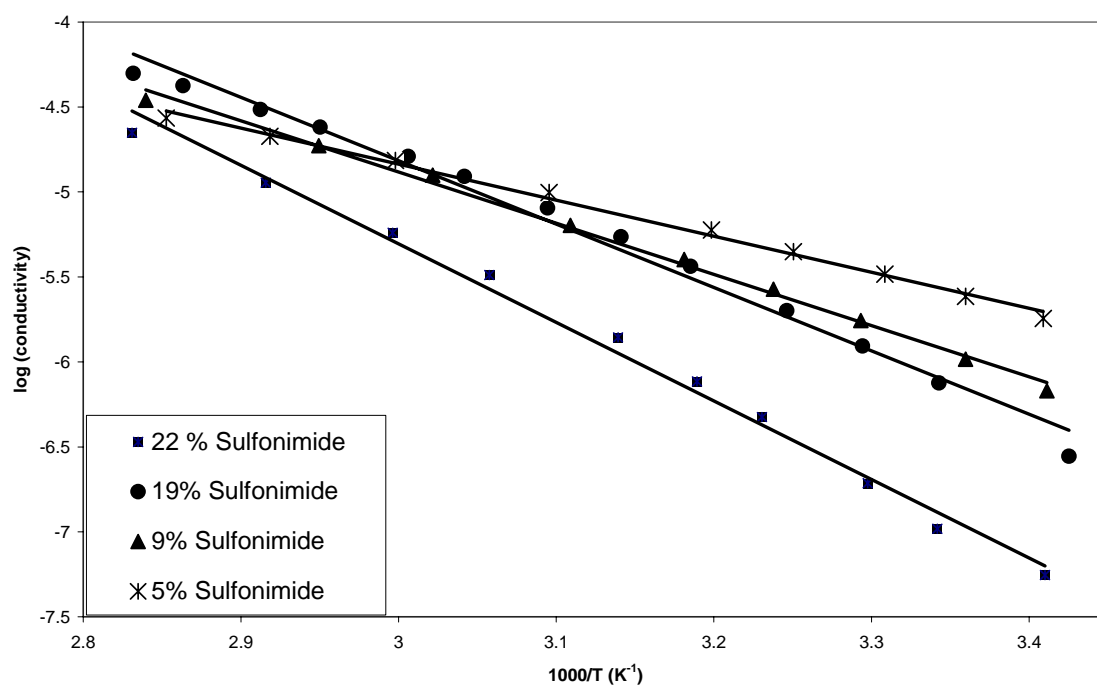


Figure 5-3: Conductivity Results for Polymers 2-5

The highest conductivity (4.99×10^{-5}) was found for polymer **4** with 19% of the lithium salt containing substituent.

4. Mechanism of Conduction

Ionic conduction in polyphosphazenes has been examined for many polymer systems with different oligoethyleneoxy side groups and high macromolecular mobility.^{24,25} The key to high ionic conduction in these polymers is weak coordination of mobile lithium ions to etheric oxygen atoms. In addition, it has also been recently shown that the nitrogen atoms in the phosphazene backbone may contribute to the conductivity of lithium ions through cooperative coordination with the oligoethyleneoxy side groups.²⁶ Polymers **1-4** did not have ionic conductivities as high as polyphosphazene polyelectrolytes with lithium salt added.²⁴ Incorporation of the sulfonimide functionalized side group hinders the macromolecular motion of the polymers by raising the T_g and this decreases ionic conduction by polymer electrolyte motion.

Gel polymer electrolyte fabrication could improve the conductivities of polymers **1-4** by increasing the macromolecular motion of the polymers. However, initial attempts to incorporate propylene carbonate into the polymers had no effect on the conductivities or T_g s of the polymers due to their immiscibility.

C. Conclusions

Co-substituted polyphosphazenes with 2-(2-methoxyethoxy)ethoxy and 5% to 22% of a sulfonimide functionalized side group were synthesized and examined as single ion conductors. The glass transition temperatures of these materials increased with higher incorporations of the sulfonimide to a maximum of -16 °C for polymer **4**.

Ionic conductivities in the range of 10^{-6} were obtained at ambient temperatures and 10^{-5} at 80 °C. The relative conductivities depended on both the amount of sulfonimide and the T_g s of the polymers. The ambient temperature conductivities decreased with sulfonimide content but the conductivities at 80 °C tended to increase with sulfonimide content due to increased macromolecular motion above the T_g . Thus, the T_g is the most important consideration at lower temperatures but the amount of lithiated sulfonimide becomes more important at higher temperatures. The conductivities obtained were comparable to those obtained for other single ion lithium conducting polymers.

