DESIGN, SYNTHESIS, AND CHARACTERIZATION OF POLYMERIC MATERIALS FOR USES IN ENERGY STORAGE APPLICATIONS

A Thesis in
Chemistry

by

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ABSTRACT

The work described in this thesis focuses on the design, synthesis, and characterization of polymeric materials for energy storage applications, which include small molecule electrolyte additives, solid polymer electrolyte, and gel polymer electrolyte systems. In addition, non-woven nanofiberous mats of a pre-ceramic polymer were examined for high-strength and temperature material applications. Chapter 2 of this thesis describes the synthesis of novel polyphosphazene single ion conductors for use in secondary lithium ion batteries. Chapters 3 and 4 details work towards the synthesis and evaluation of highly selective membranes for use in lithium-seawater batteries. The fifth chapter deals with the synthesis and characterization of a polyphosphazene-silicate solid polymer electrolyte networks for secondary lithium batteries. Chapter 6 describes the fabrications and evaluation a gel polymer electrolyte system which utilizes a phosphate-based small molecule electrolyte additive. The appendix details the electrostatic spinning of a polymeric ceramic precursor to produce a nanofiberous mat, which upon pyrolysis yield boron carbide nanofibers.

Chapter 2 describes the synthesis and characterization of novel single ion conductive polymer electrolytes developed by covalently linking an arylsulfonimide substituent to the polyphosphazene backbone. An immobilized sulfonimide lithium salt is the source of lithium cations, while a cation-solvating cosubstituent, 2-(2-methoxyethoxy)ethoxy, was used to increase free volume and assist cation transport. The ionic conductivities showed a dependence on the percentage of lithiated sulfonimide substituent present. Increasing amounts of the lithium sulfonimide component increased
the charge carrier concentration but decreased the ionic conductivity due to decreased macromolecular motion and possible increased shielding of the nitrogen atoms in the polyphosphazene backbone. The ion conduction process was investigated through model polymers that contained the non-immobilized sulfonimide – systems that had higher conductivities than their single ion counterparts.

Chapter 3 details the synthesis of novel polyoctenamers with pendent functionalized-cyclotriphosphazenes as amphiphilic lithium-ion conductive membranes. Cyclotriphosphazene monomers were functionalized with one cycloocteneoxy substituent per ring. Two different types of monomer units, one with oligoethyleneoxy cation-coordination side groups and the other with hydrophobic fluoroalkoxy side groups, were then prepared. The syntheses of these monomers, their ring-opening metathesis copolymerization, and the characteristics of the resultant polymers are discussed, with an emphasis on the dependence of ionic conductivity and hydrophobicity on polymer composition.

Chapter 4 focuses the design of novel amphiphilic single-ion conductive polynorbornenes with pendent cyclotriphosphazenes as candidates for lithium-ion conductive membranes for lithium-seawater batteries. The cyclotriphosphazene components were linked to a 5-norbornene-2-methoxy substituent to provide a polymerizable unit. 2-(2-Phenoxyethoxy)ethoxy co-substituents on the cyclotriphosphazene unit of the first co-monomer were utilized to simultaneously facilitate lithium cation transport and introduce hydrophobicity into the polymer electrolyte. 4-(Lithium carboxalato)phenoxy side groups were linked to the rings of a second co-monomer to provide tethered anions with mobile lithium cations and to
increase the dimensional stability of the final polymers. The synthesis of norbornenemethoxy-based cyclotriphosphazene monomers, their ring-opening metathesis polymerization, deprotection and lithiation of the 4-(propylcarboxalato)phenoxy side groups, and the characterization of the polymers are discussed to illustrate the dependence of ion transport and hydrophobic properties on the polymer composition.

Chapter 5 is an analysis of the ionic conduction characteristics of silicate sol-gel poly[bis(methoxyethoxyethoxy)phosphazene] hybrid networks synthesized by hydrolysis and condensation reactions. Conversion of the precursor polymers to covalently interconnected hybrid networks with controlled morphologies and physical properties was achieved. Thermal analyses showed no melting transitions for the networks and low glass transition temperatures that ranged from approximately -38 °C to -67 °C. Solid solutions with lithium bis(trifluoromethanesulfonyl)amide in the network showed a maximum ionic conductivity value of $7.69 \times 10^{-5}$ S/cm, making these materials interesting candidates for dimensionally stable solid polymer electrolytes.

Chapter 6 investigates the influence of an organophosphate electrolyte additive on poly(ethylene oxide) lithium bis(trifluoromethylsulfonyl)imide-based gel polymer electrolytes for secondary lithium battery applications. Tris(2-(2-methoxyethoxy)ethyl)phosphate, is compared to the well known gel-battery component, propylene carbonate, through a study of complex impedance analysis, differential scanning calorimetry, and limiting oxygen index combustion analysis. The conductivities of the gels at low concentrations of tris(2-(2-methoxyethoxy)ethyl)phosphate (1.9 - 4.2 mol %) are higher to those of propylene carbonate based systems with the same concentration. Despite micro-phase separation at high concentrations of tris(2-(2-
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The appendix is a pyrolysis study of electrostatically spun poly(norbornenyldecaborane), a polymeric boron carbide precursor. Electrostatic spinning techniques provided an efficient and large scale route to non-woven mats of boron-carbide/carbon nanoscale ceramic fibers with narrow size distributions. Scanning electron microscopy, x-ray diffraction analysis and diffuse reflectance infrared Fourier transform spectroscopy were used to characterize the polymer and ceramic fibers. The results suggest that electrostatic spinning followed by pyrolysis can be used as a general route to a wide variety of single-phase and hybrid non-oxide ceramic fibers.
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PREFACE

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EPIGRAPH

“Scientific concepts exist only in the minds of men. Behind these concepts lies the reality which is being revealed to us, but only by the grace of God.”

- Werner Von Braun (1912-1977), first director of NASA, pioneer of space exploration
Chapter 1

Introduction

1.1 Polymeric materials

Polymeric materials are something that we, as humans, cannot live without. They are utilized in the simplest of devices such as dental floss and tooth brushes, to the most complex devices ever built by man, the NASA space shuttles. In addition to synthetically derived polymers, there are many naturally occurring polymers such as proteins, cellulose, silk, and rubber which are utilized in our everyday lives.

The term “polymer” comes from the Greek work poly, many, and meres, parts. A polymer by definition is a long-chain molecule which contains a large number of repeating units, or monomers, of identical structure. Most polymers are linear, but there are many other types of architectures in which they exist. In combination with the polymer’s architecture, the chemical structure of the monomer directly influences the physical properties of the polymer. This allows the physical properties of polymers to be tuned for specific applications.
1.1.1 History of polymer chemistry

Polymers have been utilized by humans for as long as we have been on this earth. However, it wasn’t until recently that we learned how to make our own polymers. The birth of synthetic polymer chemistry occurred about 175 years ago. In 1839, Charles Goodyear in the United States and Thomas Hancock in Britain concurrently developed the vulcanization process which enhanced the properties of natural rubber via treatment with sulfur at elevated temperatures. Nitrocellulose, the first man-made thermoplastic, was developed in 1847, when Christian Schönbein treated cellulose with nitric acid. Then in 1907 the first synthetic polymer was invented by Leo Baekeland. This synthetic polymer, called Bakelite was a phenol-formaldehyde resin known for its high heat resistance. However, at this time, the modern definition of what a polymer is was not generally accepted in the scientific community. The prevailing theory described the distinctive properties associated with polymeric materials as intermolecular interactions between many small molecules.\(^5\) It was not until the early 20\(^{th}\) century, that this theory was challenged. In 1920, Herman Staudinger (1953 Chemistry Nobel Laureate) proposed that the unique characteristics of polymeric materials were not a result of interactions between many small molecules, but were long chain-like molecules containing covalent chemical bonds.\(^6\,^7\) Over the next decade Staudinger’s “macromolecular theory” gained acceptance and was followed by a number of experiments performed by Wallace Carothers. In these experiments Carothers utilized well characterized small molecules, monomers, to prepare high polymers, which provided support of the macromolecular theory. Carothers invented the first synthetic rubber, a polyester which goes by the
tradename of Neoprene® and later went on and developed the first silk replacement, Nylon® or poly(hexamethylene adipamide), which also became the first synthetic polymer to be commercialized.\textsuperscript{8,9}

Over the next fifty years, vast numbers of other synthetic polymers were developed and commercialized in response to the growing need for new materials in the automotive and aerospace industries. Some of these new materials include polymers like polyethylene, polypropylene, polystyrene, and polycarbonate.\textsuperscript{1} Then in the late 20\textsuperscript{th} century the field of polymer chemistry began to take its attention off of exploiting previously commercialized polymers and refocused its efforts on developing new polymers for high-performance applications.\textsuperscript{2} Next generation batteries, fuel cells, visual displays, drug delivery platforms, and fire retardants are only a few of the applications where new polymeric materials are currently being researched and developed.

1.1.2 Polymer architecture

A polymer is a long chain-like molecule composed of many small units, called monomers, which are covalently linked together. If all the monomers are similar, than the polymer is referred to as a homopolymer. Alternatively, if the monomers are not similar than the polymer is referred to as a copolymer. Although, the chemical structure of the monomer units plays an integral role in determining the physical properties of the polymer, the architecture of the polymer chain can have an equally important impact. There are five general types of polymer architectures and they include linear, branched, star, dendrimer, and cross-linked (Figure 1-1).\textsuperscript{2,10,11}
Figure 1-1: Types of polymer architectures
Linear polymers have the simplest type of architecture and are generally soluble in many organic solvents. Additionally, the linear architecture allows for the polymer chains to become closely packed together favoring the formation of crystalline regions. A branched polymer contains branching sites along the polymer chain, which disrupts the ability of the chains to closely pack together and form crystalline regions.

Star and dendrimer polymer architectures are very similar because they both possess a central core which has three or more polymer chains attached to it. However, unlike a star polymer, dendrimers have regular, uniform branching points along the polymer chains, which reduce the degree of chain entanglements between polymer molecules. This usually leads to increased solubility and a less viscous solution when compared to their linear or branched counterparts.

The cross-linked polymer architecture is very similar to a branched polymer except that some of the branched chains are covalently linked to other polymer chains. This produces a polymer which is insoluble in organic solvents. However, cross-linked polymers usually can swell to many times their original volume when immersed in organic solvents.

A common way to modify the properties of a particular homopolymer is to incorporate one or two different monomers into the polymerization. This produces a copolymer, when two different monomers are polymerized, or a terpolymer, when three different monomers are used. A large majority of the commercially available synthetic polymers are copolymers presented in various monomer sequences such as those shown in Figure 1-2.
**Homopolymer**

AAAAA

**Random**

AABABBABAABABBA

**Alternating**

ABABABABABABABAB

**Block**

AAAAAABBBBBBB

**Graft**

AAAAAAABBBBBB

Figure 1-2: Various copolymer architectures (A, B = monomer units)
A random copolymer is a single polymer chain, which contains two monomers that are in no particular arrangement or sequence, whereas an alternating copolymer contains a regular alternating sequence of two monomers. Random and alternating copolymers typically exhibit properties that are intermediate of the two respective homopolymers of each monomer. The third type of copolymer architecture is a block copolymer. This type of architecture contains a polymer of one monomer linearly linked to a polymer of a different monomer. Graft copolymers result when there is a central polymer chain that has branching points to which different polymers are attached. Unique to block and graft copolymers is their ability to retain some of the properties associated with the individual homopolymers of the two monomers.

1.1.3 Polymerization type

Classification of polymers according to their architecture is one approach; however, there are still many different types of polymers within each architectural classification. This is where classification according to synthetic protocol is utilized to further delineate one polymer from another. There are three major polymerizations types used to classify polymers – this include step-growth, chain-growth, and ring-opening polymerizations.1,2,10
1.1.3.1 Step-growth polymerization

Step-growth polymerizations, or step reactions, are distinguished by the slow and stepwise style in which growth of the polymer chain occurs.\(^1\) In the earlier stages of the reaction two monomers come together to form a dimer, which then can react with any remaining monomers or other dimers to form trimers and tetramers. After this process repeats itself numerous times there is no monomer remaining, which only leaves the intermediate length polymer chains to react with each other. It is at this point an abrupt increase in molecular weight takes place. Condensation reactions are a type of step-growth polymerization where multifunctional monomers react with each other usually eliminating acid, ammonia, salt, or water.\(^10\) Some common condensation reactions include the polyesterification of terephthalic acid and ethylene glycol to produce poly(ethylene terephthalate) and the polyamidation of adipic acid and hexamethylenediamine to obtain nylon-6,6 (Figure 1-3). There are also non-condensation reactions which proceed in a step-growth manner – two examples of this are the addition polymerization of polyurethane and the oxidative coupling polymerization of 2,6-xylenol to yield poly(2,6-dimethyl-1,4-phenylene oxide) (Figure 1-4).
A

\[ n \text{HO-}C\text{-}C\text{-}OH \quad + \quad n \text{HO-}C\text{-}C\text{-}OH \]

terephthalic acid

\[ + \quad 2n \text{H}_2\text{O} \]

poly(ethylene terephthalate)

B

\[ n \text{HO-}C\text{(H}_2\text{)}\text{C}\text{-}OH \quad + \quad n \text{H}_2\text{N}\text{(H}_2\text{)}\text{C}_6\text{NH}_2 \]

adipic acid

\[ + \quad 2n \text{H}_2\text{O} \]

nylon-6,6

Figure 1-3: Step-growth polycondensation reactions - A) polyesterification of poly(ethylene terephthalate) and B) polyamidation of nylon-6,6.
Figure 1-4: Non-condensation step-growth reactions – A) addition polymerization of polyurethane and B) oxidative coupling polymerization of poly(2,6-dimethyl-1,4-phenylene oxide).
1.1.3.2 Chain-growth polymerization

The mechanism of chain-growth polymerizations proceed in an entirely different manner than step-growth polymerizations.\textsuperscript{1,2} Chain-growth polymerizations require the initiation of only a few monomers by a reactive molecule, which then propagates as monomers are added, yielding high molecular weight polymers immediately. This process can be described in three key steps: initiation, propagation, and termination. The initiation step requires the activation of a monomer from which the polymer chain will grow. The next step involves the propagation of the active chain end with additional monomers causing the chain to increase in length. Termination is when the active chain end is quenched, making it unable to grow any longer. A detrimental event that commonly occurs during chain-growth polymerizations is chain transfer. This happens when the active site on a chain end is transferred to another polymer chain or free monomer, as opposed to monomer at the end of the growing polymer chain. Upon transfer of the active site to another polymer chain, branching sites can arise causing a change in the morphology of the final polymer. On the other hand, if the active site is transferred to free monomer the previously active polymer chain is terminated and a new polymer chain is started, which causes a reduction in the final molecular weight along with a broadening of the molecular weight distribution.

There are three general mechanisms by which chain-growth polymerizations can occur – free-radical, ionic, and coordinative.\textsuperscript{2} The free-radical mechanism utilizes an unpaired electron at the propagating chain end (Figure 1-5), while the ionic mechanism employs anionic or cationic active species. Polyethylene, polypropylene, and
poly(vinylchloride) are examples of polymers which utilize free-radical techniques in their commercial production. Finally, the coordination, or insertion mechanism involves the use of transition metal catalysts which form complexes between the transition metal and \(\pi\)-electrons of the monomer. Ziegler-Natta catalysts are the most common class of transition metal catalysts, which are used in the polymerizations of polypropylene (\(i\)-PP) and high density polyethylene (HDPE).\(^ {12}\)
Initiation

\[ R^* + H_2C\equiv CH_2 \rightarrow R-\overset{H_2}{C-\overset{H_2}{C-CH_2^*}} \]

Propagation

\[ \overset{H_2}{C-\overset{H_2}{C-CH_2^*}} + H_2C\equiv CH_2 \rightarrow \overset{H_2}{C-\overset{H_2}{C-\overset{H_2}{C-CH_2^*}}} \]

Termination

\[ \overset{H_2}{C-\overset{H_2}{C-\overset{H_2}{C-\overset{H_2}{C-\overset{H_2}{C-\overset{H_2}{C-\overset{H_2}{C-CH_2^*}}}}}}}} + \overset{H_2}{C-\overset{H_2}{C-\overset{H_2}{C-\overset{H_2}{C-\overset{H_2}{C-\overset{H_2}{C-\overset{H_2}{C-\overset{H_2}{C-CH_2^*}}}}}}}} \]

Figure 1-5: Free-radical chain polymerization of polyethylene.
1.1.3.3 Ring-opening polymerization

Ring-opening polymerizations (ROPs) are utilized to convert cyclic monomers into linear polymer chains (Figure 1-6).\textsuperscript{2,10,13} ROP is a type of chain polymerization that consists of the initiation, propagation, and termination steps. However, unlike the typical chain polymerizations of carbon-carbon double-bond monomers, the propagation rate constants are similar to those in step-growth polymerizations, which lead to a slow rate of molecular weight increase. The ability of a cyclic monomer to be initiated and undergo chain propagation is primarily governed by thermodynamics, having to do with the relative stabilities of the cyclic monomer (ring-strain) and linear polymer structure. Typical initiation in ROP occurs via cationic or anionic means by the use of ionic initiators. Some inorganic polymers like polysiloxanes and polyphosphazenes also are synthesized via ROP via acid/base catalysis or thermal treatment, respectively. Additionally, new methods have been developed which utilize olefin metathesis catalysts usually based on early transition metals like tungsten, molybdenum, rhodium, and ruthenium. Polymerizations which utilize these catalysts are termed as ring-opening metathesis polymerizations (ROMPs) and mechanistically proceeds by the propagation of a metal-carbene complex as shown in Figure 1-7.\textsuperscript{13}
Figure 1-6: Ring-opening polymerization of various monomers
Figure 1-7: Mechanism of ring-opening metathesis polymerization
1.1.4 Polymer composition

A third approach to the classification of polymers is according to their elemental composition. The majority of polymers utilized in everyday life contain mostly organic elements, like carbon, nitrogen, and oxygen, in their backbone. However, there are two additional classes of polymers that are broadly employed in everyday life – inorganic and hybrid inorganic-organic polymers.

1.1.4.1 Organic polymers

The defining characteristic of organic polymers is their carbon-based backbone. Poly(ethylene) is one of the simplest organic polymers containing only -CH\textsubscript{2}- units in its backbone. Some common uses of polyethylene include electrical insulation, fibers and films.\textsuperscript{2} However, there are many other polymers derived from ethylene, which have made a large impact in commercial industry. Poly(tetrafluoroethylene), or Teflon® is a highly water resistant polymer which is used as a surface lubricant in machine parts, nonstick cooking utensils, and protective liners. Plexiglas® is another ethylene-based polymer known scientifically as poly(methylmethacrylate). Other classes of organic polymers contain heteroatoms such as oxygen, sulfur, or nitrogen in the polymer chain. Carbon-oxygen polymers include polycarbonates, polyethers, polyesters, and polyanhydrides. Polythioethers and polysulfones comprise carbon-sulfur polymers and carbon-nitrogen polymers consist of polyamines, polyimines, polyamides, and polyureas (Figure 1-8).\textsuperscript{1}
poly(tetrafluoroethylene) (PTFE, Teflon®)

poly(methyl methacrylate) (PMMA, Plexiglas®)

bisphenol-A poly(carbonate (PC, Lexan®)

poly(aryletherketone) (PEEK, Victrex®)

Figure 1-8: Various commercial organic polymers
1.1.4.2 Inorganic polymers

Inorganic polymers are heavily used as construction and building materials, abrasives and cutting materials, coatings, lubricants, catalysts, flame retardants, and fibers. The most common inorganic polymer today is silicon dioxide (silica), otherwise known as glass. There is also a version of silica which incorporates aluminum into its polymeric structure called alumina. Another inorganic polymer known for causing serious medical problems in humans is asbestos. Asbestos’s unique fire resistance characteristics are a result of a specific grouping of various minerals that form soft thread-like fibers. For example white asbestos, or Chrysotile, has a chemical formula of \( \text{Na}_2\text{Fe}^{2+}_3\text{Fe}^{3+}_2\text{Si}_8\text{O}_{22}(\text{OH})_2 \). Polysilicates and polyphosphates also represent two additional types of inorganic polymers, which are hydrolytically unstabe.

1.1.4.3 Hybrid inorganic-organic polymers

Hybrid inorganic-organic polymers have become one of the most widely researched areas in polymer science because of the many advantages they offer over organic polymers. By incorporating inorganic elements into the backbone of a polymer chain a far greater range of properties are realized compared to organic polymers. Properties such as catalytic activity, electrical conduction, wider operational temperatures, increased strength and thermal stabilities, as well as, improved chemical and oxidative resistances have all been demonstrated in these types of polymers. Some prominent classes of hybrid polymers are polysiloxanes, polysilanes, polycarbosilanes,
and polyphosphazenes illustrated in Figure 1-6. The unique ability for hybrid inorganic-organic polymers to combine properties associated with inorganic and organic elements has led to there increased exploration in order to meet the technological challenges in today’s world.

1.2 Polyphosphazenes

Polyphosphazenes are a specific class of hybrid inorganic-organic polymers, which have been heavily explored since the mid-1960s. This class of materials is differentiated by the alternating nitrogen and phosphorus atoms in the backbone to which two organic side units are attached to each phosphorus atom. This is similar to polysiloxanes, which also possess two organic side units attached to the silicon atoms in the backbone. However, the primary difference between polyphosphazenes and polysiloxanes lies in the synthesis of these two materials. Polysiloxanes are typically polymerized from siloxane ring structures that have the organic side units already attached to the silicon atoms. In contrast, a reactive intermediate, poly(dichlorophosphazene), is utilized to synthesize polyphosphazenes by replacement of the labile chlorine atoms with a nucleophile. This unique ability has led to the synthesis of well over 700 different polyphosphazenes with various chemical and physical properties.\textsuperscript{15}
Figure 1-9: Structure of hexachlorocyclotriphosphazene, (NPCl₂)₃, and poly(dichlorophosphazene), (NPCl₂)ₙ
1.2.1 History of polyphosphazenes

In 1834, Liebig and Rose reacted phosphorus pentachloride with ammonia which yielded a white crystalline solid.\textsuperscript{16,17} A decade later Gerhardt and Laurent determined the empirical formula of this white crystalline solid to be NPCl\textsubscript{2}.\textsuperscript{18} However, the exact structure was not determined until the 1860s when Gladstone and Holmes\textsuperscript{19-21} and Wichelhaus\textsuperscript{22} performed vapor density measurements that showed it was a trimeric molecule, hexachlorocyclotriphosphazene, (NPCl\textsubscript{2})\textsubscript{3} (Figure 1-9). It was not until thirty years later that cyclic structure of hexachlorocyclotriphosphazene was suggested by Stokes.\textsuperscript{23-26} Additionally, he identified a number of other higher cyclic homologues up to seven repeating units of NPCl\textsubscript{2}. Furthermore, he detailed a description on how to thermally polymerize these chlorophosphazenes to produce an insoluble, elastic “inorganic rubber”, which was found to be hydrolytically unstable. Then in 1924 a new method for the synthesis of hexachlorocyclotriphosphazene was proposed by Schlenk and Romer, where phosphorus pentachloride was reacted in solution with ammonium chloride.\textsuperscript{27} This alternative route gave higher yields and is currently the principal method for the synthesis hexachlorocyclotriphosphazene.

It was not until the 1960s, when Allcock, Kugel, and Valan published work which demonstrated that soluble polyphosphazenes could be prepared.\textsuperscript{30-32} They showed that by controlling the conditions of the thermal polymerization of hexachlorocyclotriphosphazene, soluble poly(dichlorophosphazene) (Figure 1-9) could be produced before it formed the insoluble “inorganic rubber”. Later work reported that the chlorine atoms on poly(dichlorophosphazene) could be replaced with a vast array of
nucleophiles to produce hydrolytically stable poly(organophosphazenes). These crucial
discoveries made by Allcock, Kugel, and Valen were integral in creating a foundation of
science which has led to the contemporary state of phosphazene chemistry.

1.2.2 Polyphosphazene architecture

As illustrated in Figures 1-1 and 1-2, the polymer and copolymer architectures are
also accessible with phosphazenes. The linear polymer architecture comprises the
majority of the polyphosphazenes synthesized to date; however, in the last decade a
variety of other polymeric architectures have been explored utilizing the phosphazene
system (Figure 1-10). Block and graft copolymers allow for various types of organic
polymers to be incorporated into polyphosphazenes. Some examples of organic polymers
which have been blocked or grafted with polyphosphazenes include polystyrene, polymethylmethacrylate, polyethylene oxide, polydimethylsiloxane and polynorbornene. Polyphosphazene star polymers have also been synthesized by
cationically growing phosphazene chains from a trifunctional monomer. Additionally,
unique hybrid architectures have been synthesized by incorporating cyclophosphazene
rings into polyethylene-like backbones and as pendant groups from various types of
organic polymers including polyethylene, polystyrene, polynorbornene, and polyoctenamer. Finally, three-dimensional cross-linked networks termed “cyclomatrix
polymers” have been synthesized also using cyclophosphazenes.
Figure 1-10: Polyphosphazene and organic polymer cyclotiposphazene architectures
1.2.3 Synthesis of polyphosphazenes

There are several methods by which the reactive macromolecular intermediate, poly(dichlorophosphazene), is synthesized. The oldest and most common method is the thermal ring-opening polymerization of hexachlorocyclotriphosphazene developed by Allcock and Kugel. However, due to molecular weight control issues a number of other methods have been developed in the last decade that attempt to produce poly(dichlorophosphazene) in a well-defined manner. The main synthetic feature of polyphosphazenes which distinguishes them from all others polymer systems is macromolecular substitution. This process utilizes a single reactive macromolecular intermediate to generate all polyphosphazenes.

1.2.3.1 Thermal ring-opening polymerization

The thermal ring-opening polymerization (TROP) method is a melt polymerization utilized to produce high molecular weight poly(dichlorophosphazene) (Figure 1-11). This polymerization is performed by heating hexachlorocyclotriphosphazene to 250°C in an evacuated sealed glass tube. Termination of the polymerization is carried out when a highly viscous melt is obtained by allowing the reaction mixture to cool to room temperature. This usually occurs after 8-10 hours, where as, prolonged heating will eventually turn the reaction into the cross-linked “inorganic rubber” previously made by
Polymeriation yields of 70-75% are typically obtained where the molecular weights are over 500 kDa with broad polydispersity indices.

The mechanism by which TROP proceeds is not fully understood, but it is believed to occur via a cationic route (Figure 1-12). Initially, one of the phosphorus-chlorine bonds in hexachlorocyclotriphosphazene undergoes thermal ionization to produce a phosphazenum ion.\textsuperscript{15,53,54} A lone pair of electrons on another trimer molecule’s nitrogen then attacks the phosphazenum ion, which concurrently causes ring cleavage, transfer of the cationic charge to the terminal phosphorus, and chain propagation, which leads to high molecular weight poly(dichlorophosphazene).

There is a significant amount of experimental evidence which supports the cationic pathway of this polymerization. First, conductivity measurements have shown that there is a substantial decrease in the resistivity of molten hexachlorocyclotriphosphazene when the temperature is raised indicating that charged species have been formed. Electron-spin resonance experiments have also indicated the absence of free-radicals, which further supports a cationic route over a free-radical path. Finally, the required polymerization temperature rises with increasing phosphorus-halogen bond strength, thus, indicating the necessity of phosphorus-halogen bond ionization in the TROP.
Figure 1-11: Synthesis of poly(dichlorphosphazene) and macromolecular substitution
Figure 1-12: Proposed mechanism for the thermal ring-opening polymerization of hexachlorocyclotriphosphazene
1.2.3.2 Alternative polymerization methods

Despite the utilization of the thermal ring-opening polymerization method as the primary route to poly(dichlorophosphazene) there are a number of inherent disadvantages, which include poor molecular weight control, high polydispersity indices (broad molecular weight distribution), and elevated polymerization temperature. These drawbacks are what stimulated exploration into new methods that can produce poly(dichlorophosphazene) in a controlled, well-defined manner. Lewis acid catalysts, such as borontrichloride-triphenylphosphate, toluenesulfonic acid, and sulfamic acid, have been utilized in melt and solution polymerizations, which have produced higher yields and lower polydispersity indices. Although, high molecular weight poly(dichlorophosphazene) was not obtained.\(^{53,56}\) Additionally, the exact mechanism by which the polymerization proceeds in the presence of these catalysts still is unclear. However, it is generally accepted that the catalyst assists in the ionization of the phosphorus-chlorine bond.

Recently, an ambient temperature solution synthesis of poly(dichlorophosphazene) was developed by Allcock, Manners, and coworkers.\(^{57,58}\) This polymerization first involves the treatment of trichloro(trimethylsilyl)phosphoranimine (Cl\(_3\)P=NSiMe\(_3\)) with trace amounts of cationic initiator, phosphorus pentachloride (PCl\(_5\)) (Figure 1-11). The PCl\(_5\) first dissociates in solution yielding a PCl\(_4^+\) PCl\(_6^-\) ion pair, which then leads to the attack of the lone pair electrons on the nitrogen atom of another monomer by the PCl\(_4^+\) cation, resulting in displacement of the trimethylsilyl group. The
polymerization then proceeds by addition of more monomer which results in chain propagation and eventually produces poly(dichlorophosphazene). The development of this method, the cationic polymerization of phosphoranimines, has led to the synthesis of telechelic, block, and graft copolymers of polyphosphazenes with various organic polymers.33-42

1.2.3.3 Macromolecular substitution

As mentioned previously, the macromolecular substitution process sets polyphosphazenes apart from all other polymer synthesis methods.15 The hydrolytic instability of the phosphorus-chlorine bonds in poly(dichlorophosphazene) makes them susceptible to nucleophilic attack by a variety of types of nucleophiles such as alkoxides, aryloxides, primary amines, and secondary amines. As shown in Figure 1-11 single nucleophiles can be added, as well as, two nucleophiles in a sequential or simultaneously manner yielding single- and di-substituted polyphosphazenes, respectively. The reactivity of the phosphorus-chlorine bond is such that it allows for the displacement of effectively every chlorine atom, which results in hydrolytically stable polyphosphazenes with a wide array of bulk properties. Bulk properties, which have been modified, include solvent solubility, hydrophobicity, hydrophilicity, biocompatibility, glass transition temperature, thermal and oxidative stability, chemical and mechanical stability, ionic conductivity, and refractive index.

The primary advantage of polyphosphazene’s macromolecular substitution step over conventional organic polymer synthesis is the ability to systematically control the
final polymer’s properties by the treatment of the reactive macromolecular intermediate, poly(dichlorophosphazene), with various nucleophiles. In contrast, for the properties of a conventional organic polymer to be altered, the chemical structure of the monomer must be modified, which may require different polymerization conditions than the original monomer. Thus, modification of organic polymers can be a timely and costly process.

1.2.4 General structure-property relationships

There are a number of unique characteristics resultant from the phosphorus-nitrogen backbone that are not found in the common organic polymer backbones. The first unusual property is the flexibility of the polyphosphazene backbone, which is a result of the high torsional mobility of the backbone bonds. The barrier to torsion in the phosphorus-nitrogen bonds is well below 1 kcal/bond/repeat. This has led to glass transition temperature ($T_g$) values as low as -105ºC. Similarly, poly(dimethylsiloxane) has a $T_g$ of -130ºC and is known to be one of the most flexible polymer backbones in existence. The low barrier to torsion of the phosphorus-nitrogen bond is best explained in terms of bonding electronics. It is known that the polyphosphazene backbone is electronically insulative, which suggests that long-range π-bond delocalization does not occur. Instead, it is thought that short-range delocalization exists over a phosphorus-nitrogen-phosphorus three bond arrangement with a node at each phosphorus separating each “island” of electron density (Figure 1-13). This bonding structure allows the nitrogen 2p-orbitals to overlap with the five possible phosphorus d-orbitals during bond
torsion which allows for a 360° rotation without experiencing a decrease in π-bond overlap.\textsuperscript{59}

An alternative explanation for the high degree of flexibility in the polyphosphazene backbone also exists, which deals with the alternating phosphorus-nitrogen atoms bearing positively and negatively charged, respectively. This zwitterionic arrangement is thought to be induced by negative hyperconjugation, which involves electron donation from the nitrogen’s π-orbitals to the σ*-bonds of the phosphorus.\textsuperscript{60,61}

Increased thermo-oxidative stability and resistance to visible, ultraviolet, and high-energy radiation are other unique characteristics of the polyphosphazene backbone which improve over conventional organic carbon-based polymers.\textsuperscript{15} Most organic polymers tend to undergo homolytic cleavage to give free radicals when exposed to high temperatures and various types of radiation.\textsuperscript{2} In addition, many organic polymers are completely degraded at temperatures well below 250ºC, the temperature which most polyphosphazenes start to degrade. There are a number of reasons that explain the increased thermo-oxidative stability of polyphosphazenes: (1) the high bond energy in the backbone (>70 kcal/mol), (2) the resistance of the backbone to undergo homolytic cleavage, and (3) the phosphorus (pentavalent) and nitrogen (trivalent) atoms are already in their most stable oxidative state. The resistance to visible, ultraviolet, and high-energy radiation is also a notable characteristic of polyphosphazenes, which shows radiation transparency from the near infrared to the mid-ultraviolet region (220 nm) of the electromagnetic spectrum. As a result, the backbone has a high resistance to cleavage either by direct photolytic or photo-oxidative means. Furthermore, high bond strength of the polyphosphazene backbone is most likely related to its high-energy radiation stability.
Figure 1-13: Out-of-plane $d_{\pi}(P) - p_{\pi}(N)$ bonding in polyphosphazenes
The final unique characteristic of the polyphosphazene backbone pertains to its fire retardant properties. It is well known that compounds containing phosphorus and nitrogen have increased fire retardant properties. There are two theories which attempt to explain why polyphosphazenes have increased fire resistance. The first theory centers on the phosphazenes ability to decompose and form a “char”, which then acts to insulate unburned materials from the heat and chemical reactions which allow the flame to propagate. Secondly, phosphazenes have the capability to retard the oxidative chain reactions that occur at the flame front and, thus, hinder flame propagation.

1.2.5 Applications

By combining the advantages of the phosphorus-nitrogen backbone and the synthetic tailorability via macromolecular substitution many different applications have targeted for polyphosphazenes. Figure 1-14 shows various polyphosphazenes which have completely different properties and applications. The first polymer shown bears 2-(2-methoxyethoxy)ethoxy side units, which impart a high degree of free volume into the polymer producing very low a $T_g$ value. Polymers with these types of oligoethyleneoxy side units are also extremely good solvents for metal salts, such as lithium bis(trifluoromethanesulfonyl)imide. These polymer-salt complexes are useful as solid electrolytes in energy storage devices. Polymers that bear fluoroalkoxy side units exhibit hydrophobicity, fire resistance, and relatively low $T_g$ values. Additionally, these types of side units usually result in the polymers containing crystalline domains due to side unit interactions. Polymers bearing these types of side units are good for modifying
existing surfaces to make them more hydrophobic. Two polymers, with the tradenames Eypel-F® and PN-F®, have been patented as solvent resistant, low temperature fluoroelastomers for military applications. The third polymer shown contains aryloxy side units with acidic sulfonamide functional groups. Various other acidic functional groups, such as sodium carboxylate and phosphonic acid have also been examined. Polymers containing the carboxylate groups have been used for cross-linking sites in bone-regeneration composites. The phosphonic acid and protonated sulfonamide polymers have been tested as polymeric fuel cell membranes, while the lithiated derivative of the sulfonamide polymer can be used as a single ion polymer electrolyte in energy storage devices. The final polymer depicted is an amino acid ester side unit bearing polyphosphazene, which is utilized to impart hydrolytic instability into the polymer. This leads to polymer degradation into biologically benign amino acids, phosphates, and ammonia. Depending on the type of amino acid ester group attached the rate at which these polymers degrade can be tailored, allowing their utilization in a number of biomedical applications including tissue engineering and bone-regeneration composites.

Other applications for polyphosphazenes that have been explored include photonic polymers which exhibit high refractive indices, non-linear optic or electroluminescence behaviors. These types of polyphosphazenes contain halogenated aryloxy, mesogen-like, or electronically conductive units linked to the polymer, respectively. Polyphosphazenes and cyclic phosphazenes also have much potential to function in other application areas such as gas, liquid, and ion separation, solid filtration,
antimicrobial materials, fire retardants and additives, protective surface coatings, photoresists, adhesives, lubricants, and hydraulic fluids.
Figure 1-14: Various polyphosphazenes
### 1.3 Polymer electrolytes

Polymer electrolytes are a class of electrolyte materials which, as the name would suggest, contain a polymer as the main component with a metal salt dissolved within.\(^\text{80}\) Electrolytes utilized in conventional battery technology typically are liquid-based, but polymer-based electrolytes are becoming more common in the commercial market.\(^\text{81}\) Polymers have many advantages over their liquid counterparts.\(^\text{80-82}\) First, energy storage devices that are fabricated using polymers will not have the leakage or gassing problems associated with liquids, which are usually toxic, flammable, and corrosive. The second advantage of polymers is their flexibility and ability to be easily processed which allow for energy storage devices to be fabricated into various geometries depending on the desired application. Thirdly, energy storage devices made with polymers will be much lighter than liquid-based devices because the casing required to contain a polymer is rather simple compared to the much more robust and heavier casings needed for liquids. The one major disadvantage of polymer electrolytes is their low ionic conductivity values, which are typically 100 to 1000 times less than liquid electrolytes.\(^\text{80}\) In order for polymer electrolytes to compete with liquid electrolytes in the commercial market they must have ionic conductivities of \(10^{-3}\) S/cm or greater at room temperature.\(^\text{83}\) Thus, research and development has been driven by the desire to improve the ionic conductivity polymer electrolytes from both an engineering approach and by the design and synthesis of new polymer electrolytes. The latter approach is where the focus of this thesis lies.

A battery is an energy storage device which provides electricity as a result of an electrochemical reaction. There are to two main categories of batteries, primary and
A primary battery is non-rechargeable and intended to be used only once after which it is disposed. Batteries of this type comprise the vast majority of batteries on the commercial market today. In contrast, a secondary battery is a rechargeable battery and has the ability to be recharged once drained by supplying an electrical current that reverses the initial electrochemical reaction. The modern lead-acid car battery is a common secondary battery used today. The volumetric and gravimetric energy densities of various battery technologies are presented in Figure 1-15. Lead-acid batteries, shown in the lower right corner, are very heavy and bulky per unit energy. On the other hand, lithium-based battery technologies offer a much lighter and smaller battery per unit energy making them very attractive in the portable electronics industry. Lithium metal is the lightest (equivalent weight $M = 6.94$ g/mol, specific gravity $\rho = 0.53$ g/cm$^3$) and most electropositive element that has a very high oxidation potential (3.04 V versus a standard hydrogen electrode), making it useful in the design of energy storage devices with high energy densities.

Shown in Figure 1-16, is a schematic of a lithium secondary battery. There are four main components to this type of battery – anode/cathode current collectors, lithium metal anode, electrolyte layer, and intercalation cathode. The power generation process starts at the lithium metal anode, where the lithium oxidation reaction ($x \text{Li}^0 \rightarrow x \text{Li}^+ + x \text{e}^-$) takes place, releasing lithium cations and electrons. The electrons are harnessed by the anode current collector and directed through an external circuit to provide power for a specific device. Simultaneously, the lithium cations are transported through the electrolyte material where they undergo a reduction and subsequent incorporation into an
intercalation compound \((x \text{ Li}^+ + x \text{ e}^- + \text{MO}_2 \rightarrow \text{Li}_x\text{MO}_2)\). The intercalation compounds are typically metal oxides based on manganese, vanadium, or cobalt.
Figure 1-15: Various battery technologies in terms of volumetric and gravimetric energy densities\textsuperscript{33}
Figure 1-16: Schematic of a lithium secondary battery
1.3.1 History

Polymer electrolytes is a relatively new field of science which only began about 25 years ago. In 1973, P.V. Wright studied the interactions of poly(ethylene oxide) (PEO) (Figure 1-17) with metal thiocyanate salts. The outcome of this study led M.B. Armand to suggest that PEO could be utilized as electrolytes in lithium batteries. This stimulated research pertaining to the ionic conduction of PEO with different salt at numerous concentrations and temperatures. Although, PEO is the most heavily studied polymer electrolyte is has an inherent disadvantage preventing its commercial use – crystallinity. At room temperature the crystalline domains present in PEO (about 60%) inhibit efficient ionic conduction. However, when heated above its crystalline melting temperature (66ºC), practical ionic conductivities are obtained. In order to improve room temperature ionic conductivity, past and current research has focused on the development polymer electrolytes based on the structure of PEO, but with no crystallinity. In addition to other solid polymer electrolyte systems, gel polymer electrolytes, and polyelectrolytes have received much attention.
Figure 1-17: Structures of poly(ethylene oxide) (PEO) and poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (MEEP)
1.3.2 Types of polymeric electrolytes

Polymer electrolytes can be classified into three categories: solid polymer electrolytes (SPEs), gel polymer electrolytes (GPEs), and polyelectrolytes. A SPE is a solution of a metal salt (solute) that is dissolved in a polymer (high molecular weight solvent). In order for a polymer to effectively dissolve a metal salt it must be capable of coordinating the metal cation of the salt. This would make polyethers, polyesters, polyimines, and polythiols ideal for polymer electrolytes because of the lone pair electrotens located on the oxygen, nitrogen, or sulfur atoms. GPEs are similar to SPEs except they contain an organic small molecule additive that serves to plasticize the polymer and increase ion dissociation of the metal salt, thus, increasing the ionic conductivity. Various commercially used small molecule additives are shown in Figure 1-18. Typically, GPEs require an additive content of more than 50 % to obtain ionic conductivities comparable to that of liquid electrolytes. The third type of polymer electrolyte is a polyelectrolyte, also called a single ion conductor. Here, the anion of a salt is incorporated directly into the polymer backbone or as a pendant group attached to the polymer backbone. By immobilizing the anion it is possible to fabricate electrochemical devices that are less vulnerable to increased resistance associated with salt concentration gradients at the electrode-electrolyte interfaces during charging and discharging.

The hard/soft acid/base principle can be used to describe how well various polymer will solvate metal salts. A hard acid is a small cation with no valence electrons which
are easily polarizable or removable, while a soft acid is a larger cation that has many valence electrons that are easily polarizable or removable. Similarly, a hard base has highly electronegative ligands which are non-polarizable and a soft base does not. The strongest interactions occur by having a hard acid with hard base or a soft acid with a soft base. Therefore, hard cations, such as lithium, sodium, magnesium, and calcium are best solvated by a polyether, while a silver cation would be best solvated by a polyimine. The anion of a metal salt also plays an integral role is allowing dissociation of the cation from the anion. Anions which are large and contain electron withdrawing groups can delocalize the negative charge much easier, thus, requiring little solvation to gain adequate charge separation which facilitates cation transport.
Figure 1-18: Various commercially used small molecule additives for gel polymer electrolytes
Figure 1-19: Mechanism of ionic conduction in liquid electrolytes
Figure 1-20: Ionic conduction mechanisms in solid polymer electrolytes

Intrachain hopping

Interchain hopping

Intrachain hopping via ion cluster

Intercluster hopping

Figure 1-20: Ionic conduction mechanisms in solid polymer electrolytes

80
1.3.3 Mechanisms of ion transport

The understood mechanisms for the transport of cations in liquid, solid polymer, and gel polymer electrolytes are very different from each other. Liquid electrolytes act by dissolving the metal salt to produce a cation-anion separated ion pair. The solvated cation is then transported to the cathode by diffusive movement as shown in Figure 1-19. Conversely, SPEs utilize macromolecular motion to transport cations. In order for a polymer to be effective at macromolecular motion it must be able to dissolve the metal salt. Typically, heteroatoms with lone pair electrons, such as etheric oxygen, nitrogen and sulfur atoms are effective.\(^{80,82}\) Macromolecular motion of the polymer then allows for the passing of the cations or ion clusters from coordination site to coordination site via intra- and interchain hopping. Schematic representations of these mechanisms are shown in Figure 1-20.\(^{80}\) Efficient macromolecular motions are usually a result of the polymer possessing a low glass transition temperature. Furthermore, the mechanism of ion transport in GPEs is similar to that of SPEs at lower concentrations of small molecule additive. However, at concentrations higher than 50 % the mechanism is predominately via diffusive motion.