D. Experimental Section

1. Materials

Trifluoromethanesulfonamide, 98+% was obtained from TCI and used as received. 4-methoxybenzenesulfonyl chloride, 99%, 4-methylphenol, 99%; 3-methylphenol, 99%, tetra(*n*-butyl)ammonium bromide, 99%; sodium hydride 95%; sodium methoxide, 0.5M in methanol; sodium ethanethiolate, tech., 80%; *N,N*-dimethylformamide (DMF), 99%, lithium chloride 99+%, and 2,2,2-trifluoroethanol,

98%, were obtained from Aldrich and used as received. Di(ethylene glycol)methyl ether, 99%, was obtained from Aldrich and distilled over calcium hydride prior to use. Propylene carbonate, 99.7%, and lithiumbis(trifluoromethanesulfonyl)imide, 99.995%, were obtained from Aldrich and used in an argon filled glove box. Poly(dichlorophosphazene) (**1**) was prepared via thermal ring-opened polymerization of hexachlorocyclotriphosphazene at 250 °C in a vacuum sealed tube. Tetrahydrofuran was distilled from sodium benzophenone ketyl under an inert atmosphere of dry argon.

All reactions were carried out using standard Schlenk techniques under an atmosphere of dry argon.

2. Equipment

^1H , ^{13}C , and ^{31}P spectra were recorded on a Bruker AMX-360 NMR spectrometer operated at 360, 90.56 and 90.27 MHz, respectively. ^1H and ^{13}C NMR were referenced to external tetramethylsilane. ^{31}P proton decoupled chemical shifts were relative to external 85% phosphoric acid. Molecular weights and polydispersities were estimated using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector, Phenomenex Phenogel 10 μm linear columns, and calibrated versus polystyrene standards. Sample elution was carried out at 40 °C with a 0.1 wt % solution of tetra-*n*-butylammonium nitrate (Aldrich) in THF (OmniSolv). Thermal transitions were determined through analysis via a TA Q10 differential scanning calorimeter. Calibration was accomplished with an indium, water and cyclohexane standards. All analyses were conducted over a range of -120 °C to 100 °C at a heating

rate of 10 degrees per minute. The purge gas was nitrogen, flowing at 50 ml/min. Elemental analysis were carried out by QTI. Flame Atomic Absorption analysis were obtained using a Buck Scientific Atomic Absorption Spectrometer, Model 210. A sodium lamp at 589 nm was also used. Conductivity measurements were obtained using a Hewlett Packard 4192A LF Impedance Analyser with an ac frequency range of 5 Hz to 13 MHz in an argon filled drybox.

3. Synthesis of Polymers (2-6)

A solution of $\text{NaO}(\text{CH}_2\text{CH}_2)_2\text{OCH}_3$ in THF was added to a solution of poly(dichlorophosphazene) in THF and allowed to react for 72 hours at room temperature. A solution in THF of $\text{NaOC}_6\text{H}_4\text{SO}_2\text{N}(\text{Na})\text{SO}_2\text{CF}_3$ was then added and also reacted for 72 hours. The polymer slowly precipitated from solution after addition of the sulfonimide sodium salt. The THF supernatant solution was decanted and the polymer was dissolved in acidic water (pH \sim 5) and placed in a 12-14000 MWCO dialysis tube for two days, changing the water twice per day. The dialysis tube was then placed in 0.1 M LiCl solution in deionized water for three days with the solution changed twice each day. To remove excess salts, the dialysis tube was dialyzed against deionized water for five days. The solvent was then changed to methanol for two days. The polymer solution was then filtered, concentrated on a rotary evaporator and transferred to a 120 mL vial. All glassware was rinsed with a 0.1 M aqueous lithium chloride solution for ten minutes and then rinsed several times with deionized water. The polymer was dried under

vacuum at 60 °C before storage. Table 5-2 shows the specific quantities of reagents used for each polymer.

For polymer **2**: Obtained 2.61 g product (74% yield). ^1H NMR (d_4 -methanol): $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ (s, 3H, $\delta = 3.5$; overlapping mlts, 6H, $\delta = 3.7, 3.8, 3.9$; broad mlt, 2H, $\delta = 4.3$), $\text{OC}_6\text{H}_4\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{CF}_3$ (broad d, 2H, $\delta = 7.6$; broad d, 2H, $\delta = 8.0$). ^{13}C NMR (d_4 -methanol): $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ ($\delta = 59.7, 67.1, 71.8, 73.5$), $\text{OC}_6\text{H}_4\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{CF}_3$ ($\delta = 122.8, 123.9, 129.9, 142.1, 156.8$), ^{31}P NMR (d_4 -methanol): $\delta = -6.5, -12.4$.

For polymer **3**: Obtained 2.21 g product (81% yield). ^1H NMR (d_4 -methanol): $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ (s, 3H, $\delta = 3.5$; overlapping mlts, 6H, $\delta = 3.7, 3.8, 3.9$; broad mlt, 2H, $\delta = 4.3$), $\text{OC}_6\text{H}_4\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{CF}_3$ (broad d, 2H, $\delta = 7.6$; broad d, 2H, $\delta = 8.0$). ^{13}C NMR (d_4 -methanol): $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ ($\delta = 59.7, 67.1, 71.8, 73.5$), $\text{OC}_6\text{H}_4\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{CF}_3$ ($\delta = 122.8, 123.9, 129.9, 142.1, 156.8$), ^{31}P NMR (d_4 -methanol): $\delta = -6.5, -12.4$.