1.3.4 Phosphazene polymer electrolytes

Polyphosphazenes were first investigated for polymer electrolyte applications in 1984.\(^{63-65}\) Figure 1-18 shows the chemical structure of poly[bis(2-(2-
methoxyethoxy)ethoxy)phosphazene] (MEEP), the phosphazene analog of poly(ethylene oxide) (PEO). MEEP, when combined with a lithium salt, showed ionic conductivities three to four orders of magnitude higher than PEO primarily because of its amorphous nature and greater number of etheric oxygen atoms per repeat unit. The low ionic conductivity of PEO is attributed to its large crystalline component (40%), which acts as a barrier to ion transport.\textsuperscript{80,82} The flexibility of the phosphazene backbone of MEEP also imparts a low glass transition temperature ($T_g$) (-84°C), which aids the ion transport via increased macromolecular motion. However, the low $T_g$ of MEEP also causes poor dimensional stability which affects its utility in an energy storage device. This led to the further investigation of polyphosphazenes for polymer electrolyte applications by the design new polymeric systems.

There have been many approaches taken in an attempt to maintain the high ionic conductivity of MEEP while improving its dimensional stability. First, $\gamma$-ray and ultraviolet irradiation, and sol-gel cross-linking techniques have been utilized to introduce cross-links between MEEP side units.\textsuperscript{98,99,100} Longer oligoethyleneoxy side units, as well as, branched derivatives have also been investigated to see how side unit entanglement affects the physical and ionic conduction properties of the polymers.\textsuperscript{101,102} The effect of arm length of MEEP tri-star polyphosphazenes compared to their corresponding linear derivative has been examined. In addition to star polymers, block copolymers of MEEP and PEO have been studied in order to incorporate the properties of both systems.\textsuperscript{103} Both the polyphosphazene\textsuperscript{104} and various organic polymers\textsuperscript{47-50} with pendant substituted-cyclotriporphosphazene units have been analyzed by utilizing several polymerization techniques including the thermal ring-opening polymerization and
macromolecular substitution, free-radical, and ring-opening metathesis polymerization. Furthermore, single ion conductive and composite polyphosphazenes have also been synthesized and their ionic conductive properties characterized. Single ion conductive polyphosphazenes have linked sulfonamide\textsuperscript{69} and sulfonate\textsuperscript{89,105,106} anions to the polymer backbone. The composite polyphosphazene systems have involved blending MEEP with other polymers\textsuperscript{107,108} such as PEO and poly(propylene oxide) or creating interpenetrating networks\textsuperscript{108,109} of MEEP with other organic polymers including poly(styrene), poly(acylic acid), poly(acrylonitrile), poly(methyl methacrylate), poly(ethylene glycol diacrylate), and poly(vinylpyrrolidinone). In addition, MEEP has been combined with sol-gel silicates\textsuperscript{110} and other inorganic materials like layered silicate montmorillonite.\textsuperscript{111}

MEEP-based gel polymer electrolytes with various commercially used organic solvents like N-methylpyrrolidone and propylene carbonate have been explored in an effort to increase the ionic conductivity of the MEEP-based systems to the $10^{-3}$ S/cm value required for commercial applications.\textsuperscript{112} Other additives, including oligoethyleneoxy-substituted phosphates\textsuperscript{113} and functionalized-cyclotriphosphazenes\textsuperscript{112} have also been synthesized and combined with MEEP to increase ionic conductivity and fire retardancy.
1.4 References


(49) Allcock, H.R.; Bender, J.D.; Morford, R.V.; Berda, E.B. *Macromol.* 2003, 36, 3563.


(51) Devadoss, E.; Reghunadhan C.P. *Polymer* 1985, 26, 1895.


Chapter 2

Single ion conductors - polyphosphazenes with sulfonimide functional groups

2.1 Introduction

Secondary lithium batteries are lightweight systems with high power densities. Compared to lead-acid or nickel-based batteries they offer a solution to numerous energy storage problems.\textsuperscript{1,2} Traditional lithium ion battery systems contain salts dissolved in organic liquid electrolytes. These give good conductivities due to high ion mobility.\textsuperscript{1} However, liquid-based systems have inherent disadvantages such as flammability, the need for electrolyte containment, and possible reactions of the liquid electrolytes with the anode.\textsuperscript{2} For these reasons, solid-state lithium battery systems have been the subject of intense research.\textsuperscript{1,3}

Solid polymer electrolytes (SPEs) are materials that transport ions without the aid of a liquid electrolyte. Many commercial liquid-based lithium ion battery cells use lithium hexafluorophosphate (LiPF\textsubscript{6}) mixed with a polymer electrolyte to increase both the charge carrier concentration and the overall lithium ion transport.\textsuperscript{4} However, lithium cations and hexafluorophosphate anions tend to associate in solution, which decreases the ionic conductivity. Moreover, LiPF\textsubscript{6} is susceptible to thermal decomposition at temperatures above 30 °C.\textsuperscript{1} These problems have stimulated research into the use of
large, highly delocalized anions in order to decrease the strength of coordination between
the cation and anion, thereby increasing the lithium ion transport.\(^5\)

Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) is one of the most weakly
coordinating salts known.\(^6\) Weak coordination between the lithium cation and the TFSI
anion provides access to a high concentration of charge carriers which, in turn, leads to
an increase in ion transport. To further limit ion association and increase cation mobility
in SPEs, several research groups have attempted to immobilize the anion by a covalent
linkage to the polymer to produce a single ion conductive polymer electrolyte.\(^6-9\) Ideally,
the anion bound to the polymer electrolyte should have a highly delocalized charge and
be a weak conjugate base.\(^5\) Of course, if the anion is a significant charge carrier, anion
immobilization would result in a decrease in ionic conductivity.

Previous work by Watanabe and co-workers used a polymeric analogue, poly(2-
oxo-1-difluoroethylene lithium sulfonimide), of LiTFSI salt as a single ion conductive
polymer and achieved maximum ambient temperature conductivity in the range of \(10^{-7}\)
S/cm.\(^10\) Shriver and coworkers synthesized siloxane-based polymers with ethyleneoxy
and trifluoromethanesulfonamide functionalized side chains and obtained a maximum
ambient temperature conductivity in the range of \(10^{-6}\) S/cm.\(^4\)

A small molecule analog of TFSI, 4-hydroxy-N-[(trifluoromethyl)sulfonyl]-benzenesulfonamide (HOC\(_6\)H\(_4\)SO\(_2\)N(H)SO\(_2\)CF\(_3\)) was developed in our laboratories for
use in proton conducting fuel cell membranes.\(^11,12\) This molecule can be adapted for
battery applications via lithiation of the nitrogen atom. The work described in this paper
utilizes a lithiated derivative of this molecule, with the anion covalently linked to a
polyphosphazene that also bears 2-(2-methoxyethoxy)ethoxy substituents. The 2-(2-
methoxyethoxy)ethoxy substituent has previously been shown to provide excellent properties for lithium ion transport, probably because the lone pair electrons on each oxygen atom function as weak lithium ion coordination sites. Lithium ion transport is also increased by the large free volume generated by the highly flexible 2-(2-methoxyethoxy)ethoxy substituents. The percentage of lithium sulfonimide substituent in the new polymers was varied from 5 mol % to 22 mol % in order to study the effect of the substituent ratios on the ion conductive properties. In addition, 2-(2-methoxyethoxy)ethoxy / phenoxy cosubstituted polyphosphazenes with unbound LiTFSI were synthesized to compare the single ion conductive polymers with their unbound salt analogues. Gel polymer electrolyte samples were also fabricated in order to illustrate the effect of a plasticizer on the ionic conductivity of a single ion conductive solid polymer electrolyte.

2.2 Experimental

2.2.1 Materials

Trifluoromethanesulfonamide (98+ %) was obtained from TCI and was used as received. 4-Methoxybenzenesulfonyl chloride (99 %), sodium hydride (95 %), sodium methoxide (0.5 M in methanol), sodium ethanethiolate (80 %); N,N-dimethylformamide (99 %), lithium chloride (99+ %), and 2,2,2-trifluoroethanol (98 %), propylene carbonate (99.7 %), and N-methyl-2-pyrolidinone were obtained from Aldrich and were used as received. 2-(2-methoxyethoxy)ethanol (99 %) (Aldrich) and was distilled over calcium
hydride before use. Phenol (99+ %) (Acros Organics) was used as received. Lithium trifluoromethanesulfonimide (LiTFSI) (3M Corp.) was used as received. Poly(dichlorophosphazene) was prepared via the thermal ring-opening polymerization of hexachlorocyclotriphosphazene at 250 °C in a sealed evacuated tube. Tetrahydrofuran was distilled from sodium benzophenone ketyl under an inert atmosphere of argon. The synthesis of 4-hydroxy-N-[(trifluoromethyl)sulfonyl]-benzenesulfonamide mono-sodium salt was carried out according to a literature procedure. Poly[bis(trifluoroethoxyphosphazene)] (6) and poly[bis(2-(2-methoxyethoxy) ethoxyphosphazene)] (7) were synthesized according to literature procedure. All reactions were carried out using standard Schlenk techniques under an atmosphere of argon.

2.2.2 Equipment

High-field $^1$H (360 MHz), $^{13}$C (90.56 MHz), and $^{31}$P (90.27 MHz) NMR spectra were recorded using a Bruker AMX-360 NMR spectrometer. $^1$H and $^{13}$C NMR spectra were referenced to external tetramethysilane, while $^{31}$P NMR spectra were referenced to external 85% phosphoric acid. $^{13}$C and $^{31}$P NMR spectra were proton decoupled. 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 (Alfa Aesar) in THF (OmniSolv). Thermal transitions were
determined through analysis via a TA Q10 differential scanning calorimeter. Calibration was accomplished with indium, water, and cyclohexane standards. All analyses were performed over a range of -120 °C to 100 °C at a heating rate of 10 °C/min. Elemental analysis were carried out by Quantitative Technologies, Inc.. Flame atomic absorption analyses were obtained using a Buck Scientific Atomic Absorption Spectrometer (Model 210) with a sodium lamp at 589 nm. Ionic conductivity measurements were obtained using a Hewlett Packard 4192A LF Impedance Analyzer at a potential of 0.1 V with an alternating current frequency range of 5 Hz to 1 MHz. The samples were placed between platinum electrodes with a Teflon o-ring spacer. The electrolyte cell was compressed between aluminum blocks held in a Teflon fixture. Electrical leads were attached between the impedance analyzer and the electrolyte cell sample holder. Multiple measurements were made to ensure the accuracy and precision of the ionic conductivity values. All ionic conductivities measurements were carried out over a temperature range of 20 °C to 80 °C (5 °C increments) under an inert atmosphere of argon.

### 2.2.3 Synthesis of \([\text{NP}((\text{OCH}_2\text{CH}_2)_2\text{OCH}_3)_x(\text{OC}_6\text{H}_4\text{SO}_2\text{N(Li)SO}_2\text{CF}_3)_y]_n\) (2-5)

For polymer 2: 2-(2-methoxyethoxy)ethanol (2.07 g, 17.2 mmol) was added dropwise to a suspension of 95 % sodium hydride (0.403 g, 16.8 mmol) in THF (100 mL) at room temperature. The reaction was complete in a period of 5 h. This sodium salt solution was then added to a solution of poly(dichlorophosphazene) (1.0 g, 8.6 mmol) in THF (100 mL) at room temperature and the reaction was allowed to proceed for 72 h. In a separate reaction vessel a solution of 4-hydroxy-N-[(trifluoromethyl)sulfonyl]-
benzenesulfonamide mono-sodium salt (0.422 g, 1.29 mmol) in THF (25 mL) was added to a suspension of 95 % sodium hydride (0.021 g, 0.86 mmol) in THF (25 mL) at room temperature and allowed to react for a period of 12 h. The sulfonimide di-sodium salt was then added to the solution of poly(dichlorophosphazene) at room temperature and allowed to react for 72 h. The substituted polymer precipitated slowly from solution after addition of the sulfonimide di-sodium salt. The THF supernatant solution was then removed by decantation and the precipitated polymer was dissolved in acidic water (pH ~5). Once dissolved, it was placed in 12-14000 MWCO dialysis tubing for two days against deionized water. A 0.1 M LiCl\textsubscript{(aq)} solution was then used to dialyze the polymer solution for three days. Deionized water was then used to remove excess salts. Once complete, the polymer solution was filtered, concentrated to a viscous liquid and transferred to a polypropylene vial. The remaining solvent was removed under reduced pressure at 60 °C to produce a solid material. To eliminate the exchange of lithium cations from the polymer with sodium cations present in the glassware, all glassware was rinsed with a 0.1 M LiCl\textsubscript{(aq)} solution. The product (2.61 g, 74 % yield) was isolated as a brown gum. $^1$H NMR (d\textsubscript{4}-methanol): δ (ppm) 3.5 (s, 57H), 3.7 (m, 38H), 3.8 (m, 38H), 3.9 (m, 38H), 4.3 (m, 38H), 7.6 (br d, 2H), 8.0 (br d, 2H); $^{13}$C NMR (d\textsubscript{4}-methanol): δ (ppm) 59.7, 67.1, 71.8, 73.5, 122.8, 123.9, 129.9, 142.1, 156.8; $^{31}$P NMR (d\textsubscript{4}-methanol): δ (ppm) -6.5 (br s, 9P), -12.4 (br s, 1P). Similar chemical shifts were observed for polymers 3, 4, and 5.

For polymer 3: The same synthetic procedure was used as for polymer 2 to obtain 2.21 g product (81 % yield). Reagent quantities: 2-(2-methoxyethoxy)ethanol (1.96 g, 16.4 mmol), 95 % sodium hydride (0.382 g, 15.9 mmol); 4-hydroxy-N-
[(trifluoromethyl)sulfonyl]-benzenesulfonamide mono-sodium salt (0.703 g, 2.15 mmol), 95 % sodium hydride (0.041 g, 1.72 mmol); poly(dichlorophosphazene) (1.0 g, 8.6 mmol).

For polymer 4: The same synthetic procedure was used as for polymer 2 to obtain 2.68 g product (87 % yield). Reagent quantities: 2-(2-methoxyethoxy)ethanol (1.76 g, 14.6 mmol), 95 % sodium hydride (0.341 g, 14.2 mmol); 4-hydroxy-N-[(trifluoromethyl)sulfonyl]-benzenesulfonamide mono-sodium salt (1.27 g, 3.87 mmol), 95 % sodium hydride (0.083 g, 3.34 mmol); poly(dichlorophosphazene) (1.0 g, 8.6 mmol). Elemental analysis (calcd, found): % H (5.21, 5.20), % C (35.66, 35.76), % N (5.82, 5.62), % Li (0.79, 0.72).

For polymer 5: The same synthetic procedure was used as for polymer 2 to obtain 2.56 g product (81 % yield). Reagent quantities: 2-(2-methoxyethoxy)ethanol (1.65 g, 13.8 mmol), 95 % sodium hydride (0.320 g, 13.4 mmol); 4-hydroxy-N-[(trifluoromethyl)sulfonyl]-benzenesulfonamide mono-sodium salt (1.55 g, 4.73 mmol), 95 % sodium hydride (0.103 g, 4.30 mmol); poly(dichlorophosphazene) (1.0 g, 8.6 mmol).

2.2.4 Synthesis of [NP((OCH$_2$CH$_2$)$_2$OCH$_3$)$_x$(OC$_6$H$_5$)$_y$]$_n$ (8-11)

The synthesis of poly[(2-(2-methoxyethoxy)ethoxy-co-phenoxypophosphazene] copolymers was carried out according to a literature procedure.$^{18}$ The following 2-(2-methoxyethoxy)ethoxy / phenoxy side group ratios were used: 95/5 (8), 90/10 (9), 85/15
(10), and 80/20 (11). The $^1$H, $^{13}$C, and $^{31}$P NMR chemical shifts agreed with literature values.\textsuperscript{18}

2.2.5 Preparation of solid polymer electrolytes

Polymers 2-5 were dried under vacuum at 40 °C for 1 week before fabrication. Approximately 0.10 g of each polymer was used for impedance measurements. Polymers 8-11 were dried under vacuum at 40 °C for 1 week and each polymer (0.3 g) was combined with 5 mol \% (8), 10 mol \% (9), 15 mol \% (10), or 20 mol \% (11) LiTFSI salt and dissolved in THF. The THF was air-evaporated in a dry environment and the samples were dried under a vacuum for 72 h at 40 °C to remove any residual THF. Approximately 0.1 g of each sample was used for each impedance measurement.

2.2.6 Preparation of gel polymer electrolytes

Polymer 4 with 20, 30, 40 or 50 wt. \% NMP was dissolved in methanol. The methanol was air-evaporated in a dry environment and the samples were dried under reduced pressure (0.1 mm Hg) for ~2 h at room temperature to remove any residual methanol. Approximately 0.10 g of each GPE was for impedance measurements at 25 °C and 80 °C.
2.3 Results and discussion

2.3.1 Synthesis of $[\text{NP}((\text{OCH}_2\text{CH}_2)_{2}\text{OCH}_3)_3(\text{OC}_6\text{H}_4\text{SO}_2\text{N(Li)}\text{SO}_2\text{CF}_3)_y]_n$ (2-5)

Sequential addition of solutions of sodium 2-(2-methoxyethoxy)ethoxide and the di-sodium salt of the sulfonimide derivative allowed control of the substituent ratios in the final polymers (Figure 2-1). This sequence of addition was utilized because of the insolubility of sodium sulfonimide-chlorophosphazene polymers in the reaction medium. Replacement of the chlorine atoms in poly(dichlorophosphazene) (1) was monitored by $^{31}\text{P}$ NMR spectroscopy. The fully substituted mixed substituent polymers precipitated slowly from solution in THF as the sulfonimide groups were introduced.

Following completion of the reaction and subsequent purification of the polymer, the sulfonimide substituent was lithiated. Initially, lithium carbonate was investigated as a reagent for lithiation of the sulfonimide substituent, but several broad peaks near 0 ppm in the $^{31}\text{P}$ NMR spectra suggested that polymer degradation had occurred from exposure to the basic aqueous medium. Therefore, lithiation of the sulfonimide substituent was accomplished with lithium chloride. This aqueous medium is less basic than the lithium carbonate solutions and the sulfonimide substituent was lithiated without decomposition of the polyphosphazene.
Figure 2-1: Synthesis of the 2-(2-methoxyethoxy)ethoxy / lithium sulfonamide co-substituted polyphosphazenes
Table 2-1: Thermal, activation energy, and ionic conductivity data of polymers 2-5

<table>
<thead>
<tr>
<th>Polymer</th>
<th>% lithium sulfonimide</th>
<th>$T_g$ (°C)</th>
<th>$E_a$ (kJ/mol)</th>
<th>$\sigma$ at 25°C ($10^{-5}$ S/cm)</th>
<th>$\sigma$ at 80°C ($10^{-5}$ S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>5</td>
<td>-64</td>
<td>5.3</td>
<td>$0.25 \pm 1.2 %$</td>
<td>$2.8 \pm 0.9 %$</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>-45</td>
<td>7.5</td>
<td>$0.11 \pm 0.6 %$</td>
<td>$3.5 \pm 1.1 %$</td>
</tr>
<tr>
<td>4</td>
<td>19</td>
<td>-31</td>
<td>9.2</td>
<td>$0.075 \pm 0.4 %$</td>
<td>$5.0 \pm 1.6 %$</td>
</tr>
<tr>
<td>5</td>
<td>22</td>
<td>-16</td>
<td>13.6</td>
<td>$0.011 \pm 0.1 %$</td>
<td>$2.2 \pm 0.7 %$</td>
</tr>
</tbody>
</table>
2.3.2 Polymer characterization

Polymers 2-5 (Table 2-1) were characterized by $^{31}$P, $^{13}$C and $^1$H NMR spectroscopy to determine the purity of the materials and the ratios of the substituents. Two broad peaks were detected in the $^{31}$P NMR spectra of polymers 2-5, at -6.4 ppm which corresponds to di-(2-(2-methoxyethoxy)ethoxy) substituted phosphorus and at -12.4 ppm from mono-(2-(2-methoxyethoxy)ethoxy) / mono-(lithium sulfonimide) substituted phosphorus. Integration of these peaks then allowed the ratios of the two substituents to be estimated. The substituent ratios were also confirmed through $^1$H NMR spectroscopic integration of the aromatic protons of the lithium sulfonimide substituent and the aliphatic proton peaks of the 2-(2-methoxyethoxy)ethoxy substituent.

Polymers 8-11 were characterized by $^1$H, $^{13}$C and $^{31}$P NMR spectroscopy to determine purity and the ratios of the substituents. All chemical shifts agreed with related literature values. Integration of the $^1$H and $^{31}$P NMR peaks confirmed that the target side group ratios were obtained to within 1 mol %.

In order to confirm lithiation of polymers 2-5, sodium flame atomic absorption spectroscopy (FAA) was performed. In all cases, FAA showed that the amount of sodium present was below the detection limit (0.2 ng/mL) of the instrument, which corresponds to less than 2 x $10^{-5}$ % sodium present in each polymer. Elemental analyses for hydrogen, carbon, nitrogen, and lithium, were obtained for polymer 4 to further demonstrate lithiation of the polymer and to confirm the polymer structure.

As mentioned previously, polymers 2-5 were insoluble in THF. Therefore, gel permeation chromatography (GPC) could not be used directly to obtain molecular weight data. Instead, poly[bis(trifluoroethoxy)phosphazene] (6), was synthesized from the same
batch of polymeric precursor (1), and molecular weight values were measured for this THF-soluble polymer. Polymer 6 had a number average molecular weight ($M_n$) of $1.52 \times 10^5$ g/mol and a weight average molecular weight ($M_w$) of $4.22 \times 10^5$ g/mol, giving a polydispersity index (PDI) of 2.8. These values suggest the approximate chain lengths (average number of repeating units = ~625) and molecular weight distributions that might be expected for the lithium sulfonimide system. Polymers 8-11 were synthesized from a separate batch of 1 and were THF soluble. Their structure is shown in Figure 2-2. $M_n$ values of $1.31 \times 10^5$ – $2.02 \times 10^5$ g/mol and $M_w$ values of $3.36 \times 10^5$ – $5.28 \times 10^5$ g/mol with PDIs of 2.6 – 2.8 were obtained.
Figure 2-2: Structure of the 2-(2-methoxyethoxy)ethoxy / phenoxy cosubstituted polyphosphazenes
2.3.3 Ionic conductivity as a function of $T_g$ and $E_a$

Ionic conductivities in the range of $10^{-6}$ S/cm at 25 °C and $10^{-5}$ S/cm at 80 °C were obtained for polymers 2-5 (Table 2-1). These results are comparable to those from other single ion lithium conductive polymers. In addition, the ambient temperature and high temperature (80 °C) ionic conductivities of polymers 2-5 were an order of magnitude higher than the values obtained for a polymer system with a sulfonimide functionality incorporated into the backbone of the polymer. This is due to the higher level of macromolecular motion in the polyphosphazene system compared to poly(2-oxo-1-difluoroethylene lithium sulfonimide) which has a glass transition temperature ($T_g$) of 140 °C.

DSC analysis was performed on polymers 2-5 and on a sample of poly[bis(2-(2-methoxyethoxy)ethoxyphosphazene)] [MEEP] (7) to compare the ionic conductivity values with the $T_g$ values. The $T_g$ increased significantly from -84 °C, for polymer 7, to a maximum of -16 °C, for polymer 5 (Figure 2-3). The $T_g$ values for polymers 2 to 5 increased in parallel with increases in the amount of lithium sulfonimide substituent. However, the ambient temperature ionic conductivity decreased as the amount of lithium sulfonimide substituent increased (Figure 2-4). In addition, the activation energy ($E_a$) values of polymers 2-5 increased from 5.3 kJ/mol, for polymer 2, to 11.5 kJ/mol, for polymer 5 (Table 2-1). The $E_a$ values were calculated by using the Arrhenius equation and the slope of the ionic conductivity-temperature dependence lines for each polymer in Figure 2. The ionic conductivities at 25 °C ranged from $2.5 \times 10^{-6} \pm 1.2$ % S/cm (polymer 2) to $1.1 \times 10^{-7} \pm 0.1$ % S/cm (polymer 5) (Table 2-1). By contrast, the solid polymer
electrolyte counterpart of polymer 5 with unbound salt (MEEP:lithium triflate) had an ionic conductivity at 25 °C of $2.7 \times 10^{-5}$ S/cm.\textsuperscript{15} At 80 °C, increased ionic conductivities for polymers 2-5 were measured in the range of $10^{-4.5}$ S/cm.
Figure 2-3: DSC data for polymers 2-5 and 7
Figure 2-4: Ionic conductivity data for polymers 2-5
The ionic conductivities of polymers 8-11 (with unbound salt) showed typical behavior associated with lithium salt loading and \( T_g \) (Table 2-2). The \( T_g \) of polymer 8 with no LiTFSI salt was -77 °C. As the phenoxy content increased a parallel increase occurred in \( T_g \) to -66 °C for polymer 11. A more pronounced increase in \( T_g \) was seen in polymers 8-11 with dissolved LiTFSI salt. Polymer 8 with dissolved LiTFSI salt had a \( T_g \) of -72 °C, which increased to -45 °C for polymer 11. However, the ionic conductivities increased from \( 2.5 \times 10^{-5} \pm 1.3 \% \) S/cm (polymer 8), and showed a maximum of \( 4.8 \times 10^{-5} \pm 1.6 \% \) S/cm with polymer 9. The values for polymers 10 and 11 then decreased to \( 3.0 \times 10^{-5} \pm 1.3 \% \) S/cm and \( 2.1 \times 10^{-5} \pm 0.7 \% \) S/cm, respectively. The \( E_a \) values showed a similar trend relative to the ionic conductivity values. Polymer 8 had an \( E_a \) value of 4.3 kJ/mol, which then decreased to 3.7 kJ/mol for polymer 9. Polymer 10 and 11 then had increased \( E_a \) values of 5.5 kJ/mol and 6.6 kJ/mol, respectively (Table 2-2).
Table 2-2: Thermal, activation energy, and ionic conductivity data of polymers 8-11

<table>
<thead>
<tr>
<th>Polymer</th>
<th>mol % LiTFSI</th>
<th>$T_g$°C with no LiTFSI</th>
<th>$T_g$°C with LiTFSI</th>
<th>$E_a$ (kJ/mol)</th>
<th>$\sigma$ at 25 °C ($10^{-5}$ S/cm)</th>
</tr>
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<tbody>
<tr>
<td>8</td>
<td>5</td>
<td>-77</td>
<td>-72</td>
<td>4.3</td>
<td>4.0 ± 1.3 %</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>-73</td>
<td>-65</td>
<td>3.7</td>
<td>5.0 ± 1.6 %</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
<td>-69</td>
<td>-54</td>
<td>5.5</td>
<td>4.0 ± 1.3 %</td>
</tr>
<tr>
<td>11</td>
<td>20</td>
<td>-66</td>
<td>-45</td>
<td>6.6</td>
<td>2.7 ± 0.7 %</td>
</tr>
</tbody>
</table>
2.3.4 Mechanism of ionic conductivity

Ionic conductivity in polyphosphazenes has been studied for many polymer systems with different oligoethyleneoxy substituents, all of which are characterized by high macromolecular mobility.\textsuperscript{23-25} The key to high ionic conductivity in these polymers is the weak coordination of mobile lithium cations to etheric oxygen atoms, which facilitates their transport through inter- and intrachain hopping mechanisms. It has also been suggested that nitrogen atoms in the polyphosphazene backbone may contribute to the ionic conduction of lithium cations through cooperative coordination with oligoethyleneoxy substituents, which leads to a backbone-centered transport mechanism.\textsuperscript{26,27} Polymers 2-5 and 8-11 had ambient temperature ionic conductivities lower than those of di-oligoethyleneoxy polyphosphazenes with unbound lithium salts probably due to their restricted macromolecular motion and higher $T_g$ values. This results from the presence of bulky aryloxy lithium sulfonimide (polymers 2-5) and phenoxy (polymers 8-11) substituents.\textsuperscript{18,23} In addition, steric shielding of the backbone by the lithium sulfonimide group in polymers 2-5 and the phenoxy group in polymers 8-11 would reduce the backbone nitrogen participation if this is a factor.

Thus, the decrease in ambient temperature ionic conductivity from polymer 2 to polymer 5 can be explained in terms of decreased macromolecular motion, possibly by steric shielding of the polyphosphazene backbone, and by the change in $E_a$. In polymers 2-5, the increase in lithium sulfonimide content is directly paralleled by a rise in $T_g$ and $E_a$. At 80 °C, the ionic conductivities of polymers 2-5 are similar, and are in the range of $10^{-4.5}$ S/cm. Under these conditions the elevated temperature and corresponding increase
in macromolecular motion facilitates enhanced lithium transport. Skeletal nitrogen atoms in the polymer would also become more exposed due to the enhanced molecular motion.

Polymers 8-11, with the dissolved but unbound salt, showed a small increase in ambient temperature ionic conductivity over that of polymers 2-5 perhaps caused by both cation and anion transport and/or the increased macromolecular motion associated with the less bulky phenoxy substituents. This is evident when comparing their $T_g$ values. A maximum ionic conductivity was detected for polymer 9, despite its higher phenoxy content over polymer 8. This increase in ionic conductivity and parallel decrease in $E_a$ from polymer 8 to 9 is almost certainly a result of the increase in LiTFSI salt content, which provides more lithium ions for transport. However the decrease in ionic conductivity, despite the increase in LiTFSI salt content in polymers 10 and 11, is attributed to the presence of transient O-Li-O crosslinks. This is evident from the increase in $T_g$ and $E_a$ for these polymers as LiTFSI salt is added. Thus, the relationship of $T_g$ and $E_a$ to ionic conductivity is strongly influenced by the loading of LiTFSI salt in the polymer.

Further support for an ionic conduction mechanism governed by macromolecular motion and possible nitrogen participation is illustrated in a previous study. Here, single-substituent polyphosphazenes with aryloxy groups that bore 2-(2-methoxyethoxy)ethoxy units in the para position of the aromatic rings were used to fabricate LiTFSI solid polymer electrolytes. The structure of this polymer is shown in Figure 2-5. The presence of the aryloxy units along the polyphosphazene backbone effectively shields the nitrogen atoms from lithium cation coordination. The maximum ionic conductivity of this polymer was shown to be $4.4 \times 10^{-7}$ S/cm ($T_g = -16 \, ^\circ$C), which
is significantly lower than $2.9 \times 10^{-5}$ S/cm ($T_g = -76 \, ^\circ\text{C}$) measured from a MEEP:lithium triflate SPE. Aryloxy units adjacent to the polyphosphazene backbone stiffen the polymer, cause an increase in $T_g$, and probably shield the nitrogen atoms in the backbone from lithium cation coordination.
Figure 2-5: Structure of a 4-(2-(2-methoxyethoxy)ethoxy)phenoxy substituted polyphosphazene
2.3.5 Gel polymer electrolytes of polymer 4 with N-methyl-2-pyrrolidinone

Polymer 4 was used for the preparation of gel polymer electrolytes (GPEs) with N-methyl-2-pyrrolidone (NMP). This polymer was used because of its higher ionic conductivity in the solid state than polymers 2, 3 and 5. The ionic conductivities of these GPE samples were significantly higher than that of solid polymer 4. Moreover, the ionic conductivities increased as the wt. % of NMP was increased (Table 2-3). Maximum ionic conductivities were measured at 50 wt. % NMP (1.1 x 10^{-3} ± 1.5 % S/cm at ambient temperature, 6.0 x 10^{-3} ±1.7 % S/cm at 80 °C).

The DSC results for each gel electrolyte showed a single $T_g$ at a lower temperature than that of solid polymer 4 ($T_g = -31 ^\circ C$) (Table 2-3). The $T_g$ decreased to a minimum value of -62 °C for the 30, 40 and 50 wt. % GPEs. Thus, the primary increase in ionic conductivity corresponds to a higher degree of macromolecular motion of the polymer, which results from the plasticization effect of NMP. Solvation of the lithium cations by NMP, which would decrease ion-ion interactions, appeared to play a less significant role in the increase in ionic conductivity. Mechanically, GPEs containing 30-50 wt. % NMP were extremely viscous liquids, whereas the GPE with 20 wt. % NMP is a gum.

Other liquids considered for GPE fabrication were propylene carbonate, DMF, DMAC, glyme, and diglyme. However, these liquids are immiscible with polymer 4 and had no affect on ionic conductivity.
Table 2-3: Thermal and ionic conductivity data for GPEs of polymer 4

<table>
<thead>
<tr>
<th>wt. % NMP</th>
<th>$T_g$ (°C)</th>
<th>$\sigma$ at 25 °C ($10^{-5}$ S/cm)</th>
<th>$\sigma$ at 80°C ($10^{-5}$ S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>-51</td>
<td>5.2 ± 0.9%</td>
<td>41 ± 1.3 %</td>
</tr>
<tr>
<td>30</td>
<td>-62</td>
<td>11 ± 1.2%</td>
<td>79 ± 1.6%</td>
</tr>
<tr>
<td>40</td>
<td>-62</td>
<td>14 ± 1.3%</td>
<td>160 ± 1.6%</td>
</tr>
<tr>
<td>50</td>
<td>-62</td>
<td>110 ± 1.5%</td>
<td>600 ± 1.7%</td>
</tr>
</tbody>
</table>
2.4 Conclusions

Mixed-substituent polyphosphazenes with 2-(2-methoxyethoxy)ethoxy and 5 mol % to 22 mol % of a lithium sulfonimide substituent were synthesized and examined as single ion conductors. A comparison was also made to polyphosphazenes with 2-(2-methoxyethoxy)ethoxy side groups and 5 mol % to 20 mol % phenoxy substituents together with unbound dissolved LiTFSI. Ionic conductivities of the single ion conductive polymer electrolytes were in the range of $10^{-6}$ S/cm at ambient temperature and $10^{-5}$ S/cm at 80 °C. The ambient temperature ionic conductivities actually decreased as the amount polymer bound lithium sulfonimide was increased. Macromolecular motion and possible steric shielding of the polymer backbone by bulky aryloxy groups appear to be influential factors that affect ionic conductivity at ambient temperature. Comparison model systems with 2-(2-methoxyethoxy)ethoxy and phenoxy side groups plus unbound lithium sulfonimide gave higher ionic conductivities than the single ion systems, a result that could reflect the contribution of anion charge transport and/or higher macromolecular flexibility. For these systems also, the significant increase in macromolecular motion at elevated temperatures and perhaps greater exposure of the backbone nitrogen atoms resulted in higher ionic conductivities. Gel polymer electrolytes that contained N-methyl-2-pyrrolidinone showed excellent ionic conductivities, in the range of $10^{-3}$ S/cm at 50 wt. % loadings.
2.5 References


Chapter 3

Synthesis of pendent functionalized-cyclotriphosphazenes polyoctenamers: hydrophobic lithium-ion conductive materials

3.1 Introduction

The purpose of this work was the synthesis and investigation of new polymers that are both hydrophobic and lithium ion conductive. A reason for the growing interest in polymers that have this unusual combination of properties is their possible use as lithium anode membranes in lithium / seawater batteries. The hydrophobic character is needed to prevent water ingress to the lithium anode where parasitic lithium-water reactions may occur. An approach to solving this problem involves the utilization of a hydrophobic organic polymer to which is attached both hydrophobic and (hydrophilic) lithium ion conductive side units. Because of the ease with which different groups can be linked to cyclic six-membered phosphazene rings, these units were chosen as the pendent side groups linked to a polyoctenamer main chain.

Numerous hybrid polymers that contain organic polymer components and either linear or cyclic phosphazenes are known, and several polymers with phosphazene rings pendent to organic polymer chains have been described. Allen and coworkers utilized addition reactions to polymerize vinyl and allyl-substituted cyclotriphosphazenes. Polystyrene with pendent oligo(ethyleneoxy)
cyclotriphosphazenes, which have applications as polymer electrolytes, was synthesized by Inoue and coworkers using free-radical methods.\textsuperscript{12,14} Van de Grampel and coworkers were able to introduce cyclotriphosphazenes into polysiloxanes via hydrosilation techniques.\textsuperscript{15} In addition, cyclotriphosphazenes have been linked to polyurethanes by De Jaeger and Dez.\textsuperscript{16}

Previous research in our program has demonstrated that ring-opening metathesis polymerization can be used to synthesize polynorbornenes with pendent cyclotriphosphazenes.\textsuperscript{17,18} These polymers have the general structure shown in Figure 3-1. In that earlier work the pendent cyclotriphosphazene was functionalized with various types of oligoethyleneoxy units in order to produce lithium ion-based polymer electrolytes with better dimensional stability than the classical linear poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (MEEP).

Polyoctenamers are macromolecules prepared by the ring-opening metathesis polymerization (ROMP) of cyclooctene. These polymers have commercial uses in pure and blended elastomers.\textsuperscript{19,20} The two stereoisomers associated with this system, cis-polyoctenamer and trans-polyoctenamer, have very different physical properties, as illustrated by their glass transition temperatures at -108 °C and -65 °C respectively.\textsuperscript{21} Polymers of this type are unique because the backbone can contain various structural repeat units, such as butadiene, ethylene, and substituted ethylene.\textsuperscript{19} Although polyoctenamers have the potential to serve as an excellent platform for producing polymers with highly tailored properties, only a limited amount of research has been published on the ring-opening metathesis polymerization of cyclooctene-functionalized monomers.\textsuperscript{22-26}
Here we describe the synthesis, characterization, structure-property relationships, and ionic conductivity of amphiphilic lithium-ion conductive solid polymer electrolytes synthesized via the ring-opening copolymerization of cyclooctene-based cyclotriphosphazene monomers. These monomers bear cyclotriphosphazenes units with either cation-solvating etheric or hydrophobic fluoroalkoxy side groups.

The monomers used for copolymerization differed with respect to the side groups linked to the cyclotriphosphazene rings. These side groups were (1) 2-(2-methoxyethoxy)ethoxy substituents to provide a solvation source for lithium cations and (2) fluoroalkoxy chains with varying lengths and fluorine content to impart hydrophobicity. Two alternative hydrophobic monomers were utilized. The first bore five 2,2,2-trifluoroethoxy substituents per cyclotriphosphazene ring, while the second had five 2,2,3,3,4,4,5,5-octafluoropentoxy substituents. Differences in the ratios of the two copolymer types were investigated in an attempt to study the relationship of ionic conductivity and hydrophobicity with composition.
Figure 3-1: Structure of pendent cyclotriphosphazene polynorbornenes.
3.2 Experimental

3.2.1 General

High-field $^1$H (360.14 MHz), $^{13}$C (90.56 MHz), and $^{31}$P (145.79 MHz) NMR spectra were recorded using a Bruker AMX-360 NMR spectrometer. $^1$H and $^{13}$C NMR spectra were referenced to external tetramethylsilane, while $^{31}$P NMR spectra were referenced to external 85 % phosphoric acid. $^{13}$C and $^{31}$P NMR spectra were proton decoupled. Mass spectra were collected using a Micromass Quattro-II triple quadrupole mass spectrometer. 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 $\mu$m 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 (Alfa Aesar) in THF (EMD). Thermal transitions were determined through analysis via a TA Q10 differential scanning calorimeter. Calibration was accomplished with indium, water, and cyclohexane standards. All analyses were performed over a range of -100 °C to 100 °C at a heating rate of 10 °C/min. Ionic conductivity measurements were obtained using a Hewlett Packard 4192A LF Impedance Analyzer at a potential of 0.1 V with an alternating current frequency range of 5 Hz to 1 MHz. The samples were placed between platinum electrodes with a Teflon o-ring spacer and the polymer electrolyte cell was compressed between aluminum blocks held in a Teflon fixture. Electrical leads were attached between the impedance analyzer and the polymer electrolyte cell sample holder. All ionic
conductivity measurements were carried out over a temperature range of 20 °C to 80 °C under an inert atmosphere of dry argon. Static water contact angle measurements were obtained using a Rame-Hart, Inc., model 100-00 contact angle goniometer. Five static water contact angles were obtained for each solid polymer electrolyte and an average and standard deviation value was calculated. All reactions were performed under an inert atmosphere of argon gas.

3.2.2 Materials

*Cis*-1,5-cyclooctadiene (99+ %), *m*-chloroperoxybenzoic acid (77 %), lithium aluminum hydride (95 %), 2-(2-methoxyethoxy)ethanol (99 %), 2,2,2-trifluoroethanol (99 %), ethyl vinyl ether (99 %), (bis(tricyclohexylphosphine)benzylidene ruthenium(IV)dichloride) (97 %), tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene] [benzyldiene]ruthenium(IV)dichloride (97 %), sodium hydrogen carbonate (99 %), sodium hydrogen sulfate (99 %), magnesium sulfate (98 %), sodium hydride (95 %) were obtained from Sigma-Aldrich Co. and used as received. Potassium tert-butoxide (98+ %) was obtained from Acros Organics and used as received. 2,2,3,3,4,4,5,5-octafluropentanol (99 %) was obtained from TCI, Inc. and used as received. Lithium tetrafluoroborate (99.9985 %) was obtained from Alfa Aesar and used as received. Hexachlorocyclotriphosphazene was obtained from Ethyl Corp./Nippon Fine Chemical and was recrystallized from heptane and sublimed at 0.1 mm Hg at 30 °C before use. All solvents were anhydrous and were obtained from EM Science and used as
received unless otherwise noted. *Polyoctenamer* was synthesized according to literature procedure.\textsuperscript{22}

### 3.2.3 Preparation of cyclotriphosphazene-functionalized monomers

Synthesis of cycloocten-5-epoxide (2). The synthesis of cycloocten-5-epoxide was carried out as described previously.\textsuperscript{22} A solution of *m*-chloroperoxybenzoic acid (357 g, 2.07 mol) in chloroform (4 L) was added dropwise to a solution of *cis*-1,5-cyclooctadiene (280 g, 2.59 mol) in tetrahydrofuran (THF) (400 mL) with stirring. The reaction mixture was stirred at room temperature for 18 h and the resultant 3-chlorobenzoic acid was filtered off. The organic layer was washed with an aqueous solution of 20 % (w/v) NaHSO\textsubscript{3}, 10 % (w/v) NaHCO\textsubscript{3}, and brine solution. The organic layer was then concentrated via rotary evaporation and purified via column chromatography (silica, 70/30 hexanes / ethyl acetate) to yield 257 g (90 % yield) a colorless oil (2).

Synthesis of cycloocten-5-ol (3). The synthesis of cycloocten-5-ol was carried out as described previously.\textsuperscript{22} A solution of 2 (257 g, 2.07 mol) in THF (2.5 L) at 0 °C was added dropwise to a solution of lithium aluminum hydride (39.3 g, 1.04 mol) in THF (1 L) at room temperature. The reaction mixture was stirred for 24 h at room temperature under argon, cooled to 0 °C, and quenched with 30 mL water. The reaction mixture was allowed to warm to room temperature and filtered. The resultant solution was concentrated via rotary evaporation, and residual THF and water were removed under
reduced pressure (room temperature, 0.1 mm Hg). Purification via vacuum distillation was performed to yield 240 g (89 % yield) of a colorless oil (3).

For 3, $^1$H NMR (CDCl$_3$): $\delta$ (ppm) 5.74 (q, $J = 7.8$ Hz, -CH=CH-, 1H), 5.63 (q, $J = 7.8$ Hz, -CH=CH-, 1H) 3.81 (dt, -CH$_2$CH(OH)CH$_2$-, $J = 8.1$, 5.1 Hz, 1H), 2.29 (s, -OH, 1H), 1.58-2.35 (br m, -CH$_2$-, 10H); $^{13}$C NMR (CDCl$_3$): $\delta$ (ppm) 130.14 (C-2), 129.51 (C-1), 72.86 (C-5), 37.63 (C-4), 36.51 (C-6), 25.66 (C-3), 24.91 (C-8), 22.80 (C-7); MS = m/z 127 (MH$^+$).