For polymer **4**: Obtained 2.68 g product (87% yield). ^1H NMR (d_4 -methanol): $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ (s, 3H, $\delta = 3.5$; overlapping mlts, 6H, $\delta = 3.7, 3.8, 3.9$; broad mlt, 2H, $\delta = 4.3$), $\text{OC}_6\text{H}_4\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{CF}_3$ (broad d, 2H, $\delta = 7.6$; broad d, 2H, $\delta = 8.0$). ^{13}C NMR (d_4 -methanol): $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ ($\delta = 59.7, 67.1, 71.8, 73.5$), $\text{OC}_6\text{H}_4\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{CF}_3$ ($\delta = 122.8, 123.9, 129.9, 142.1, 156.8$), ^{31}P NMR (d_4 -methanol): $\delta = -6.5, -12.4$. Elemental analysis (calcd, found): H (5.21, 5.20), C (35.66, 35.76), N (5.82, 5.62), Li (0.79, 0.72).

Table 5-2: Quantities of Reagents for Synthesis of Polymers 2-5

<i>Polymer</i>	<i>methoxyethoxyethanol</i>	<i>NaH</i>	<i>Sulfonylimide</i>	<i>NaH for</i>
	<i>g(mmol)</i>	<i>g(mmol)</i>	<i>Derivative</i>	<i>Derivative</i>
			<i>g(mmol)</i>	<i>g(mmol)</i>
2	2.13	0.447	0.347	0.023
	(17.9)	(17.7)	(1.1)	(0.9)
3	2.04	0.427	0.621	0.043
	(17.1)	(16.9)	(1.9)	(1.7)
4	1.81	0.379	1.24	0.091
	(15.2)	(15.0)	(3.8)	(3.6)
5	1.74	0.364	1.43	0.106
	(14.6)	(14.4)	(4.4)	(4.2)

For polymer **5**: Obtained 2.56 g product (81% yield). ^1H NMR (d_4 -methanol): $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ (s, 3H, $\delta = 3.5$; overlapping mlts, 6H, $\delta = 3.7, 3.8, 3.9$; broad mlt, 2H, $\delta = 4.3$), $\text{OC}_6\text{H}_4\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{CF}_3$ (broad d, 2H, $\delta = 7.6$; broad d, 2H, $\delta = 8.0$). ^{13}C NMR (d_4 -methanol): $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ ($\delta = 59.7, 67.1, 71.8, 73.5$), $\text{OC}_6\text{H}_4\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{CF}_3$ ($\delta = 122.8, 123.9, 129.9, 142.1, 156.8$), ^{31}P NMR (d_4 -methanol): $\delta = -6.5, -12.4$.

4. Synthesis of Poly[bis(trifluoroethoxyphosphazene)] (6)

An excess of sodium trifluoroethoxide in THF was added slowly to a solution of poly(dichlorophosphazene) in THF and the mixture was stirred at room temperature for 18 hours. The polymer solution was concentrated on a rotary evaporator and the polymer was precipitated into acidic water (pH~5). The polymer was then precipitated from THF into deionized water and twice from THF into hexane. The polymer was then dried in a vacuum oven at 60 °C.

5. Preparation of SPEs

The mixed-substituent polymers **1-4** were dried under vacuum at 40 °C for 1 week before fabrication. Approximately 0.10 g of each polymer was then placed in the impedance analyzer sample holder and impedance measurements were obtained over a temperature range from 20 °C to 80 °C.

E. References

- 1) Vincent, C.; Scrosati, B. *Modern Batteries: An Introduction To Electrochemical Power Sources*; John Wiley and Sons, Inc.: New York, 1997.
- 2) Vincent, C. *Solid State Ionics*. **2000**, 134, 159-167.
- 3) Tarascon, J.; Armand, M. *Nature*, **2001**, 414, 359-367.
- 4) Jasinski, R. *High-Energy Batteries*; Plenum Press: New York, 1967.
- 5) Shriver, D.F.; Siska, D.P. *Chem. Mater.*, **2001**, 13, 4698-4700.
- 6) Hardy, L.C.; Shriver, D.F. *J. Am. Chem. Soc.* **1985**, 107, 3823-3828.
- 7) Tsuchida, E.; Ohno, H.; Kobayashi, N. *Macromol.* **1988**, 21, 96-100.
- 8) Tada, Y.; Sato, M.; Takeno, N.; Nakacho Y.; Shigehara, K. *Chem. Mater.* **1994**, 6, 27-30.
- 9) Fujinami, T.; Tokimune, A.; Mehta, M. A.; Shriver, D. F.; Rawsky, G. C.; *Chem. Mater* **1997**, 9, 2236-2239.
- 10) Matsushita, K.; Shimazaki, Y.; Mehta, M.A.; Fujinami, T. *Solid State Ionics*, **2000**, 133, 295-301.
- 11) Watanabe, M.; Suzuki, Y.; Nishimoto, A. *Electrochim. Acta*, **2000**, 45, 1187-1192.
- 12) Hofmann, M.A.; Ambler, C.M.; Maher, A.E.; Chalkova, E.; Zhou, X.Y.; Lvov, S.N.; Allcock, H.R. *Macromol.*, **2002**, 35, 6490-6493.
- 13) Chalkova, E.; Zhou, X.Y.; Ambler, C.A.; Hofmann, M.A.; Weston, J.A.; Allcock, H.R.; Lvov, S.N. *Electrochemical and Solid State Letters*, **2002**, 5, A221.
- 14) Blonsky, P.M.; Shriver, D.F.; Austin, P.; Allcock, H.R. *J. Am. Chem. Soc.*, **1984**, 106, 6854-6855.

- 15) Allcock, H.R.; Austin, P.E.; Neenan, T.X.; Sisko, J.T.; Blonsky, P.M.; Shriver, D.F. *Macromol.*, **1986**, *19*, 1508-1512.
- 16) Blonsky, P.M.; Shriver, D.F.; Austin, P.; Allcock, H.R. *Solid State Ionics*, **1986**, *19*, 258-264.
- 17) Allcock, H.R.; Maher, A.E.; Ambler, C.M. *Macromol.* **2003**, *36*, 5566-5572.
- 18) Allcock, H.R.; Kim, Y.B. *Macromol.*, **1994**, *27*, 3933-3942.
- 19) Xu, W.; Williams, M.D.; Angell, C.A. *Chem. Mater.*, **2002**, *14*, 401-409
- 20) Onishi, K.; Matsumoto, M.; Nakacho, Y., Shigehara, K. *Chem. Mater.* **1996**, *8*, 469-472.
- 21) Dérand, H.; Wesslén, B.; Mellander, B. *Electrochimica Acta*, **1998**, *43*, 1525-1531.
- 22) Chovino, C.; Frere, Y.; Gramain, P. *J. Poly. Sci. Part A: Poly. Chem.*, **1997**, *35*, 2719-2728.
- 23) Ganapathiappan, S.; Chen, K.; Shriver, D.F. *J. Am. Chem. Soc.*, **1989**, *111*, 4091-4095.
- 24) Allcock, H.R. *Chemistry and Applications of Polyphosphazenes*; Wiley-Interscience: Hoboken, NJ, 2003.
- 25) Allcock, H.R.; Kellam, E.C.; Morford, R.V. *Solid State Ionics*, **2001**, *143*, 297-308.
- 26) Luther, T.A.; Stewart, F.F.; Budzien, J.L.; LaViolette, R.A.; Bauer, W.F.; Harrup, M.K.; Allen, C.W.; Elayan, A. *J. Phys. Chem. B*, **2003**, *107*, 3168-3176.

Chapter 6

Possible Future Research Directions

A. Future Research Directions

Work described in this thesis dealt with the synthesis of mixed-substituent polyphosphazenes. Chapters 2 through 4 examined polymers with fluoroalkoxy side groups and chapter 5 examined the synthesis of sulfonimide functionalized polyphosphazenes as single ion conductors.

The results of chapters 2 and 3 showed that it is possible to synthesize mixed-substituent polyphosphazenes by exchange of fluoroalkoxy side groups with alkoxide or fluoroalkoxide nucleophiles. The phenomena of side group exchange of fluoroalkoxy substituents could be examined through reactions with aryloxy and amine nucleophiles. Alternatively, polyphosphazenes with aryloxy and amine side groups could also be examined to ascertain if any of these types of polymers can undergo side group exchange.

The work on low temperature elastomers in chapter 4 could be extended in a variety of ways. For example, polymers with small amounts of alkoxy substituents could be examined in attempts to decrease the glass transition temperature of the polymers and thus increase the temperature range of operation. Another direction would be the examination and comparison of other mixed substituent poly(fluoroalkoxyphosphazenes) systems in terms of thermal and mechanical properties. Finally, experiments on cross-linking and compounding could be performed to improve mechanical properties.

Lastly, the sulfonimide functionalized side group in chapter 5 could be modified to incorporate an oligoethyleneoxy spacer to connect to the polyphosphazene backbone. This should lower the glass transition temperatures of the polymers and increase the conductivities.

Appendix

Synthesis of a Sulfonimide Side Group and Its Incorporation into Polyphosphazenes

A. Introduction

Proton conductive polymers are attractive materials for a wide variety of applications.¹ Over the past two decades, the potential use of these materials in devices for power generation, namely polymer electrolyte fuel cells (PEFCs) has received considerable attention.²⁻⁵ However, the number of prospective candidates for use as membrane materials in PEFCs is significantly limited by a host of demanding membrane requirements including; good chemical and mechanical stability, high ionic conductivity, and low reactant permeability (i.e. hydrogen or methanol, and oxygen). For the most part, research to date has mainly focused on sulfonic acid functionalized polymers, in particular, the perfluorosulfonic acid membranes typified by Nafion™.⁶