Synthesis of cycloocten-5-oxypentakis(chloro)cyclotriphosphazene (monomer 4). The synthesis of 4 and subsequent substitution was adapted from a similar procedure.$^{18}$ Compound 3 (59.0 g, 469 mmol) was added to a solution of potassium tert-butoxide (49.4 g, 431 mmol) in THF (2.25 L) and the mixture was stirred at room temperature for 18 h. A solution of hexachlorocyclotriphosphazene (NPCl$_2$)$_3$ (250.0 g, 720 mol) in THF (2.75 L) at -78 °C was added dropwise to the solution of the potassium salt of 3 cooled to -78 °C. The reaction mixture was stirred and allowed to warm to room temperature overnight. THF was removed via rotary evaporation and the crude product was dissolved in diethyl ether (1 L) and washed with water (2 x 200 mL). The aqueous layers were combined and washed with diethyl ether (600 mL). The diethyl ether layers were then combined, dried over MgSO$_4$ overnight, and filtered. The solution was concentrated via rotary evaporation and the crude product was sublimed (0.1 mm Hg at 40 °C for 24 h) to leave the product (4) as a viscous oil (163.7 g, 86.6 % yield).

For 4, $^1$H NMR (CDCl$_3$): $\delta$ (ppm) 5.64 (m, -CH=CH-, 2H), 4.69 (m, -CH$_2$CH(O-)CH$_2$-, 1H), 1.56-2.43 (br m, -CH$_2$-, 10H); $^{13}$C NMR (CDCl$_3$): $\delta$ (ppm) 130.23 (C-2), 129.78 (C-1), 80.75 (C-5), 34.76 (C-4), 33.84 (C-6), 25.61 (C-3), 24.63 (C-8), 22.46 (C-
\( ^{31} \text{P NMR (CDCl}_3\): } \delta \text{ (ppm) 22.42 (d, } J = 61.5 \text{ Hz, 2P), 13.45 (t, } J = 61.7 \text{ Hz, 1P); MS } = m/z 436 (\text{MH}^+). \\

Synthesis of cyclooctene-5-oxypentakis(2-(2-methoxyethoxy)ethoxy)cyclotriphosphazene (monomer 5). 2-(2-Methoxyethoxy)ethanol (51.43 g, 428 mmol) was added dropwise to a suspension of sodium hydride (9.86 g, 411 mmol) in THF (500 mL) and the mixture was stirred for 5 h. The sodium 2-(2-methoxyethoxy)ethoxide solution was then added dropwise to a solution of 4 (30.0 g, 68.5 mmol) in THF (500 mL) and the reaction mixture was stirred overnight under low heat. THF was then removed via rotary evaporation and the crude product reaction mixture was dissolved in methylene chloride (CH\(_2\)Cl\(_2\)) (500 mL). The CH\(_2\)Cl\(_2\) solution was washed with water (3 x 100 mL). The aqueous layers were combined and washed with CH\(_2\)Cl\(_2\) (700 mL). The CH\(_2\)Cl\(_2\) layers were combined, dried over MgSO\(_4\) overnight, and filtered. The CH\(_2\)Cl\(_2\) was removed via rotary evaporation and under reduced pressure (room temperature, 0.1 mm Hg) to produce 26.4 g (67.5 % yield) of viscous oil (5).

For 5, \(^1\text{H NMR (CDCl}_3\): } \delta \text{ (ppm) 5.61 (m, -CH=CH-, 2H), 4.39 (m, -CH\(_2\)CH(O-CH\(_2\)-, 1H), 4.06 (m, OCH\(_2\)CH\(_2\)-O-, 10H), 3.69 (m, -OCH\(_2\)CH\(_2\)-O-, 10H), 3.63 (m, -OCH\(_2\)CH\(_2\)OCH\(_3\), 10H), 3.52 (m, -OCH\(_2\)CH\(_2\)OCH\(_3\), 10H), 3.36 (s, -OCH\(_3\), 15H), 1.49-2.35 (br m, -CH\(_2\)-, 10H); \(^{13}\text{C NMR (CDCl}_3\): } \delta \text{ (ppm) 129.71 (C-2), 129.46 (C-1), 78.56 (C-5), 71.90 (-OCH\(_2\)CH\(_2\)-O-), 70.52 (-OCH\(_2\)CH\(_2\)OCH\(_3\), 70.05 (-OCH\(_2\)CH\(_2\)OCH\(_3\), 64.91 (-OCH\(_2\)CH\(_2\)-O-), 58.99 (-OCH\(_3\), 35.37 (C-4), 34.36 (C-6), 25.54 (C-3), 24.66 (C-8), 22.32 (C-7); \(^{31}\text{P NMR (CDCl}_3\): } \delta \text{ (ppm) 17.5 (m, 3P); MS } = m/z 856 (\text{MH}^+). \\

Synthesis of cycloocten-5-oxypentakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (monomer 6). The same synthetic procedure used for monomer 5 was used to produce
48.3 g of monomer 6 (71.7 % yield). Reagent quantities: 2,2,2-trifluoroethanol (55.71 g, 557 mmol), sodium hydride (13.15 g, 548 mmol), monomer 4 (40.0 g, 91.3 mmol).

For 6, 1H NMR (CDCl₃): δ (ppm) 5.66 (m, -CH=CH-, 2H), 4.44 (m, -CH₂CH(O-)CH₂-, 1H), 4.27 (s, OCH₂CF₃, 10H), 1.43-2.41 (m, -CH₂-, 10H); ¹³C NMR (CDCl₃): δ (ppm) 129.92 (C-2), 129.15 (C-1), 122.45 (q, J = 271.7, -CH₂CF₃), 81.22 (C-5), 62.85 (m, -OCH₂CF₃), 35.14 (C-4), 34.67 (C-6), 25.56 (C-3), 24.57 (C-8), 21.96 (C-7); ³¹P NMR (CDCl₃): δ (ppm) 17.1 (m, 3P); MS = m/z 756 (MH⁺).

Synthesis of cycloocten-5-oxy pentakis(2,2,3,3,4,4,5,5-octafluoro-1-pentoxy) cyclotriphosphazene (monomer 7). The same synthetic procedure used for monomer 5 was used to produce 47.2 g of monomer 7 (73.0 % yield). Reagent quantities: 2,2,3,3,4,4,5,5-octafluoro-1-pentanol (64.75 g, 279 mmol), sodium hydride (6.58 g, 274 mmol), monomer 4 (20.0 g, 45.7 mmol).

For 7, ¹H NMR (CDCl₃): δ (ppm) 6.05 (m, -CF₂CF₂H, 5H), 5.65 (m, -CH=CH-, 2H), 4.44 (m, -CH₂CH(O-)CH₂-, 1H), 4.42 (s, OCH₂CF₂-, 10H), 1.25-2.50 (m, -CH₂-, 10H); ¹³C NMR (CDCl₃): δ (ppm) 129.74 (C-2), 129.19 (C-1), 110.43 (m, -CF₂-), 81.40 (C-5), 67.97 (-CF₂CF₂H), 62.23 (m, -OCH₂CF₂-), 35.05 (C-4), 34.41 (C-6), 25.41 (C-3), 24.41 (C-8), 21.93 (C-7); ³¹P NMR (CDCl₃): δ (ppm) 17.3 (m, 3P); MS = m/z 1416 (MH⁺).

3.2.4 General procedure for ring-opening metathesis polymerization

Synthesis of polymer 8. Monomer 5 (5.00 g, 5.8 mmol) was degassed under reduced pressure (room temperature, 0.1 mm Hg), dissolved in CH₂Cl₂ (7 mL), and
heated to 50 °C. A solution of initiator, tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidene]ruthenium(IV) dichloride (1) (17.0 mg, 0.020 mmol), in CH₂Cl₂ (1 mL) was added quickly to the monomer solution and the mixture was stirred for 10 min. The reaction was terminated with ethyl vinyl ether (1 mL). The polymer solution was cooled to room temperature, concentrated under vacuum (room temperature, 0.1 mm Hg), and precipitated into hexanes three times. The polymer was collected and dried under reduced pressure (room temperature, 0.1 mm Hg) to yield 1.70 g (34 % yield) of a rubbery gum.

For 8, ¹H NMR (d₆-THF): δ (ppm) 5.46 (br m, -CH=CH-, 2H), 4.29 (br m, -CH₂CH(O-)-CH₂-, 1H), 4.00 (br m, -OCH₂CH₂O-., 10H), 3.65 (br m, -OCH₂CH₂O-, 10H), 3.58 (br m, -OCH₂CH₂OCH₃, 10H), 3.47 (br m, -OCH₂CH₂OCH₃, 10H), 3.29 (s, -OCH₃, 15H), 1.45-2.06 (br m, -CH₂-, 10H); ¹³C NMR (d₆-THF): δ (ppm) 130.08 (C-2), 127.48 (C-1), 77.67 (C-5), 71.90 (-OCH₂CH₂O-), 70.60 (-OCH₂CH₂OCH₃), 70.02 (-OCH₂CH₂OCH₃), 64.82 (-OCH₂CH₂O-), 58.03 (-OCH₃), 35.23 (C-4), 35.07 (C-6), 32.77 (C-3), 28.29 (C-8), 27.31 (C-7); ³¹P NMR (d₆-THF): δ (ppm) 18.06 (m, 3P); Mₙ = 89 kDa, Mₙ = 169 kDa, PDI = 1.9.

Synthesis of polymer 9. Polymer 9 was synthesized in a similar manner to polymer 8 using monomer 6 (5.00 g, 2.5 mmol) in CH₂Cl₂ (5.0 mL) and a solution of 1 (9.4 mg, 0.011 mmol) in CH₂Cl₂ (1 mL) to yield 1.20 g (48 % yield) of polymer 9. ¹H NMR (d₆-THF): δ (ppm) 5.43 (br m, -CH=CH-, 2H), 4.65 (br m, -CH₂CH(O-)-CH₂-, 1H), 4.43 (br m, -CH₂CF₃, 10H), 1.32-2.23 (br m, -CH₂- 10H); ¹³C NMR (d₆-THF): δ (ppm) 129.87 (C-2), 128.65 (C-1), 122.88 (m, -CF₂-), 80.10 (C-5), 62.89 (m, -CH₂CF₃), 34.33
(C-4), 32.35 (C-6), 28.06 (C-3), 26.99 (C-8), 25.23 (C-7); \(^{31}\)P NMR (\(d_6\)-THF): \(\delta\) (ppm) 17.31 (m, 3P); \(M_n = 397\) kDa, \(M_w = 866\) kDa, PDI = 2.2.

Synthesis of polymer 10. Polymer 10 was synthesized in a similar manner to polymer 8 using monomer 7 (2.59 g, 1.8 mmol) in CH\(_2\)Cl\(_2\) (5.0 mL) and a solution of 1 (5.2 mg, 0.006 mmol) in CH\(_2\)Cl\(_2\) (1 mL) to yield 0.30 g (12 % yield) of polymer 10. \(^1\)H NMR (\(d_6\)-THF): \(\delta\) (ppm) 6.54 (br m, -CF\(_2\)CF\(_2\)H, 5H), 5.42 (br m, -CH=CH-, 2H), 4.53 (br s, -CH\(_2\)CF\(_3\), 10H), 4.02 (br m, -CH\(_2\)CH(O)-CH\(_2\)-, 1H), 1.04-2.14 (br m, -CH\(_2\)-, 10H); \(^{13}\)C NMR (\(d_6\)-THF): \(\delta\) (ppm) 131.23 (C-2), 128.89 (C-1), 111.14 (m, -CH\(_2\)F), 73.15 (C-5), 64.23 (-CF\(_2\)H), 57.45 (m, -OCH\(_2\)CF\(_2\)-), 36.23 (C-4), 32.14 (C-6), 31.98 (C-3), 28.12 (C-8), 26.67 (C-7); \(^{31}\)P NMR (\(d_6\)-THF): \(\delta\) (ppm) 17.22 (m, 3P); \(M_n = 455\) kDa, \(M_w = 819\) kDa, PDI = 1.8.

Synthesis of polymer 11. Polymer 11 was synthesized in a similar manner to polymer 8 using monomer 5 (0.28 g, 0.33 mmol, 0.10 eq) and monomer 6 (2.19 g, 3.0 mmol, 0.90 eq) in CH\(_2\)Cl\(_2\) (5.5 mL) and a solution of 1 (9.3 mg, 0.011 mmol) in CH\(_2\)Cl\(_2\) (1 mL) to yield 0.88 g (35 % yield) of a rubbery gum. The average repeat unit composition was calculated from \(^1\)H NMR peak integration. Similar \(^1\)H, \(^{13}\)C, and \(^{31}\)P chemical shifts were observed for polymers 12 and 13.

For 11, average repeat unit composition (5, 11.2 %; 6, 88.8 %); \(^1\)H NMR (\(d_6\)-THF): \(\delta\) (ppm) 5.41 (br m, -CH=CH-, 4H), 4.48 (br s, -CH\(_2\)CF\(_3\)-, 18H), 4.41 (m, -CH\(_2\)CH(O-CH\(_2\)-, 2H), 4.01 (br m, -OCH\(_2\)CH\(_2\)-, 2H), 3.63 (br m, -OCH\(_2\)CH\(_2\)-, 2H), 3.59 (br m, -OCH\(_2\)CH\(_2\)OCH\(_3\), 2H), 3.48 (br m, -OCH\(_2\)CH\(_2\)OCH\(_3\), 2H), 3.28 (s, -OCH\(_3\), 3H), 1.35-2.62 (br m, -CH\(_2\)-, 20H); \(^{13}\)C NMR (\(d_6\)-THF): \(\delta\) (ppm) 129.49 (C-2), 129.23 (C-1), 123.46 (m, -CH\(_2\)CF\(_3\)), 80.06 (C-5), 71.94 (-OCH\(_2\)CH\(_2\)-), 70.36 (-OCH\(_2\)CH\(_2\)OCH\(_3\)), 70.03 (-
OCH₂CH₂OCH₃), 65.94 (-OCH₂CH₂O-), 62.49 (-CH₂CF₃), 57.97 (-OCH₃), 34.69 (C-4), 34.30 (C-6), 32.45 (C-3), 27.95 (C-8), 27.01 (C-7); ³¹P NMR (d₆-THF): δ (ppm) 18.12 (m, 6P); Mₙ = 387 kDa, Mₘ = 841 kDa, PDI = 2.2.

Synthesis of polymer 12. Polymer 12 was synthesized in a similar manner to polymer 8 using monomer 5 (0.68 g, 0.8 mmol, 0.25 eq) and monomer 6 (2.22 g, 2.5 mmol, 0.75 eq) in CH₂Cl₂ (5.5 mL) and a solution of 1 (9.3 mg, 0.011 mmol) in CH₂Cl₂ (1 mL) to yield 0.90 g (36 % yield) of polymer 12. Average repeat unit composition (5, 31.5 %; 6, 68.5 %); Mₙ = 250 kDa, Mₘ = 463 kDa, PDI = 1.9.

Synthesis of polymer 13. Polymer 13 was synthesized in a similar manner to polymer 8 using monomer 5 (1.11 g, 1.3 mmol, 0.40 eq) and monomer 6 (1.40 g, 1.9 mmol, 0.60 eq) in CH₂Cl₂ (5.5 mL) and a solution of 1 (9.3 mg, 0.011 mmol) in CH₂Cl₂ (1 mL) to yield 1.09 g (44 % yield) of polymer 13. Average repeat unit composition (5, 44.0 %; 6, 56.0 %); Mₙ = 279 kDa, Mₘ = 632 kDa, PDI = 2.3.

Synthesis of polymer 14. Polymer 14 was synthesized in a similar manner to polymer 8 using monomer 5 (0.32 g, 0.37 mmol, 0.10 eq) and monomer 7 (4.67 g, 3.3 mmol, 0.90 eq) in CH₂Cl₂ (12 mL) and a solution of 1 (10.5 mg, 0.012 mmol) in CH₂Cl₂ (1 mL) to yield 1.51 g (30 % yield) of polymer 14. Similar chemical shifts were observed for polymers 15 and 16.

For 14, average repeat unit composition (5, 8.3 %; 7, 91.7 %); ¹H NMR (d₆-THF): δ (ppm) 6.36-6.67 (br m, -CF₂CF₂H, 9H), 5.43 (br m, -CH=CH-, 4H), 4.56 (br m, -CH₂CF₂-, 18H), 4.43 (br m, -CH₂CH(O-)-CH₂-, 2H), 4.02 (br m, -OCH₂CH₂O- 2H), 3.64 (br m, -OCH₂CH₂O-, 2H), 3.57 (br m, -OCH₂CH₂OCH₃, 2H), 3.45 (br m, -OCH₂CH₂OCH₃, 2H), 3.28 (s, -OCH₃, 3H), 1.37-2.31 (br m, -CH₂-, 20H); ¹³C NMR
(CDCl₃): δ (ppm) 133.45 (C-2), 130.11 (C-1), 110.48 (m, -CF₂-), 80.98 (C-5), 71.94 (-OCH₂CH₂O-), 70.34 (-OCH₂CH₂OCH₃), 70.02 (-OCH₂CH₂OCH₃), 64.71 (-OCH₂CH₂O-), 62.14 (-CF₂CF₂H), 62.06 (-CH₂CF₂-), 57.96 (-OCH₃), 37.45 (C-4), 34.69 (C-6), 32.57 (C-3), 27.98 (C-8), 26.74 (C-7); ³¹P NMR (d₆-THF): δ (ppm) 17.2 (m, 6P); $M_n$ = 489 kDa, $M_w$ = 1129 kDa, PDI = 2.3.

Synthesis of polymer 15. Polymer 15 was synthesized in a similar manner to polymer 8 using monomer 5 (0.83 g, 0.98 mmol, 0.25 eq) and monomer 7 (4.11 g, 2.9 mmol, 0.74 eq) in CH₂Cl₂ (12 mL) and a solution of 1 (10.5 mg, 0.013 mmol) in CH₂Cl₂ (1 mL) to yield 2.25 g (45 % yield) of polymer 15. Average repeat unit composition (5, 27.1 %; 7, 72.9 %); $M_n$ = 376 kDa, $M_w$ = 964 kDa, PDI = 2.6.

Synthesis of polymer 16. Polymer 16 was synthesized in a similar manner to polymer 8 using monomer 5 (1.45 g, 1.7 mmol, 0.40 eq) and monomer 7 (3.54 g, 2.5 mmol, 0.60 eq) in CH₂Cl₂ (4 mL) and a solution of 1 (11.9 mg, 0.014 mmol) in CH₂Cl₂ (1 mL) to yield 1.87 g (37 % yield) of polymer 16. Average repeat unit composition (5, 39.4 %; 7, 60.6 %); $M_n$ = 155 kDa, $M_w$ = 255 kDa, PDI = 1.7.

3.2.5 Preparation of solid polymer electrolytes

Polymers 8-16 were dried under vacuum at 40 °C for 1 week before fabrication. Each polymer (0.3 g) was combined with 10 mol % lithium tetrafluoroborate (LiBF₄) and was dissolved in THF. The THF was removed by air-evaporation in a dry environment, and the samples were subjected to a reduced pressure (40 °C, 0.1 mm Hg, 72 h) to remove any residual THF to yield solid polymer electrolytes (SPEs) 17-25.
3.2.6 Preparation of films for static water contact angle measurements

Polymers 8-16 were dried under vacuum at 40 °C for 1 week before fabrication. Each polymer was combined with 10 mol % LiBF₄ and was dissolved in THF (30 % (w/v)). The polymer solutions were poured onto a glass substrate and the THF was air-evaporated in a dry environment. Residual THF was removed under a reduced pressure (room temperature for 24 h, 40°C for 72 h, 0.1 mm Hg).

3.3 Results and discussion

3.3.1 Monomer synthesis

The preparation of polyoctenamers with pendant functionalized-cyclotriphosphazene rings required the synthesis of cycloocten-5-ol (3).²² An epoxidation reaction was carried out on cis-1,5-cyclooctadiene in the presence of m-chloroperoxybenzoic acid. Cycloocten-5-epoxide (2) was then reduced with lithium aluminum hydride to yield compound 3.

The synthetic route employed to produce monomers 5-7 is shown in Figure 3-2. The first step was the reaction of hexachlorocyclotriphosphazene, (NPCl₂)₃, with the potassium salt of 3 which yielded cycloocten-5-oxypentakis(chloro)cyclotriphosphazene (4). Nucleophilic replacement of the chlorine atoms by the appropriate sodium alkoxide was carried out to obtain single-substituent monomers 5-7 as transparent, viscous oils in yields of approximately 70 %.
Figure 3-2: Synthesis of cyclooctene-based cyclotriphosphazene monomers 5-7
3.3.2 Polymer synthesis

Polymers 8-16 were synthesized under an inert atmosphere of argon at 50 °C via ring-opening metathesis polymerization of the corresponding monomers (Figure 3-3 and Figure 3-4). Initially, polymerization reactions were attempted with Grubbs’ first generation catalyst (bis(tricyclohexylphosphine)benzyldiene ruthenium(IV) dichloride). However, this produced extremely low molecular weight polymers which had insufficient dimensional stability to warrant further characterization. A possible reason is the low efficiency of this catalyst with substituted cyclooctene-based monomers. Therefore, all subsequent polymerizations were carried out with tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene] [benzyldiene]ruthenium(IV) dichloride (1) at a monomer to initiator ratio of 300:1 and were terminated after a specific time by the addition of ethyl vinyl ether. The polymer solutions were then concentrated and precipitated into hexanes to yield polymers 8-16 as adhesive gums in satisfactory yields. Each polymer was readily soluble in organic solvents such as tetrahydrofuran, methylene chloride, and chloroform.