Attractive alternatives to sulfonic acid containing materials are those containing sulfonimide groups. The high acid strength of sulfonimide acids has been well documented⁷ and DesMarteau and co-workers have been preparing perfluorinated polymeric membranes containing these acid groups since the early 1990's.^{8,9} Quite recently, sulfonimide-functionalized polymers containing aromatic units have been developed. In 2000, Feiring and co-workers reported the synthesis of a novel styrene monomer bearing a pendent sulfonimide group and its homopolymerization and copolymerization with a variety of olefinic monomers as potential electrolytes for lithium

battery applications.^{10,11} DesMarteau and co-workers have also described the synthesis of various trifluorovinyl aromatic ether monomers bearing both pendent sulfonimide groups, as well as sulfonimide groups incorporated into the monomer main chain.^{12,13} These monomers undergo thermal cyclopolymerization to yield perfluorocyclobutane aromatic polyethers, and are quite interesting materials as potential fuel cell membranes.¹⁴

The present work describes the synthesis of a sulfonimide bearing phenolic compound and its use in the classical macromolecular substitution approach to produce a phosphazene (-P=N-backbones) polymer bearing pendent sulfonimide groups. Initial membranes were cast from 1,4-dioxane and characterized before and after crosslinking with respect to their proton conductivity, water swelling and thermal properties. A blended membrane of the sulfonamide functionalized polymer with poly(vinylidene fluoride) was also evaluated. These polymers appear to be excellent candidates for use as proton-conducting membranes in fuel cell applications.

B. Results and Discussion

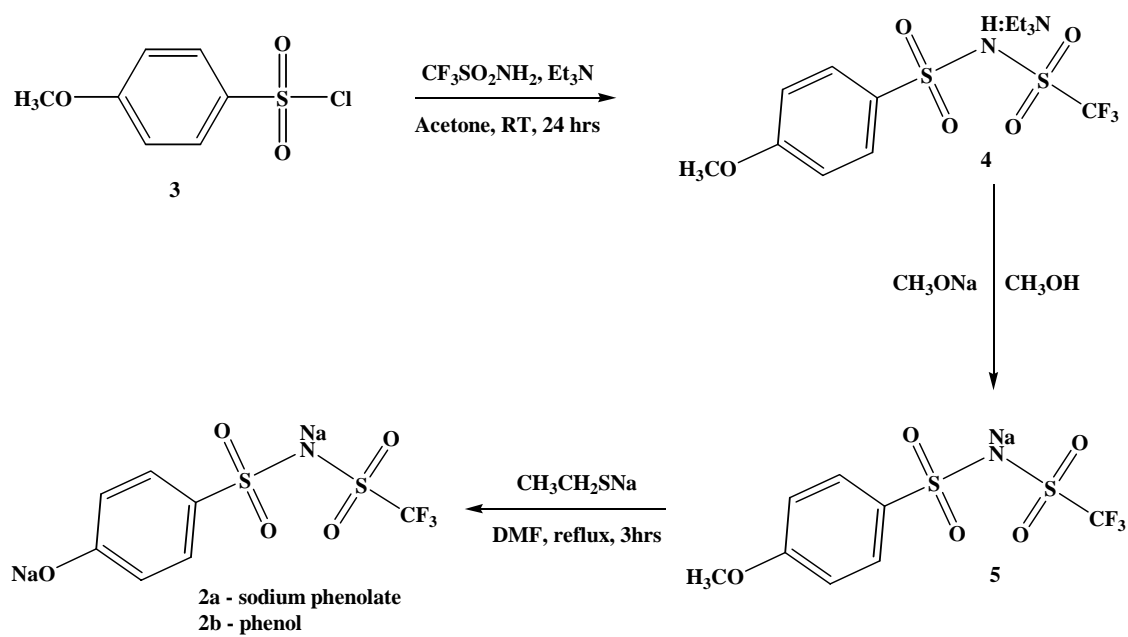
1. Incorporation of Acid Groups into Polyphosphazenes

The incorporation of carboxylic,^{15,16} phosphonic,¹⁷ and sulfonic acids^{18,19} into polyphosphazenes has been examined previously, and polyphosphazenes bearing phosphonic and sulfonic acid groups have been shown to be promising as fuel cell membrane materials, particularly for use in direct methanol fuel cells (DMFCs).²⁰⁻²² These polymers are obtained through the synthesis of poly(aryloxyphosphazenes) that are

appropriate for further modification by relatively harsh reagents (e.g. SO_3) to incorporate the acidic functionalities. This method of synthesis limits the potential choice of side groups and thus the degree of tailorability in these systems, generally considered one of the main advantages to the polyphosphazene platform.²³ It is thus desirable to have the acid functionality already incorporated into a side group that can then easily be reacted with unsubstituted (**1**) or partially substituted (**6a**) poly(dichlorophosphazene). However, sodium salts of difunctional reagents (e.g. p-hydroxybenzenesulfonic acid) are, in general, not suitable reagents for reaction with unsubstituted or partially substituted poly(dichlorophosphazene) due to the tendency of both functional sites to react, producing polymer crosslinks and insoluble products.¹⁸ The sulfonimide side group $\text{NaOC}_6\text{H}_4\text{SO}_2\text{NNaSO}_2\text{CF}_3$ (**2a**) synthesized in this work is unique in that the sulfonimide functionality is essentially non-nucleophilic, and thus allows for its use in the classical macromolecular substitution of at least a partially substituted poly(dichlorophosphazene), and potentially, the ability to easily tune final polymer properties through the choice of the cosubstituents.

2. Synthesis of Sulfonimide Side Group $\text{NaOC}_6\text{H}_4\text{SO}_2\text{NNaSO}_2\text{CF}_3$ (**2a**)

The synthesis of the sulfonimide side group is outlined in Scheme A-1. Reaction of p-methoxybenzenesulfonyl chloride (**3**) with trifluoromethanesulfonamide and triethylamine in anhydrous acetone afforded the triethylammonium sulfonimide **4** in ~60% yield (*note: subsequent work has found that careful drop-wise addition of the triethylamine can improve the yield to ~90%*). Cation exchange with sodium methoxide



Scheme A-1: Synthesis of the sulfonimide side group $\text{NaOC}_6\text{H}_4\text{SO}_2\text{NNaSO}_2\text{CF}_3$ (2a)

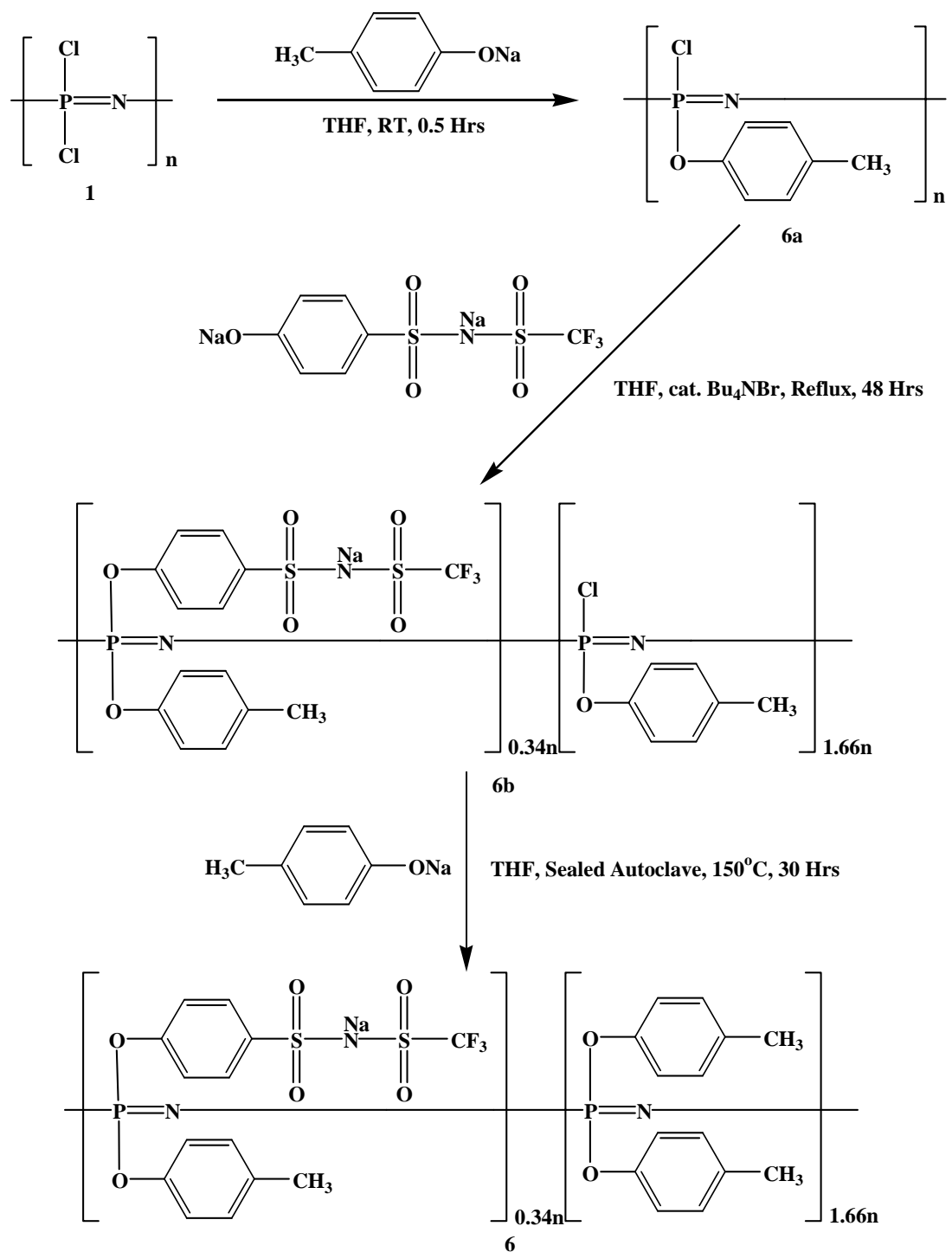
in methanol gave the sodium sulfonimide **5**. The methyl ether group of **3** was then cleaved by treatment with sodium ethanethiolate in refluxing DMF over three hours and gave the sodium sulfonimide-bearing sodium phenolate **2a**, which was isolated as the phenol **2b** in 82 % yield. The overall isolated yield based on reactant **1** was ~50 %.