The solid polymer electrolytes derived from polymers 8-16 are designated SPEs 17-25 respectively. The solid polymer electrolytes were fabricated by the addition of 10 mol % lithium tetrafluoroborate (LiBF₄).
5, 6, or 7 \( \rightarrow \)

\[
\text{CH}_2\text{Cl}_2
\]

\[
\begin{align*}
8 & (\text{SPE 17}), R = (\text{CH}_2\text{CH}_2\text{O})_2\text{CCH}_3 \\
9 & (\text{SPE 18}), R = \text{CH}_2\text{CF}_3 \\
10 & (\text{SPE 19}), R = \text{CH}_2(\text{CF}_2)_3\text{CF}_2\text{H}
\end{align*}
\]

Figure 3-3: Homopolymers from monomers 5-7 (polymers 8-10)
Figure 3-4: Copolymers from monomers 5 and 6 (polymers 11-13) and from monomers 5 and 7 (polymers 14-16)
3.3.3 Polymer characterization

Polymers 8-16 were characterized by $^1$H, $^{13}$C, and $^{31}$P NMR spectroscopy. $^1$H NMR peak integration of the aliphatic protons on the 2-(2-methoxyethoxy)ethoxy (MEE), 2,2,2-trifluoroethoxy (TFE), and 2,2,3,3,4,4,5,5-octafluoropentoxy (OFP) substituents were used to confirm their ratios on the cyclotriphosphazene units. Attempts to utilize $^{13}$C NMR to examine the influence of the pendent cyclotriphosphazene on the regio- and stereospecificity of the polyoctenamer backbone were inconclusive due to unresolved peaks in the olefinic region. However, the $^{13}$C NMR spectra of unsubstituted polyoctenamer showed two resonances in the olefinic region of the spectra, which correspond to the cis and trans isomers. Therefore, due to the asymmetric substitution of the cyclotriphosphazene-functionalized cyclooctene monomers, head-to-head, head-to-tail, and tail-to-tail repeat units are possible. In addition, analysis of the alkyl region in the $^{13}$C NMR spectra eliminated the possibility of a diblock structure, which suggests that the distribution of each type of cyclotriphosphazene unit is random. The $^{31}$P NMR spectra for the monomers showed typical A$_2$B splitting patterns, while the spectra of the polymers were inconclusive due to signal broadening and peak overlap.

Gel permeation chromatography was used to estimate the molecular weights of polymers 8-16. For polymers 8-10, the number average molecular weight ($M_n$) values ranged from 89 kDa to 455 kDa and the weight average molecular weight ($M_w$) values ranged from 169 kDa to 819 kDa. For polymers 11-13, the $M_n$ values ranged from 250 kDa to 387 kDa and the $M_w$ values were from 460 kDa to 841 kDa. For polymers 14-16, the $M_n$ values ranged from 155 kDa to 489 kDa and the $M_w$ values were from 255 kDa to
1129 kDa. The polydispersity index (PDI) values of polymer 8-16 were from 1.8 to 2.6. PDI values around 2.0 are typical for equilibrium-controlled polymerizations.\textsuperscript{27}

3.3.4 Thermal analysis

The morphological properties of polymers 8-16 and of the corresponding solid polymer electrolytes (SPEs) with lithium tetrafluoroborate 17-25 were examined by differential scanning calorimetry (Table 3-1).

Polymers 8-16 and SPEs 17-25 were amorphous over the temperature range of -100 °C to 100 °C. The linkage of the cyclotriphosphazene units to the polyoctenamer backbone led to $T_g$ values similar to or higher than unsubstituted trans-polyoctenamer ($T_g = -65 $ °C) for all polymers. This suggests that the polyoctenamer backbone is predominately trans. In addition the bulky cyclotriphosphazene units likely caused a reduction in backbone mobility which contributed to the increase in $T_g$ values for polymers 8-16 compared to unsubstituted trans-polyoctenamer.

The glass transition temperature ($T_g$) values of polymers 14-16 and SPEs 23-25 were lower than those of polymers 11-13 and SPEs 20-22. A similar decrease in the $T_g$ values is observed when comparing homopolymer 9 to 10. The $T_g$ decrease is attributed to the increase in free volume of the system induced by the presence of longer OFP substituents linked to the cyclotriphosphazene rings.

Surprisingly, the $T_g$ values for these polymers showed no change following addition of LiBF$_4$. Typically, the addition of a salt to a coordinative polymer causes an increase in the $T_g$ due to transient cross-link formation between lithium cations and
coordination sites in the polymer. However, in the systems studied, the MEE substituents, which are capable of coordination to lithium cations, are sufficiently distanced from the polyoctenamer backbone that any transient cross-links that form may not significantly affect the segmental motion of the polymer backbone.
Table 3-1: Thermal, ionic conductivity, and static water contact angle (sWCA) data for solid polymer electrolytes (SPEs) 17-25. * Data for polymers 8-16 (with no LiBF$_4$).

<table>
<thead>
<tr>
<th>SPE</th>
<th>$T_g$(°C)*</th>
<th>$T_x$(°C)</th>
<th>$\sigma$ (10$^{-5}$ S/cm) (25 °C)</th>
<th>$\sigma$ (10$^{-5}$ S/cm) (80 °C)</th>
<th>sWCA (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>-68</td>
<td>-65</td>
<td>1.15</td>
<td>4.45</td>
<td>31 ± 2</td>
</tr>
<tr>
<td>18</td>
<td>-34</td>
<td>-31</td>
<td>0.01</td>
<td>0.04</td>
<td>105 ± 2</td>
</tr>
<tr>
<td>19</td>
<td>-58</td>
<td>-63</td>
<td>0.02</td>
<td>0.13</td>
<td>113 ± 1</td>
</tr>
<tr>
<td>20</td>
<td>-36</td>
<td>-41</td>
<td>0.11</td>
<td>1.32</td>
<td>104 ± 1</td>
</tr>
<tr>
<td>21</td>
<td>-31</td>
<td>-35</td>
<td>0.12</td>
<td>1.26</td>
<td>99 ± 1</td>
</tr>
<tr>
<td>22</td>
<td>-39</td>
<td>-40</td>
<td>0.23</td>
<td>2.92</td>
<td>95 ± 2</td>
</tr>
<tr>
<td>23</td>
<td>-49</td>
<td>-50</td>
<td>0.08</td>
<td>0.69</td>
<td>111 ± 1</td>
</tr>
<tr>
<td>24</td>
<td>-51</td>
<td>-48</td>
<td>0.07</td>
<td>0.66</td>
<td>112 ± 1</td>
</tr>
<tr>
<td>25</td>
<td>-51</td>
<td>-47</td>
<td>0.08</td>
<td>0.72</td>
<td>111 ± 1</td>
</tr>
</tbody>
</table>
3.3.5 Ionic conductivity and hydrophobicity

Ionic conductivity and static water contact angle values for SPEs 17-25 are shown in Table 3-1. The highest ambient temperature ionic conductivity was found for SPE 17 (1.15 x 10^{-5} S/cm) – which was the most hydrophilic polymer. This SPE contained the highest concentration of MEE-functionalized cyclotriphosphazene units, and these facilitated lithium ion transport. By contrast, SPE’s 18 and 19, which contained only the hydrophobic TFE or OFP-functionalized cyclotriphosphazene units, had the lowest ionic conductivities (1-2 x 10^{-7} S/cm).

The temperature-dependent ionic conductivity studies carried out on SPEs 20-25 are shown in Figure 3-5. A non-linear increase in ionic conductivity was detected for each SPE as the temperature was raised. This type of temperature-dependent behavior is typical of solid polymer electrolytes. The ionic conductivity values for SPEs 20-22 were lower than SPE 17 because they contained a smaller amount of MEE-functionalized cyclotriphosphazene units and were higher than SPE 18 which contained only TFE-functionalized cyclotriphosphazene units (Table 3-1). In addition, the ambient temperature ionic conductivity values increased from SPE 20 to 22 (Figure 3-6) as the content of MEE-functionalized cyclotriphosphazene units was increased. This increase is presumably due to a larger number of lithium cation coordination sites provided by the MEE groups, which generated more efficient conductive pathways.
Figure 3-5: Temperature-dependent ionic conductivity for solid polymer electrolytes 20-25.
Figure 3-6: Ambient temperature ionic conductivity and static water contact angle relationship to composition for solid polymer electrolytes 20-22.
Figure 3-7: Ambient temperature ionic conductivity and static water contact angle relationship to composition for solid polymer electrolytes 23-25.
Again, SPEs 23-25 had lower ionic conductivities than SPE 17, but higher than SPE 19 (Table 3-1). In addition, they had lower ionic conductivities than SPEs 20-22. Moreover, no increase in ambient temperature ionic conductivity was detected as the MEE-functionalized cyclotriphosphazene content in the polymer was increased from SPE 23 to 25 (Figure 3-7). This is presumably due to the long OFP substituents, which served to disrupt conductive pathways at all ratios.

Static water contact angle (sWCA) values were measured to evaluate the hydrophobicity of SPEs 17-25 (Table 3-1). Figures 3-6 and 3-7 illustrate the relationship between static water contact angle and polymer composition for SPEs 20-22 and 23-25. As shown in Figure 3-6, the sWCA values for SPEs 20-22 increased as the content of the hydrophobic TFE-functionalized cyclotriphosphazene in the system was increased. By comparison, the sWCA value for SPE 17, which contained all MEE-functionalized cyclotriphosphazene units showed the lowest value. The sWCA value for SPE 18, which contained all TFE-functionalized cyclotriphosphazene units, was similar to that of SPE 20, which contained approximately 90% TFE-functionalized cyclotriphosphazene units.

SPEs 23-25, with OFP instead of TFE side groups as the hydrophobic substituents, had similar sWCA values (111° to 112°), in spite of the variation in the OFP-functionalized cyclotriphosphazene content (Figure 3-7). Presumably, the extent of phase separation in these three SPEs is similar, so that, the hydrophobicity of the surface remained the same, even though the overall fluorine content of the polymer varied over a broad range. This premise is supported by the sWCA value for SPE 19, which contained all OFP-functionalized cyclotriphosphazene units and no MEE-functionalized cyclotriphosphazene units. Here, the sWCA was similar to the values observed for SPE
This leads us to believe that the surfaces of these SPEs are dominated by hydrophobic OFP units.

### 3.4 Conclusions

The development of polyoctenamer copolymers with pendent functionalized-cyclotriphosphazenes was accomplished via the ring-opening metathesis copolymerization of cyclooctene-based cyclotriphosphazene monomers with 2-(2-methoxyethoxy)ethoxy (MEE), and 2,2,2-trifluoroethoxy (TFE) or 2,2,3,3,4,4,5,5-octafluoropentoxy (OFP) substituents. Dimensionally stable high molecular weight polymers were obtained in satisfactory yields. The linkage of the pendent cyclotriphosphazene units to the polyoctenamer backbone resulted in glass transition temperatures similar to or slightly higher than unsubstituted trans-polyoctenamer. In addition, the cyclotriphosphazene units allowed both lithium cation solvation and hydrophobicity to be imparted to the final polymers. The temperature-dependent ionic conductivities were typical of solid polymer electrolyte behavior. Different effects on the ionic conductivity and static water contact angle were detected depending on the type of hydrophobic substituent present. The 2,2,2-trifluoroethoxy-containing solid polymer electrolytes (20-22) showed decreased ambient temperature ionic conductivity and increased static water contact angle as the amount of the fluorinated unit was increased. Those polymers with 90-60 % 2,2,2-trifluoroethoxy groups and 10-40 % 2-(2-methoxyethoxy)ethoxy groups showed the best compromise between ionic conductivity and hydrophobicity with values in the range of $1-2 \times 10^{-6}$ S/cm, and static water contact
angles of 95°-104°. However, the 2,2,3,3,4,4,5,5-octafluoropentoxy-containing solid polymer electrolytes (23-25) underwent no significant change in ambient temperature ionic conductivity (7-8 x 10^{-7} \text{ S/cm}) or static water contact angle (111°-112°) as the amount of this longer fluoroalkoxy group was changed. This is attributed to the ability of the 2,2,3,3,4,4,5,5-octafluoropentoxy substituents to disrupt lithium cation conductive pathways in the polymer matrix by phase separation and to the concentration of the fluorinated units at the polymer surface. Polymers of the types discussed here are prototype candidates for lithium anode membranes in lithium/seawater batteries. Further optimization of the property balances is anticipated with the use of mixed substituent monomers in which each pendent cyclotriphosphazene ring contains both lithium-ion solvating and hydrophobic side groups. In addition, alternative ion-transport and hydrophobic side groups are being investigated.
3.5 References


Chapter 4

Lithium-ion conductive polymers as prospective membranes for lithium-seawater batteries

4.1 Introduction

The objective of this work was the synthesis and characterization of new amphiphilic single ion conductive polymers for possible applications as anode membranes in lithium-seawater batteries. Previous work has demonstrated the utility of organic-phosphazene hybrid polymers for electrolyte and membrane applications.\textsuperscript{1-3} This class of polymers has the unique ability to combine two different competing properties by the utilization of various side groups on the pendent cyclotriphosphazene units attached to the polymer backbone. Polymeric electrolyte anode membranes when used in aqueous environments require the unusual combination of lithium ion conduction (which usually generates hydrophilicity) while simultaneously providing a hydrophobic barrier between water and the lithium metal anode.

Autonomous marine systems such as remote sea buoys, emergency signal beacons, underwater sensors, and navigation aids typically employ conventional primary batteries as their source of power.\textsuperscript{4} However, primary battery systems are typically bulky, heavy, and expensive because of the protection required for operation in the harsh ocean
Metal-seawater battery technology offers a solution to this problem by utilizing the ambient seawater as a battery component. Metal-seawater batteries use a metal anode and seawater as the electrolyte/oxidant solution. For this reason and because it is an open system, this type of design can also be defined as a semi-fuel cell. The following electrochemical reactions take place in a metal-seawater primary cell.

Anodic reaction: \( M^0 \rightarrow M^{n^+} + n e^- \)

Cathodic reaction: \( O_2 + 2 H_2O + 4 e^- \rightarrow 4 OH^- \)

Utilization of seawater as an oxidant in the battery, allows the size and weight to be drastically reduced because no protection from the ocean environment is required. In addition, metal-seawater batteries are stored dry, allowing them to be stored for long periods of time and subsequently activated by immersion in seawater.

Lithium metal is a preferred anode material to increase the power density of the battery system. In addition, lithium metal has a high oxidation potential (-3.0 V) and high energy density making it ideal for this application. Despite, the advantages of metallic lithium, one major obstacle exists: a parasitic lithium-water reaction occurs when lithium metal and water come into contact.

Parasitic reaction: \( 2 Li^0 + \frac{1}{2} H_2O \rightarrow H_2 + 2 LiOH(s) \)
As this reaction progresses a layer of lithium hydroxide forms on the surface of the lithium anode inhibiting further oxidation of the lithium metal. Eventually, the layer becomes so thick that the battery ceases to function. Thus, in order to eliminate the parasitic lithium water reaction, all contact of the lithium anode surface with water must be prevented. In principle, this can be accomplished by the use of a highly selective polymeric membrane which acts as a barrier between the lithium metal anode and seawater but allows lithium ions to pass through. Figure 4-1 illustrates the general concept. There are four main components (1) anode and cathode current collectors, (2) seawater electrolyte/oxidant, (3) lithium metal anode, and (4) polymer electrolyte anode membrane. The most important operational factor of a device of this type is the performance of the polymer electrolyte anode membrane.

In addition to preventing the ingress of water to the lithium metal anode, the other primary function of the polymeric membrane is to conduct lithium cations. The membrane must also protect the lithium anode surface from direct reaction with dissolved gases and ions in seawater such as O₂, CO₂, N₂, Fe³⁺, and HCO₃⁻. Moreover, it must maintain adherence to the lithium anode surface and retain structural, mechanical, and chemical integrity during storage and normal operation. Thus, a hybrid polymer system, that combines seemingly conflicting properties, is needed to meet all the requirements of an anode membrane material. This is a major challenge for both the design and synthesis of polymeric materials.

Previous work in our program utilized ring-opening metathesis polymerization methods to produce polynorbornenes¹ and polyoxanorbornenes² with pendent cyclotriphosphazenes as solid polymer electrolytes (Figure 4-2a). In these studies
oligoethyleneoxy side chains of various lengths were linked to a cyclotriphosphazene unit, which was itself connected to the backbone of polynorbornene or polyoxanorbornene. The cyclotriphosphazene units possess five sites per polymer repeat unit available for property tuning. The ability to utilize five side groups per a repeat unit gives a higher density of functional side units than can be obtained for nearly all other polymers (Figure 4-2). Therefore, a wider variation in polymer properties can be generated by small compositional changes within the side group array. However, oligoethyleneoxy units are hydrophilic, which caused the earlier membranes to transmit water as well as lithium ions.
Figure 4-1: Schematic of a lithium-seawater battery
Figure 4-2: Structure of substituted a) polynorbornenes / polyoxanorbornenes and b) polyphosphazenes
Figure 4-3: Schematic structures of a) backbone-incorporated and b) pendent-incorporated single ion conductors
Other studies in our program utilized pendent-cyclotriphosphazene polyoctenamers. Each cyclotriphosphazene groups bore both hydrophobic (2,2,2-trifluoroethoxy or 2,2,3,3,4,4,5,5-octafluoropent oxy) and lithium ion conductive (2-(2-methoxyethoxy)ethoxy) side chains. Polymers with these side groups conducted lithium cations at modest ionic conductivities (10^{-6} S/cm) and showed good surface hydrophobicity (static water contact angle range, 95-112º). However, a disadvantage of these membranes proved to be the need for a free-salt dissolved in the membrane to generate measurable ionic conductivities. The addition of a “mobile” salt to the polymer matrix provides an increased likelihood of diffusion-induced concentration gradients, which lead to increased resistance through the polymer electrolyte matrix. Leaching of the salt to the surface of the membrane is also possible over extended periods of storage time. An attractive alternative is the use of single ion conductors, which incorporate an anion of a salt either into the polymer backbone (Figure 4-3a) or in a pendent group that is covalently linked to the polymer backbone (Figure 4-3b).\textsuperscript{12-15} Immobilization of the anion should prevent diffusion and leaching. Thus, this class of materials could be promising anode membrane materials.

Here we report the synthesis, characterization, ionic conductivity and hydrophobicity of prototype lithium-based amphiphilic single ion conductive polymer electrolytes. Ring-opening metathesis polymerization (ROMP) techniques were used to copolymerize two different types of pendent cyclotriphosphazene norbornenemethoxy-based monomers. The cyclotriphosphazene unit of one co-monomer bore 2-(2-phenoxyethoxy)ethoxy (PhEE) side groups. These groups were utilized because of their similarity to 2-(2-methoxyethoxy)ethoxy units, which are known to readily support ion
transport. However, the terminal phenyl group was expected to increase both the hydrophobicity and the glass transition temperature of the polymer to produce a more water-resistant and robust material. The second type of co-monomer carried single ion conductive side groups linked to the cyclotriphosphazene unit. These provided a lithium cation source. For this purpose, 4-(lithium carboxalato)phenoxy (LiOOCPh) side groups were used because (1) the phenoxy unit should increase the polymer glass transition temperature\(^{20}\), and (2) polymerization may be carried out with the use of the propylcarboxylato (protected) derivative to allow a more controlled polymerization due to the absence of the free carboxylic acid units. A free carboxylic acid group could coordinate with the polymerization catalyst and, thus, reduce its efficiency. Various ratios of the co-monomers were copolymerized to investigate how the change in composition alters the thermal, ionic conductive and hydrophobic properties.

4.2 Experimental

4.2.1 Materials

5-Norbornene-2-methanol (95%) was obtained from City Chemicals L.L.C. and was used as received. 2-(2-Chloroethoxy)ethanol (99%), potassium carbonate (99+%), propyl 4-hydroxybenzoate (99+%), ethyl vinyl ether (99%), (bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride) (97%), sodium hydride (60%, mineral oil dispersion), magnesium sulfate (98%), lithium hydroxide (98+%) were obtained from Sigma-Aldrich Co. and used as received. Phenol (99+%),
lithium tert-butoxide (98+%), potassium tert-butoxide (98+%) were obtained from Acros Organics and used as received. Hexachlorocyclotriphosphazene was obtained from Ethyl Corp./Nippon Fine Chemical and was recrystallized from heptane and sublimed at 0.1 mm Hg at 30 °C before use. Polybis(2-(2-methoxyethoxy)ethoxy)phosphazene (MEEP) was synthesized according to literature procedures. All solvents were anhydrous and were obtained from EM Science unless otherwise noted.

4.2.2 Equipment

High-field $^1$H (360.14 MHz), $^{13}$C (90.56 MHz), and $^{31}$P (145.79 MHz) NMR spectra were recorded using a Bruker AMX-360 NMR spectrometer. $^1$H and $^{13}$C NMR spectra were referenced to external tetramethylsilane, while $^{31}$P NMR spectra were referenced to external 85% phosphoric acid. $^{13}$C and $^{31}$P NMR spectra were proton decoupled. Mass spectra were collected using a Micromass Quattro-II triple quadrupole mass spectrometer. Molecular weights and polydispersity indices 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 (Alfa Aesar) in stabilized THF (EMD) at a flow rate of 1.0 mL/min. Thermal transitions were determined through analysis via a TA Q10 differential scanning calorimeter. Calibration was accomplished with indium, water, and cyclohexane standards. All analyses were over a range of -100 °C to 100 °C at a heating rate of 10 °C/min. Static water contact angle measurements were obtained using a
Rame-Hart, Inc., model 100-00 contact angle goniometer. Five static water contact angles were obtained for each solid polymer electrolyte and an average and standard deviation value was calculated. All reactions were carried out under an inert atmosphere of argon gas. Ionic conductivity measurements were obtained using a Hewlett Packard 4192A LF Impedance Analyzer at a potential of 0.1 V with an alternating current frequency range of 5 Hz to 1 MHz. The samples were placed between platinum disc electrodes with a Teflon o-ring spacer, and the polymer electrolyte cell was compressed between aluminum blocks held in a Teflon fixture. Electrical leads were attached between the impedance analyzer and the polymer electrolyte cell sample holder. All ionic conductivity measurements were carried out over a temperature range of 25 to 80 °C under an inert atmosphere of dry argon.