3. Reaction of **2a** with Partially Substituted Chlorophosphazenes

The synthesis of the sulfonimide-functionalized polymer **6** is outlined in Scheme A-2. Poly(dichlorophosphazene) was treated with sufficient sodium 4-methylphenoxide to displace ~50% of the initial chlorine atoms (polymers **6a**). A suspension of **2a** in THF with tetrabutylammonium bromide as a phase transfer agent was then added and the reaction refluxed over 48 hours. The remaining chlorine atoms of polymer (**6b**) were then displaced by treatment with 4-methylphenoxide in a sealed autoclave at 150 °C over 30 hours. The sulfonimide groups on the polymers were converted to their acid form by multiple precipitations into concentrated HCl. Purification was afforded by dialysis and precipitation into pentane to give polymer **6**.

4. Membrane Characterization for Polymer **6**

Characterization data for membranes of polymer **6** are given in table A-1. The experimentally measured ion-exchange capacity (IEC) of polymer **6** was 0.99 meq/g, which translated to an acid content of ~32% per polymer repeat unit. This was in good agreement with the acid content calculated from the ¹H NMR spectrum (~34%). The equilibrium water swelling of a non-crosslinked membrane was measured at 119% (based on membrane dry weight). As seen in table A-1, crosslinking via gamma radiation had a significant effect on membrane swelling resulting in a 40% and 65% reduction in water uptake after exposure to 20 and 40 Mrad radiation dosages, respectively. The water



Scheme A-2: Reaction of 2a with partially substituted chlorophosphazenes

Table A-1: Membrane Data

Membrane	Membrane Thickness (cm)	IEC (meq/g)	Water Swelling (%)	Proton Conductivity (S/cm)	Crosslinking (Mrad)
6	0.013	0.99	119	0.049	0
6	0.011	0.99	73	0.071	20
6	0.093	0.99	42	0.065	40
PVDF / 6 Blend	0.015	---	41	0.060	0
Nafion 117	0.020	0.91	30	0.100	0

swelling of the non-crosslinked membrane was significantly higher than the value reported for a non-crosslinked, sulfonated polyphosphazene membrane (42% for IEC = 0.96 meq/g).²⁴ The higher swelling of the polyphosphazene sulfonimide membrane when compared to the sulfonated polyphosphazene membrane is not overly surprising. Previous work by DesMarteau and coworkers had shown that a sulfonyl imide ionomer that is structurally similar to Nafion 117 with a similar IEC, had an equilibrium water swelling of 116% compared to the value reported for Nafion 117 of 31%.²⁵

Proton conductivities in fully hydrated membranes of polymer **6** were measured at room temperature via a four-electrode electrochemical impedance spectroscopy method.²⁶ As shown table A-1, it was clear that after crosslinking with 20 Mrad radiation the conductivity increased significantly from 0.049 to 0.071 S/cm. This was most likely due to the acid groups being kept in fairly close proximity to one another due to the polymer crosslinks introduced. While further crosslinking had a significant affect on water swelling, the effect on the proton conductivity was not as dramatic. The slight decrease observed could possibly be due to either restricted polymer mobility, or insufficient hydration due to the decreased water content. These values compared favorably to those reported for a crosslinked, sulfonated polyphosphazene membrane (0.04 S/cm).²¹

5. Membrane Characterization for Polymer 6 Blended with PVDF

Pintauro and coworkers have found substantial improvements in the mechanical properties of sulfonated polyphosphazene membranes when blended with poly(vinylidene fluoride).²⁷ Membranes of polymer **6** blended with PVDF were fabricated by solution casting from DMAC. The blended membranes were translucent when dry and

transparent when hydrated, indicating true blend formation rather than a phase separated mixture. Initial characterization by differential scanning calorimetry also supports this conclusion and will be included in a future detailed investigation into the blending of the new sulfonimide polymers. As shown in table A-1, blending of the sulfonimide polymer with PVDF gave similar results to those found for the pure sulfonimide membrane after a crosslinking dosage of 40 Mrad. However, the blended membranes appeared to have significantly improved mechanical properties. The measured proton conductivity also compared quite favorably to that reported for a crosslinked membrane that consisted of 75% sulfonated polyphosphazene (IEC = 1.8 meq/g) blended with 25% of a copolymer of vinylidene fluoride and hexafluoropropylene (0.014 S/cm).²⁷

C. Conclusions

A method for the synthesis of the sulfonimide containing side group, $\text{HOC}_6\text{H}_4\text{SO}_2\text{NNaSO}_2\text{CF}_3$, for incorporation into phosphazene polymers has been developed. This side groups was used to prepare a sulfonimide-functionalized phosphazene polymer with an ion-exchange capacity of 0.99 meq/g. Initial membranes were found to have good proton conductivities and moderate water swelling depending on crosslink density. A blend of the sulfonimide polymer with PVDF had improved mechanical properties, low water swelling, and good proton conductivity. An advantage of this synthesis protocol is the freedom to tune the polymer composition and properties by variations in the choice of co-substituent and the side group ratios. These polymers are currently being evaluated as membrane materials for fuel cell applications. Ongoing studies with this synthetic route will examine: 1) a variety of cosubstituents 2) blends

with a variety of polymers, including PVDF, 2) the development of MEA fabrication procedures, and 3) evaluation in a fuel cell test stand. Moreover, polymers are being prepared with oligoethyleneoxy co-substituents and will be evaluated for lithium battery applications.