4.2.3 Synthesis of 2-(2-phenoxyethoxy)ethanol (2)

Potassium carbonate (216.4 g, 1.57 mol) was suspended in N,N-dimethylformamide (1.75 L). A solution of phenol (108.0 g, 1.15 mol) in N,N-dimethylformamide (250 mL) was added and stirred via mechanical means. 2-(2-Chloroethoxy)ethanol (130.0 g, 1.04 mol) was added dropwise and the reaction mixture and heated to 140°C for 24 h. The reaction solution was cooled to room temperature, filtered, and the solvent was distilled under reduced pressure (100 °C, 0.1 mm Hg). The crude product was dissolved in diethyl ether (600 mL) and washed with a 0.5 M aqueous sodium hydroxide solution (3 x 150 mL). The aqueous layers were combined and washed with diethyl ether (600 mL). The diethyl ether layers were combined and dried over
magnesium sulfate, filtered, and the solvent was removed under reduced pressure (slight heat, 0.1 mm Hg) to yield 75.0 g of 2 (39 % yield). $^1$H NMR (CDCl$_3$): $\delta$ (ppm) 7.18 (t, -CH$_2$OAr, $J$ = 7.0 Hz, 2H), 6.86 (t, -CH$_2$OAr, $J$ = 7.1 Hz, 1H), 6.83 (t, -OCH$_2$OAr, $J$ = 7.0 Hz, 2H), 4.01 (t, -OCH$_2$CH$_2$OAr, $J$ = 4.7 Hz, 2H), 3.73 (t, -OCH$_2$CH$_2$OAr, $J$ = 4.7 Hz, 2H), 3.64 (t, HOCH$_2$CH$_2$O-, $J$ = 4.5 Hz, 2H), 3.55 (t, HOCH$_2$CH$_2$O-, $J$ = 4.4 Hz, 2H), 2.76 (s, -OH, 1H); $^{13}$C NMR (CDCl$_3$): $\delta$ (ppm) 158.74 (C-Ar), 129.64 (C-Ar), 121.02 (C-Ar), 114.72 (C-Ar), 72.80 (C-2), 69.65 (C-4), 67.33 (C-3), 61.56 (C-1); MS = m/z 183 (MH$^+$).

4.2.4 Synthesis of 5-norbornene-2-methoxy-pentakis(chloro)cyclotriphosphazene (monomer 3)

The synthesis of 3 and subsequent substitution was adapted from a similar procedure.$^9$ 5-Norbornene-2-methanol (75.0 g, 604 mmol) was added to a solution of potassium tert-butoxide (72.6 g, 647 mmol) in tetrahydrofuran (THF) (1.5 L) and the mixture was stirred at room temperature for 16 h. The potassium salt solution of 5-norbornene-2-methanol was cooled to -78 °C and added dropwise to a solution of hexachlorocyclotriphosphazene (NPCl$_2$)$_3$ (300.0 g, 863 mol) in THF (2.5 L) at -78 °C. The reaction mixture was then stirred and warmed to room temperature overnight. THF was removed via rotary evaporation and the crude product was dissolved in diethyl ether (700 mL) and washed with water (2 x 500 mL). The aqueous layers were combined and washed with diethyl ether (700 mL). The diethyl ether layers were combined, dried over magnesium sulfate, and filtered. The solution was then concentrated via rotary evaporation and excess hexachlorocyclotriphosphazene was removed by sublimation (0.1
mm Hg at 40°C for 24 h) to leave the product (3) as a viscous oil. $^1$H NMR (CDCl$_3$): $\delta$ (ppm) 6.01 (br m, -H$_2$C=CH-, 2H), 4.75 (br s, -OCH$_2$Nb, 2H), 1.04-3.28 (unresolvable, exo and endo isomers of norbornene, 7 H); $^{13}$C NMR (CDCl$_3$): $\delta$ (ppm) (exo and endo isomers of norbornene) 137.56, 133.22, 131.18, 127.68, 66.76, 49.36, 44.56, 43.04, 42.13, 41.52, 39.01, 34.43 30.75, 28.72; $^{31}$P NMR ($d_6$-THF): $\delta$ (ppm) 24.44 (d, $J = 55.2$ Hz, 2P), 16.29 (t, $J = 55.3$ Hz, 1P); MS = m/z 434 (MH$^+$).

4.2.5 Synthesis of 5-norbornene-2-methoxy-pentakis(2-(2-phenoxyethoxy)ethoxy)cyclotriphosphazene (monomer 4)

A solution of 2 (54.7 g, 350 mmol) in THF (300 mL) was added dropwise to a suspension of 60% sodium hydride (14.0 g, 344 mmol) in THF (300 mL) and stirred for 16 h. The solution of sodium salt of 2 was then added dropwise to a solution of 3 (25.0 g, 57.4 mmol) in THF (750 mL) and stirred for 18 h. THF was then removed via rotary evaporation and the crude product reaction mixture was dissolved in diethyl ether (1 L). The solution was washed with water (3 x 200 mL). The diethyl ether layers were combined, dried over magnesium sulfate, and filtered. The diethyl ether was removed via rotary evaporation and the residual diethyl ether was removed under reduced pressure (room temperature, 0.1 mm Hg) to leave 60.1 g (89.9 % yield) as a viscous oil (4). $^1$H NMR (CDCl$_3$): $\delta$ (ppm) 7.26 (m, -OCH$_2$CH$_2$OAr, 2H), 6.93 (m, -OCH$_2$CH$_2$OAr, 1H), 6.89 (m, -OCH$_2$CH$_2$OAr, 2H), 6.04 (br m, -H$_2$C=CH-, 2H), 4.09 (m, -POCH$_2$CH$_2$OCH$_2$CH$_2$OAr, 4H), 3.82 (m, -OCH$_2$CH$_2$OAr, 2H), 3.74 (m, -POCH$_2$CH$_2$O-, 2H), 3.61 (br s, -OCH$_2$Nb, 2H), 0.71-2.12 (unresolvable, exo and endo isomers of norbornene, 7 H); $^{13}$C NMR (CDCl$_3$): $\delta$ (ppm) (exo and endo isomers) 160.01, 137.63,
4.2.6 Synthesis of 5-norbornene-2-methoxy-pentakis(4-propylcarboxalatophenoxy)cyclotriphosphazene (monomer 5)

The same synthetic procedure was used as for monomer 4 to produce 45.6 g of product (86.0 % yield). Reagent quantities: propyl 4-hydroxybenzoate (50.5 g, 280 mmol), 60% sodium hydride (11.0 g, 275 mmol), monomer 3 (20.0 g, 45.9 mmol). $^1$H NMR (CDCl$_3$): δ (ppm) 7.95 (m, -PO$_2$ArCOOPr, 2H), 7.18 (m, -PO$_2$ArCOOPr, 2H), 4.28 (t, -OC$_2$H$_2$CH$_2$CH$_3$, 2H), 6.05 (br m, -HC=CH-, 2H), 1.78 (q, -OCH$_2$CH$_2$CH$_3$, 2H), 1.05 (t, -OCH$_2$CH$_2$CH$_3$, 3H), 3.40 (br s, -OC$_2$H$_2$Nb, 2H), 0.79-1.98 (unresolvable, aliphatic-Nb, 7 H); $^{13}$C NMR (CDCl$_3$): δ (ppm) (exo and endo isomers) 165.65, 137.56, 132.03, 131.92, 127.65, 120.72, 115.34, 66.79, 49.41, 45.27, 43.72, 42.35, 41.49, 38.91, 33.91, 30.98, 29.78, 28.57, 22.03, 10.50; $^{31}$P NMR (CDCl$_3$): δ (ppm) 10.32 (m, 3P); MS = m/z 1154 (MH$^+$).

4.2.7 Procedure for ring-opening metathesis polymerization

Monomer 4 (9.01 g, 7.74 mmol, 0.90 eq) and monomer 5 (0.99 g, 0.86 mmol, 0.10 eq) were combined, degassed under reduced pressure (room temperature, 0.1 mm Hg), and dissolved in THF (20 mL). A solution of initiator, (bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride) (Grubbs’ first
generation catalyst) (1) (28 mg, 0.035 mmol, 300:1 monomer: initiator), in CH$_2$Cl$_2$ (1 mL) was added quickly to the monomer solution and stirred for 90 min. The reaction was then terminated with ethyl vinyl ether (1 mL). The polymer solution was concentrated under vacuum (room temperature, 0.1 mm Hg) and dialyzed (12K-14K MWCO) against THF for 3 days. The polymer solution was then concentrated and precipitated into hexanes where the product was collected and dried under reduced pressure (room temperature, 0.1 mm Hg) to yield 4.80 g (48 % yield) of polymer 6. The average repeat unit composition was calculated from $^1$H NMR peak integration. Similar chemical shifts were observed for polymers 7-9.

For 6, average repeat unit composition (4, 89.1 %; 5, 10.9 %); $^1$H NMR (CDCl$_3$): δ (ppm) 7.91 (br m, -POArCOOPr, 2H), 7.80 (br m, -POArCOOPr, 2H), 7.20 (br m, -CH$_2$OAr, 2H), 7.93 (br m, -CH$_2$OAr, 1H), 6.83 (br m, -CH$_2$OAr, 2H), 5.24 (br m, -HCC=CH-, 2H), 4.23 (br m, -OCH$_2$CH$_2$CH$_3$, 2H), 4.06 (br s, -OCH$_2$CH$_2$OAr, 2H), 3.97 (br s, -POCH$_2$CH$_2$O-, 2H), 3.82 (br m, -OCH$_2$Nb, 2H), 3.65 (br s, -POCH$_2$CH$_2$OCH$_2$CH$_2$OAr, 4H), 1.75 (br m, -OCH$_2$CH$_2$CH$_3$, 2H), 1.03 (br m, -OCH$_2$CH$_2$CH$_3$, 3H), 0.87-2.61 (unresolvable, exo and endo isomers of norbornene, 7H);
$^{13}$C NMR (CDCl$_3$): δ (ppm) 167.75, 158.71, 137.87, 137.21, 132.98, 131.94, 129.44, 123.12, 120.81, 115.12, 114.55, 70.21, 69.63, 67.27, 66.87, 65.08, 61.45, 49.84, 43.89, 40.69, 35.21, 30.01, 22.11, 11.05; $^{31}$P NMR (CDCl$_3$): δ (ppm) 18.3 (s, 6P); $M_n = 106$ kDa, $M_w = 123$ kDa, PDI = 1.16.

Polymer 7 was synthesized in a similar manner to that described for polymer 6 using monomer 4 (8.50 g, 7.30 mmol, 0.85 eq) and monomer 5 (1.49 g, 1.29 mmol, 0.15 eq) in a solution of THF (20 mL) and a solution of 1 (28 mg, 0.035 mmol) in CH$_2$Cl$_2$ (1
mL). After purification via dialysis, the THF was removed under reduced pressure (room temperature, 0.1 mm Hg) to yield 3.3 g (33 % yield) of polymer 7. The average repeat unit composition (4, 86.3 %; 5, 13.7 %); \( M_n = 105 \text{ kDa}, M_w = 122 \text{ kDa}, \text{PDI} = 1.16. \)

Polymer 8 was synthesized in a similar manner to polymer 6 using monomers 4 (8.01 g, 6.90 mmol, 0.80 eq) and 5 (1.98 g, 1.72 mmol, 0.20 eq) in a solution of THF (20 mL) and a solution of 1 (28 mg, 0.035 mmol) in CH\(_2\)Cl\(_2\) (1 mL). After purification via dialysis, the THF was removed under reduced pressure (room temperature, 0.1 mm Hg) to yield 4.5 g (45 % yield) of polymer 8. Average repeat unit composition (4, 81.2 %; 5, 18.8 %); \( M_n = 94 \text{ kDa}, M_w = 109 \text{ kDa}, \text{PDI} = 1.16. \)

Polymer 9 was synthesized in a similar manner to polymer 6 using monomer 4 (7.52 g, 6.50 mmol, 0.75 eq) and monomer 5 (2.48 g, 2.15 mmol, 0.25 eq) in a solution of THF (20 mL) and a solution of 1 (28 mg, 0.035 mmol) in CH\(_2\)Cl\(_2\) (1 mL). After purification via dialysis the THF was removed under reduced pressure (room temperature, 0.1 mm Hg) to yield 4.9 g (49 % yield) of polymer 9. Average repeat unit composition (4, 78.0 %; 5, 22.0 %); \( M_n = 105 \text{ kDa}, M_w = 124 \text{ kDa}, \text{PDI} = 1.18. \)

### 4.2.8 General procedure for deprotection and lithiation of polymers 6-9

Deprotection of the propyl ester groups in polymers 6-9 was carried out by treating a given amount of polymer in THF with 7 equivalents of potassium tert-butoxide and 2 equivalents of water for 48 h. The polymer was then acidified by precipitation into 1.0 M HCl\(_{(aq)}\), collected, and dried under reduced pressure (60 °C, 0.1 mm Hg). Acidification could not be confirmed because the carboxylic acid peak in the \(^1\)H NMR
could not be resolved. However, the disappearance of the propyl peaks in the $^1$H NMR [(CDCl$_3$) δ (ppm) 1.03 (br m, -OCH$_2$CH$_2$CH$_3$, 3H), 1.75 (br m, -OCH$_2$CH$_2$CH$_3$, 2H), 4.22 (br m, -OCH$_2$CH$_2$CH$_3$, 2H)] and $^{13}$C NMR [(CDCl$_3$) δ (ppm) 65.08 (OCH$_2$CH$_2$CH$_3$), 22.11 (OCH$_2$CH$_2$CH$_3$), 11.05 (OCH$_2$CH$_2$CH$_3$)] indicated full deprotection.

Lithiation of polymers 6-9 was accomplished by multiple precipitations of the deprotected polymer into 1.0 M LiOH$_{(aq)}$. Once the polymer was collected it was washed with water and dried under reduced pressure (60 °C, 0.1 mm Hg). The polymer was then dissolved in methanol and dialyzed (1K MWCO) against methanol for 5 days to remove any residual ions. The methanol was then removed under reduced pressure (40 °C, 0.1 mm Hg). The lithiated derivatives for polymers 6-9 were transparent light brown tough rubbery solids and were recovered in quantitative yields to their propyl ester counterpart.

### 4.2.9 Preparation of polymer electrolyte samples for impedance analysis

Lithiated polymers 6-9 were dried under vacuum at 40 °C for 1 week before fabrication. Each polymer (0.3 g) was dissolved in dry methanol and poured into a 2 cm x 2 cm mold. The methanol was then air-evaporated in a dry environment and the samples were subjected to reduced pressure (40 °C, 0.1 mm Hg, 72 h) to remove any residual methanol. Once dried, the appropriate size sample was cut from each film and a small amount of a 10 % MEEP-10 mol % LiBF$_4$ (w/v) in THF solution was painted lightly onto each side of the electrolyte sample. The polymer electrolyte cell was then assembled and exposed to vacuum (room temperature, 0.1 mm Hg, 12 h) to remove residual solvent.
Following the exposure to vacuum, the impedance analysis sample holder was assembled and measurements were carried out.

**4.2.10 Preparation of films for static water contact angle measurements**

Lithiated polymers 6-9 were dried under vacuum at 40 °C for 1 week before fabrication. Each polymer was dissolved in methanol (30 % (w/v)). The polymer solution was poured onto a glass substrate and the methanol was air-evaporated in a dry environment and dried under a reduced pressure (room temperature for 24 h, 40 °C for 72 h, 0.1 mm Hg) to remove any residual methanol.

**4.3 Results and Discussion**

**4.3.1 Synthesis of monomers**

The synthetic route employed to produce monomers 4 and 5 is shown in Figure 4-4. The first step was the reaction of hexachlorocyclophosphazene, \((\text{NPCl}_2)_3\), with the potassium salt of 5-norbornene-2-methanol, which yielded 5-norbornene-2-methoxy pentakis(chloro)cyclophosphazene (4). Nucleophilic replacement of the remaining chlorine atoms on the cyclophosphazene by the appropriate sodium alkoxide was carried out to obtain single-substituent monomers 4 and 5 as transparent, yellowish viscous oils in yields of approximately 70 %.
Figure 4-4: Synthesis of norbornene-based cyclotriphosphazene monomers 4 and 5
Figure 4-5: Copolymerization of monomers 4 and 5 to yield polymers 6-9
4.3.2 Synthesis of polymers

Polymers 6-9 were synthesized under an inert atmosphere of argon at ambient temperature via ring-opening metathesis polymerization (ROMP) of the corresponding monomers (Figure 4-5). Co-polymerization reactions were attempted with Grubbs’ 1st generation catalyst (bis(tricyclohexylphosphine)benzylidene ruthenium(IV)dichloride) (1) at a monomer to initiator ratio of 300:1, and were terminated after 90 min. by the addition of ethyl vinyl ether. The polymer solutions were then dialyzed against THF, concentrated, and precipitated into hexanes to yield polymers 6-9 in satisfactory yields (33-49 %) as transparent brown tough rubbery solids. Each polymer was readily soluble in organic solvents such as tetrahydrofuran, methylene chloride, and chloroform. The ester groups of polymers 6-9 were deprotected under basic conditions and then acidified by multiple precipitations into 1.0 M HCl(aq). Lithiation was then performed by multiple precipitations into 1.0 M LiOH(aq). Following purification via dialysis the lithiated derivatives of polymers 6-9 were obtained in quantitative yields, based on their propyl ester counterparts, as transparent light brown tough rubbery solids.

Parallel syntheses of each 5-norbornene-2-methoxy monomer was carried out with cyclooctene-5-oxy units in place of the 5-norbornene-2-methoxy units in order to examine the influence of backbone architecture on the polymer’s physical, thermal, conductive, and hydrophobic properties. However, when the cyclooctene-5-oxy monomers were copolymerized with Grubbs’ 2nd generation catalyst the molecular weights obtained were insufficient to warrant further characterization. Despite the use of this catalyst, which is significantly more active than its 1st generation predecessor, the
steric constraints of the cycloocteneoxy-based monomers probably reduced the accessibility of the monomers to the propagating chain end. This, in combination with the low ring strain of cyclooctene and low reactivity of its propagating metal-carbene complex, led to limited degrees of polymerization and low molecular weights for each polymer. Thus, all the work described here involved the norbornene-based monomers.

4.3.3 Polymer characterization

Polymers 6-9 were characterized by $^1$H, $^{13}$C, and $^{31}$P NMR spectroscopy. $^1$H NMR peak integration of the aromatic protons on the 2-(2-phenoxyethoxy)ethoxy (PhEE) and 4-propylcarboxalatophenoxy (PrOOCPh) substituents were used to confirm their ratios on the cyclotriphosphazene units. $^1$H and $^{13}$C NMR were utilized to examine the effectiveness of the deprotection protocol. Disappearance of the propyl ester $^1$H and $^{13}$C NMR peaks indicated complete deprotection.

Gel permeation chromatography of the propyl ester polymer derivatives was used to estimate the molecular weights of protected polymers 6-9, which had number average molecular weight ($M_n$) values from 94 kDa to 105 kDa and weight average molecular weight ($M_w$) values from 109 kDa to 125 kDa. Typically polydispersity index (PDI) values for equilibrium controlled polymerizations of this type are approximately 2.0; however, the PDI values for polymers 6-9 were significantly lower at 1.16-1.18. A possible explanation for the lower PDI values is that these polymerizations were terminated before they reached a high degree of polymerization (average DP = 96). At
higher degrees of polymerization branching and chain recombination can occur, which can lead to higher PDI values.

4.3.4 Solid polymer electrolytes - morphological properties

The morphological properties of polymers 6-9 and their lithiated derivatives were examined by differential scanning calorimetry. The glass transition temperature ($T_g$) values are summarized in Table 4-1. Each polymer gave a single $T_g$ and no melting transition, which suggests that the polymers are completely amorphous. The $T_g$ values of polymers 6-9 ranged from -16 °C (6) to -14 °C (9). The lithiated derivatives of polymers 6-9 had slightly higher $T_g$ values compared to their propyl ester counterparts. The $T_g$ values ranged from -8°C (6) to -5°C (9).

4.3.5 Solid polymer electrolytes - temperature-dependent ionic conductivity

Initial attempts measure the ionic conductivities of lithiated polymers 6-9 were unsuccessful due to poor contact between the electrolyte sample and the platinum disc electrodes. In order to achieve good contact between the electrolyte samples and the platinum electrodes a layered electrolyte sample was fabricated. This was accomplished by utilizing a second polymer, poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (MEEP), as an adhesive between each platinum disc electrode and the electrolyte sample. This polymer is a well studied solid polymer electrolyte with known ionic conductivity data.16-19
A control experiment was carried out to ascertain if such a layered electrolyte assembly would affect the ionic conductivity measurements of lithiated polymers 6-9. This control experiment consisted of measuring the ionic conductivity of a poly(ethylene oxide)-lithium tetrafluoroborate (PEO-LiBF₄) sample and comparing that value to a layered electrolyte sample with PEO and MEEP. PEO was used because it is one of the most widely studied solid polymer electrolytes which typically shows ionic conductivities around 10⁻⁸ S/cm.²⁸,²⁹ The ionic conductivity was initially measured without the MEEP-LiBF₄ adhesive layers and then subsequently with the MEEP-LiBF₄ adhesive layers. The difference in ionic conductivity values between the control samples was only 6.0 x 10⁻⁸ S/cm. This small variation in ionic conductivity, when compared to the orders of magnitude higher ionic conductivities for polymers 6-9, indicated that the layered electrolyte sample technique is an effective means for measuring the ionic conductivity of lithiated polymers 6-9 without causing significant discrepancies.

The temperature-dependent ionic conductivity of lithiated polymers 6-9 is shown in Figure 4-6. Room temperature ionic conductivities ranged from 5.9 x 10⁻⁶ S/cm (6) to 7.0 x 10⁻⁷ S/cm (9) and the 80 ºC ionic conductivities ranged from 3.1 x 10⁻⁵ S/cm (6) to 3.9 x 10⁻⁶ S/cm (9). The ionic conductivities of each polymer increased in a non-linear manner as the temperature was increased, which is typical of solid polymer electrolytes.³⁰ In addition, the ionic conductivities of lithiated polymers 6-9 increased as the content of LiOOCPh-substituted cyclotriphosphazene was decreased. This decrease is attributed to the deficiency of lithium cations available for transport because of inter- and intrachain transient cross-links which utilize lithium cations as bridge between polymer chains. It should be noted that the presence of transient cross-links did not cause a significant
change in the $T_g$ values for polymers 6 to 9. This phenomenon, which had previously been observed in polyoctenamer pendent-cyclotriphosphazenes\textsuperscript{3}, occurs because the cation coordinative side groups, PhEE, are adequately separated from the polynorbornene backbone and, therefore, have little or no influence on the $T_g$ of the polymer even if they participate in a transient cross-links. However, if the amount of LiOOCPh-substituted cyclotriphosphazene is increased, a critical value is reached at which the $T_g$ will be affected significantly.
Table 4-1: Glass transition temperature ($T_g$), ionic conductivity ($\sigma$) and static water contact angle (sWCA) data for polymers 6-9.