D. References

- 1) G. Inzelt; M. Pineri; J.W. Schultz and M.A. Vorotyntev *Electrochim. Acta* **2000**, *45*, 2403.
- 2) K.B. Prater *J. Power Sources* **1994**, *51*, 129.
- 3) K.V. Kordesch *Chem. Rev.* **1995**, *95*, 191.
- 4) F. Barbir and T. Gomez *Int. J. Hydrogen Energy* **1996**, *21*, 891.
- 5) J. Appleby *J. Power Sources* **1995**, *53*, 187.
- 6) G. Alberti and M. Casciola *Solid State Ionics* **2001**, *145*, 3.
- 7) I.A. Koppel; R.W. Taft; F. Anvia; S.-Z. Zhu; L.-Q. Hu; K.-S. Sung; D.D. DesMarteau; L.M. Yagupolskii; Y.L. Yagupolskii; N.V. Ignat-ev; N.V. Kondratenko; N.V. Volkonskii; V.M. Vlasov; R. Notario and P.-C. Maria *J. Am. Chem. Soc.* **1994**, *116*, 3047.
- 8) D.D. DesMarteau *J. Fluorine Chem.* **1995**, *72*, 203.
- 9) D.D. DesMarteau "Copolymers of Tetrafluoroethylene and Perfluorinated Sulfonyl Monomers and Membranes Made Therefrom," US Patent 5,463,005, 1995.
- 10) A.E. Feiring; S.K. Choi; M. Doyle and E.R. Wonchoba *Macromolecules* **2000**, *33*, 9262.
- 11) A.E. Feiring and E.R. Wonchoba *J. Fluorine Chem.* **2000**, *105*, 129.
- 12) D.D. DesMarteau; C.W. Martin; L.A. Ford and Y. Xie "Sulfonated Perfluorovinyl Functional Monomers," US Patent 6,268,532 B1, 2001.
- 13) D.W. Smith and D.D. DesMarteau *Abstr. Pap. Amer. Chem. Soc.* **2000**, *220*, 7.

- 14) L.A. Ford; D.W. Smith and D.D. DesMarteau *Abstr. Pap. Amer. Chem. Soc.* **2000**, 220, 208.
- 15) H.R. Allcock and R.J. Fitzpatrick *Chem. Mater.* **1992**, 4, 769.
- 16) H.R. Allcock and S. Kwon *Macromolecules* **1989**, 22, 75.
- 17) H.R. Allcock; M.A. Hofmann; C.M. Ambler and R.V. Morford *Macromol* **2002**, 35, 3484-3489.
- 18) H.R. Allcock; R.J. Fitzpatrick and L. Salvati *Chem. Mater.* **1991**, 3, 1120.
- 19) E. Montoneri; M. Gleria; G. Ricca and G.C. Pappalardo *Makromol. Chem.* **1989**, 190, 191.
- 20) R. Wycisk and P.N. Pintauro *J. Membr. Sci.* **1996**, 119, 155.
- 21) Q. Guo; P.N. Pintauro; H. Tang and S. O'Connor *J. Membr. Sci.* **1999**, 154, 175.
- 22) H.R. Allcock; M.A. Hofmann; C.M. Ambler; E. Chalkova; S.N. Lvov; X.Y. Zhou and J. Weston *J. Membr. Sci.* **2002**, 201, 47-54.
- 23) H.R. Allcock *Chem. Materials Review* **1994**, 6, 155.
- 24) H. Tang; P.N. Pintauro; Q. Guo and S. O'Connor *J. Appl. Poly. Sci.* **1999**, 71, 387.
- 25) J.J. Sumner; S.E. Creager; J.J. Ma and D.D. DesMarteau *J. Electrochem. Soc.* **1998**, 145, 107.
- 26) X. Ren; M.S. Wilson and S. Gottesfeld *J. Electrochem. Soc* **1996**, 143, L12.
- 27) R. Carter; R. Wycisk; P.N. Pintauro; C. Byrne and S. Mukerjee "Blended Polyphosphazene Membranes for Direct Methanol Fuel Cells: Membrane Fabrication," Joint International Meeting - the 200th Meeting of The Electrochemical Society, Inc. and the 52nd Annual Meeting of the International Society of Electrochemistry - Meeting Abstracts, San Francisco, California, 2001.

Vita

Andrew Elessar Maher was born to John and Mary Maher in St. John's Newfoundland, Canada on January 1st, 1976. He completed his Bachelor's degree in chemistry at St. Francis Xavier University in 1998. His thesis work involved synthesis, photoelectron spectroscopy and computational analysis of several heterocyclic compounds containing carbonyl acetylenic moieties. He began his graduate work under the direction of Dr. Harry Allcock at The Pennsylvania State University in the fall of 1998. He was married to Anna Johnson in May 2001 and in May 2002 their daughter Aria Eleanor was born.