<table>
<thead>
<tr>
<th>polymer</th>
<th>$T_g$ (°C)</th>
<th>$T_g$ (°C) (Li)$^a$</th>
<th>$\sigma$ at 25 °C ($10^{-5}$ S/cm)$^a$</th>
<th>$\sigma$ at 80 °C ($10^{-5}$ S/cm)$^a$</th>
<th>sWCA (°)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
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<td>3.1</td>
<td>76 ± 2</td>
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<tr>
<td>7</td>
<td>-15</td>
<td>-7</td>
<td>0.35</td>
<td>2.1</td>
<td>80 ± 3</td>
</tr>
<tr>
<td>8</td>
<td>-15</td>
<td>-7</td>
<td>0.20</td>
<td>1.6</td>
<td>76 ± 3</td>
</tr>
<tr>
<td>9</td>
<td>-14</td>
<td>-5</td>
<td>0.07</td>
<td>0.39</td>
<td>80 ± 4</td>
</tr>
</tbody>
</table>

$^a$ Analyses performed on the lithiated derivatives.
Figure 4-6: Temperature-dependent ionic conductivity behavior of polymers 6-9
4.3.6 Solid polymer electrolytes - hydrophobic properties

Static water contact angle (sWCA) measurements were utilized to investigate the hydrophobicity of each lithiated polymer. Values for lithiated polymers 6-9 are shown in Table 4-1. The sWCA values ranged from 76º (6), to 80º (9). Curiously, there were no significant differences in the sWCA values for polymers 6-9 based on the measurements and their standard deviations. This suggested that the surface of each polymer film is chemically similar, despite, the compositional variations.

The sWCA values generated by these polymers are probably 10-15º lower than those required for a practical device, although the ionic conductivities may be adequate.31,32 There are two main approaches to improving the hydrophobicity of the polymers. The first requires a modification of the amphiphilic side group (PhEE) in order to make the phenyl moiety more hydrophobic. In principle, this can be accomplished by utilizing fluorinated or trifluoromethylated phenol in the synthesis of the PhEE side group. This approach is being investigated. The second strategy employs more of an engineering approach by using a second, more hydrophobic polymer, as part of a layered membrane. The hydrophobic polymer would be located on the seawater-exposed side of the anode membrane, while the other side of the membrane would be cemented to the lithium mental anode by an ionic conductive membrane such as MEEP.
4.4 Conclusions

The membranes synthesized in this work provide encouragement for the view that polymers can be designed that combine the seemingly opposing properties of lithium ion conduction and water repellency. Two types of 5-norbornene-2-methanoxy monomers were copolymerized, (1) 4-(propylcarboxyalato)phenoxy-containing (PrOOCPh), which was subsequently lithiated to yield 4-(lithium carboxyalato)phenoxy (LiOOCPh) and (2) 2-(2-phenoxyethoxy)ethoxy-containing (PhEE). The LiOOCPh-containing cyclotriphosphazenes provided a source for lithium cations, while the PhEE-containing cyclotriphosphazenes functioned as a lithium ion solvating and hydrophobic groups. The polymers showed ionic conductivities near $10^{-6}$ S/cm at room temperature and $10^{-5}$ S/cm at elevated temperatures, with static water contact angles around 80º. Polymer 6, which contained 10 % LiOOCPh and 90 % PhEE gave the highest ionic conductivity ($5.9 \times 10^{-6}$ S/cm) with a modest static water contact angle of 76º. Although adequate ionic conductivities were obtained for anode membrane applications and the glass transition temperatures are below 0ºC, the hydrophobic properties of the polymers need to be improved. This aspect is currently being investigated through two different strategies (1) modification of the amphiphilic side groups with fluoro-organic units and (2) through the use of a hydrophobic polymer in a layered membrane assembly. In addition, alternative single ion conductive groups, which allow increased dissociation of the lithium cation, are being examined.
4.5 References


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Chapter 5

Ionic conductivity of covalently interconnected polyphosphazene-silicate hybrid networks

5.1 Introduction

Solid polymer electrolytes (SPEs) have been studied extensively since the discovery of ionic conduction in complexes of poly(ethylene oxide) (PEO) with alkali metal salts and the subsequent suggestion that such ionic conductors could be used as electrolytes in electrochemical energy storage devices.\textsuperscript{1-3} Since then, PEO has become one of the most widely studied polymers for applications in secondary batteries. However, due to the crystalline nature of PEO at room temperature, the high ionic conductivities required for commercial applications have not yet been achieved.\textsuperscript{4} Therefore, alternative polymer systems have been the subject of intense investigation during the last decade in an effort to find a polymer system with a room temperature ionic conductivity suitable for commercial applications.\textsuperscript{5,6}

Previous research has shown that poly[bis(methoxyethoxyethoxy)phosphazene] (MEEP) has many advantages over PEO.\textsuperscript{7,8} MEEP has oligoethyleneoxy side chains, which are similar to the backbone of PEO (Figure 5-1). These side chains attached to a flexible polyphosphazene backbone result in a completely amorphous polymer with a low glass transition temperature ($T_g$) of -83 °C.\textsuperscript{9} These properties allow MEEP to achieve room temperature ionic conductivities of approximately $10^{-4}$ S/cm, which is much higher
than that of PEO \((10^{-7} \text{ S/cm})\).\(^7\) MEEP is also an excellent solvent for species such as lithium trifluoromethanesulfonylimide (LiTFSI), which is a common salt used in SPEs. Each MEEP repeating unit has six oxygen atoms which can coordinate to metal cations and facilitate ion-pair separation. However, MEEP is a visco-elastic gum at room temperature and can flow like a viscous liquid when subjected to an external force.\(^9\) Therefore, various attempts have been made to improve the dimensional stability by radiation or other crosslinking methods.\(^{10,11}\)

The crosslinking of MEEP by \(\gamma\)-ray and ultraviolet irradiation has been investigated earlier in our program. However, this approach does not provide a sufficiently high degree of control over the crosslinking density. Recently, sol-gel techniques were developed in order to confer dimensional stability to MEEP. The first approach combined a silicate network with a polyphosphazene. Kim \textit{et al.} prepared a polyphosphazene/silicon oxide partial IPN-type composite as a solid electrolyte from a mixture of MEEP and tetraethylorthosilicate (TEOS).\(^{12}\) The resultant materials had no covalent connections between MEEP and the silicon oxide. Gleria \textit{et al.} attempted to overcome this limitation by the introduction of free hydroxyl functionalities on the organic side groups of a polyphosphazene, and these were then chemically bonded to the silicon oxide to form a three dimensional network.\(^{13}\) However, this method provided poor control over the density of hydroxyl functionalities within the polyphosphazene. Consequently, this sol-gel technique yielded networks which were not well-defined.

We have synthesized a sol-gel precursor of a polyphosphazene, prepared by the covalent linkage of MEEP to a silicon alkoxide. Subsequent hydrolysis and condensation of the alkoxide component generated a covalently interconnected hybrid network with a
controlled morphology and physical properties. The combination of the sol-gel derived silicate network and the polyphosphazene provides a facile synthetic route to unique hybrid materials for several different applications including solid polymer electrolytes.
Figure 5-1: Structures of poly(ethylene oxide) (PEO) and poly[bis(2-(2-methoxyethoxyethoxy)phosphazene)] (MEEP)
5.2 Experimental

5.2.1 Materials

3,4-Dihydro-2H-pyran, pyridinium \( p \)-toluenesulfonate (PPTS), 3-isocyanato propytriethoxysilane, di-\( n \)-butyltin dilaurate (DBTDL), Sodium hydride (60 % suspension in mineral oil) was obtained from Fluka and was used as received. Diethylene glycol and di(ethylene glycol) monomethyl ether were vacuum distilled over CaH\(_2\) before use. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (3M Corp.) was used as received. Hexachlorocyclotriphosphazene (Ethyl Corp./Nippon Fine Chemical Co.) was recrystallized from heptane and sublimed at 40 °C (0.05 mmHg). Poly(dichlorophosphazene) was prepared via the thermal ring-opening polymerization of hexachlorocyclotriphosphazene at 250 °C in a sealed evacuated tube. 2-(2-Tetrahydropyranoxyethoxy)ethanol was synthesized following the procedure reported by Allcock and Kim.\(^{14}\) All reactions were carried out under an inert atmosphere of dry argon.

5.2.2 Equipment

High-field \(^1\)H (360 MHz), \(^{13}\)C (90.56 MHz), and \(^{31}\)P (90.27 MHz) NMR spectra were recorded using a Bruker AMX-360 NMR spectrometer. \(^1\)H and \(^{13}\)C NMR spectra were referenced to external tetramethylsilane, while \(^{31}\)P NMR spectra were referenced to external 85% phosphoric acid. \(^{13}\)C and \(^{31}\)P NMR spectra were proton decoupled. 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 (Alfa Aesar) in THF (OmniSolv). Thermal transitions were determined through analysis via a TA Q10 differential scanning calorimeter. Calibration was accomplished with indium, water, and cyclohexane standards. All analyses were performed over a range of -140 °C to 100 °C at a heating rate of 20 and 40 °C/min. Ionic conductivity measurements were obtained using a Hewlett Packard 4192A LF Impedance Analyzer at a potential of 0.1 V with an alternating current frequency range of 5 Hz to 1 MHz. The samples were placed between platinum electrodes with a Teflon o-ring spacer. The electrolyte cell was compressed between aluminum blocks held in a Teflon fixture. Electrical leads were attached between the impedance analyzer and the electrolyte cell sample holder. Multiple measurements were made to ensure the accuracy and precision of the ionic conductivity values. All ionic conductivities measurements were carried out over a temperature range of 20 °C to 80 °C (5 °C increments) under an inert atmosphere of argon.
Figure 5-2: Synthesis of the covalently interconnected polyphosphazene-silicate hybrid networks
5.2.3 Synthesis of polyphosphazene-silicate hybrid networks

The synthesis of covalently interconnected polyphosphazene-silicate hybrid network membranes is shown in Figure 5-2 and was carried out according to literature. Structural confirmation of polymers 1-3 was carried out with $^1$H, $^{13}$C, $^{31}$P NMR and the observed chemical shifts were similar to previously published values.

For polymer 1: 2-(2-methoxyethoxy)ethanol was added dropwise to a suspension of sodium hydride in dry tetrahydrofuran (THF). This sodium salt solution was then added dropwise to a solution of poly(dichlorophosphazene) in dry THF and let to stir overnight at room temperature. In a separate reaction vessel 2-(2-tetrahydropyranloxyethoxy)ethanol was added to a suspension of sodium hydride in dry THF. This sodium salt was then added to the polymer reaction solution and let to stir for 48 h at room temperature. Full substitution of the polymer was confirmed by $^{31}$P NMR. The polymer was purified via dialysis (12-14K MWCO) against water and methanol to remove unreacted reagents and oligomeric products. The polymer solution was precipitated in to diethyl ether.

For polymer 2: A solution of pyidinium $p$-toluenesulfonate (PPTS) to a solution of polymer 1 in absolute ethanol and allowed to stir for 5 h at 60 ºC. Once cooled to room temperature, the polymer was purified via dialysis (12-14K MWCO) against water and methanol. The polymer solution was then precipitated in hexanes.

For polymers 3 and 4: Polymer 2 was treated with 3-isocyanatopropyltriethoxysilane in THF with a catalytic amount of di-$n$-butyltin dilaurate
(DBTDL) at room temperature for 5 h and at 60 °C for 5 h to yield polymer 3. Hydrochloric acid (0.15 N, 3 mL) and specific amounts of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were added to the precursor polymer 3 solution, and the mixture was stirred at 50 °C for 2 h. The solution was poured onto a flat Teflon® mold to obtain a gel film. Hydrolytic gelation was carried out at room temperature for 2 days. The gel was dried further at 60 °C for 4 days and at 40 °C under vacuum for 3 days to yield polymer 4.

5.3 Results and discussion

5.3.1 Network synthesis

As shown in Figure 5-2, the precursor polymer 3 was prepared from poly(dichlorophosphazene) using a nucleophilic substitution reaction with the sodium salt of 2-(2-methoxyethoxy)ethanol and 2-(2-tetrahydropyranyloxyethoxy)ethanol. The substituent ratio of crosslinkable units (tetrahydropyranyloxy-protected) and hydrophilic diethyleneoxy units were varied from 10:90 to 30:70 in order to obtain different degrees of increased dimensional stability. Deprotection of the tetrahydropyranyloxy group with PPTS from polymer 1 produced hydroxyl-functionalized polymer 2. For the synthesis of precursor polymer 3, fully dried polymer 2 was allowed to react with 3-isocyanatopropyltriethoxysilane in the presence of DBTDL. Hydrolytic gelation was carried out with a calculated amount of LiTFSI and an acid catalyst to yield polymer 4.

LiTFSI was used as an added salt to examine the polyphosphazene-silicate networks for possible applications in electrochemical devices. Polymer 4 (10:90) was not
utilized in the fabrication of SPEs because it did not possess the desired level of dimensional stability.

5.3.2 Thermal analysis

In Figure 5-3, the glass transition temperature ($T_g$) values of polymer 4 (15:85), 4 (20:80), and 4 (30:70) are shown as a function of LiTFSI concentration. Differential scanning calorimetry analysis, which measured enthalpy changes as a function of temperature, showed that the SPEs have no crystalline melting temperatures but have linearly increasing $T_g$ values with increased salt concentration. The $T_g$ values ranged from approximately -67 °C at 10 mol % LiTFSI to approximately -38 °C at 50 mol % LiTFSI. The increase in $T_g$ values is presumably caused by the decrease in macromolecular motion resultant from an increased number of transient crosslinks between lithium cations and etheric oxygens on neighboring MEEP side chains as the LiTFSI concentration is increased. The $T_g$ values also increased from polymer 4 (15:85) to 4 (30:70) at a given salt concentration. This is due to the progressively greater crosslink density in the hybrid networks, which increased the rigidity of the polymer backbone and restricted segmental motion.
Figure 5-3: $T_g$ values for film 4 (15:85), 4 (20:80) and 4 (30:70) as a function of mol % LiN(SO$_2$CF$_3$)$_2$. 
5.3.3 Ionic conductivity analysis

Figure 5-4 shows the ionic conductivity values for polymer 4 (15:85) at various LiTFSI concentrations as a function of temperature. A maximum ambient temperature ionic conductivity of $7.69 \times 10^{-5}$ S/cm was measured at 20 mol % LiTFSI (15 wt. %). The corresponding MEEP/TEOS composite synthesized by Kim et al. had a maximum ambient temperature ionic conductivity of $4.6 \times 10^{-5}$ S/cm at 10 wt. % TEOS and 15 wt. % lithium triflate. In addition, a comparable γ-ray radiation crosslinked MEEP polymer showed a maximum ambient temperature ionic conductivity of $2.05 \times 10^{-5}$ S/cm with 25 wt. % lithium triflate. At 10 mol % (8.0 wt. %) LiTFSI the decreased ambient temperature ionic conductivity of polymer 4 (15:85) is caused by the lower concentration of mobile lithium cations. At salt concentrations higher than 20 mol % LiTFSI, the ionic conductivity values decreased as the $T_g$ values increased, which results from the decreased macromolecular motion of the hybrid network. However, at higher temperatures (> 60 °C) more thermal motion is present, and this increased the number of mobile lithium cations by lowering the stability of the transient crosslinks. This allowed increased lithium cation transport and resulted in higher conductivity values for those networks with higher LiTFSI concentrations.

A similar trend was evident for polymer 4 (20:80) as shown in Figure 5-5. A maximum ambient temperature ionic conductivity of $6.72 \times 10^{-5}$ S/cm was measured at 20 mol % LiTFSI (15 wt. %). In the case of polymer 4 (30:70), the SPEs were brittle due to the large amount of silicon oxide units and the high crosslink density. Therefore, ionic conductivity measurements could not be obtained.
Figure 5-4: Log $\sigma$ as a function of temperature for film 4 (15:85).
Figure 5-5: Log $\sigma$ as a function of temperature for film 4 (20:80).
5.4 Conclusions

A modified silicate sol-gel precursor of a polyphosphazene and its hybrid network was synthesized. The precursor polymers were prepared by combining a MEEP-type polymer with an organometallic alkoxide (triethoxysilane group), which was incorporated into the polymer main chain by covalent bonding. After hydrolysis and condensation reactions, the system gave a covalently interconnected hybrid material with controlled morphologies and physical properties. Thermal analyses revealed no melting transitions for the networks and low glass transition temperatures that ranged from approximately -38 °C to -67 °C. A maximum ionic conductivity value of $7.69 \times 10^{-5}$ S/cm was achieved with LiTFSI as a salt, which makes these materials interesting candidates for dimensionally stable solid polymer electrolytes.
5.5 References


Chapter 6

A phosphate additive for poly(ethylene oxide)-based gel polymer electrolytes

6.1 Introduction

The development of high power and high energy density batteries with good performance, safety, and reliability has been an active area of research for the past three decades.\textsuperscript{1-3} Advances in electronics, especially portable electronics (i.e. mobile phones, portable computers, etc.), have created a demand for smaller, lighter, yet more powerful energy sources. Since Wright’s discovery of poly(ethylene oxide)-metal salt complexes\textsuperscript{1}, and Armand’s subsequent suggestion\textsuperscript{2} that solid polymer electrolytes may be useful in lightweight and powerful solid state batteries, numerous reports on their development have been published.\textsuperscript{4-8} In particular, lithium batteries have received the most attention, due to the low density and high redox potential of lithium. Several excellent reviews of the literature exist.\textsuperscript{3,9,10}

Numerous different materials have been examined as the basic components of a lithium battery: anode, electrolyte (metal salt in solid or liquid matrix), and cathode. Many safe and efficient materials have been developed for use as anodes, as well as numerous reversible intercalation cathodes.\textsuperscript{11-13} Moreover, a significant amount of
research has been focused on the development of materials for the electrolyte layer which transports lithium ions between the anode and the cathode.\textsuperscript{9,10} Polar aprotic liquid electrolytes provide good media for the transport of lithium ions.\textsuperscript{10} However, organic liquid electrolytes require bulky and sometimes heavy enclosures.\textsuperscript{14} Thus, attempts have been made to develop solid polymer electrolytes that allow the use of complex shapes, greater ease of fabrication, reduced weight for containment, lower flammability, and a lower toxicity of the battery components.\textsuperscript{14} So far no solid polymer electrolyte is known that efficiently transports lithium ions at commercially viable levels (conductivities $\sim 10^{-3}$ S/cm at 25°C).

A promising route to circumvent this problem has been to add liquids to polymers to form gel polymer electrolytes (GPEs).\textsuperscript{14} This route has produced many free-standing gel materials, with high conductivities. Examples of these systems include poly(ethylene oxide), poly(methyl methacrylate), poly(acrylonitrile), and poly(vinylidene fluoride) plasticized with organic solvents.\textsuperscript{14-16} The main disadvantage in the use of organic solvent additives is their volatility and flammability. Although many liquid electrolytes and additives are known, the greatest attention has been focused on liquid carbonates.\textsuperscript{15-17} Concern over the flammability and volatility of these compounds prompted us to prepare a new, non-volatile, fire retardant, and conductive phosphate additive initially for use in the gel polymer electrolyte layer of polyphosphazene-based lithium batteries.\textsuperscript{18,19} Recently other groups have published work detailing efforts on the development of non-flammable liquid electrolytes\textsuperscript{20,21} and polymer electrolyte additives.\textsuperscript{22}

In our earlier work we identified a new gel polymer electrolyte additive and demonstrated its utility when used in conjunction with polyphosphazene-based polymer
This compound, tris(2-(2-methoxyethoxy)ethyl)phosphate, 1, was shown to be essentially non-volatile and significantly less flammable than propylene carbonate, 2. At low additive concentrations, the phosphate-based gels were amorphous and had higher conductivities than propylene carbonate-based gels. However, at higher loadings of the additives, the phosphate GPEs generated multiple phases, and the conductivities were slightly lower than that of the propylene carbonate-based polyphosphazene gels.

In this study a comparison was made of propylene carbonate and the phosphate as additives in a more widely studied polymer, poly(ethylene oxide) (PEO) (3). Two sets of GPEs were prepared using PEO and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) (4), with 1 (5(a-e)) and 2 (6(a-e)) as the liquid additives (Figure 6-1). The GPEs were subsequently analyzed via differential scanning calorimetry, complex impedance and limiting oxygen index analysis. This work described here demonstrates that tris(2-(2-methoxyethoxy)ethyl)phosphate may be a promising replacement for organic carbonates in the more widely used PEO-based gel polymer electrolyte systems.

6.2 Experimental

6.2.1 Materials

Phosphorous oxychloride (99%), propylene carbonate (99.7%), tri(ethyl)phosphate (99%), and bis(2-methoxyethyl) ether (99%) were used as received from Aldrich Chemical Company. 2-(2-Methoxyethoxy)ethanol (99%) was obtained from Aldrich and distilled from calcium hydride before use. Triethylamine (99.5%) was
obtained from Aldrich and distilled from sodium benzophenone ketyl prior to use. Poly(ethylene oxide) (PEO) (M_w = 1,000,000) was obtained from Aldrich and was dried for 2 days at 45°C under 0.2 mm Hg before use. Tetrahydrofuran (THF) was obtained from EM Science and was distilled from sodium benzophenone ketyl before use. Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) was donated by the 3M Corporation (HQ-115) and was used as received.
Figure 6-1: Components used in GPE fabrication - tris(2-(2-methoxyethoxy)ethyl)phosphate (1), propylene carbonate (2), poly(ethylene oxide) (PEO) (3), and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) (4).
6.2.2 Equipment

Complex impedance analysis was performed in a constant flow argon glovebox. The gel polymer electrolyte was placed between two platinum electrodes supported by a Teflon® spacer. The platinum electrode-gel polymer electrolyte sandwich was held in place in a Teflon® fixture by aluminum blocks. Leads were connected from the aluminum blocks to a Hewlett-Packard 4192A LF impedance analyzer, controlled by a PC, and tested with an AC frequency range of 5 Hz to 1 MHz and amplitude of 0.1 V. Thermal data were obtained through differential scanning calorimetry (DSC) using a Perkin-Elmer-7 thermal analysis system equipped with a PC computer. Calibration of the Perkin-Elmer-7 thermal analysis system was achieved through use of an indium standard. Polymer samples were heated from -100°C to 100°C under an atmosphere of dry nitrogen. 30 Mg samples were sealed in aluminum pans and heated at 10, 20, and 40°C/min. The final $T_g$ was determined through extrapolation to 0°C/min heating rate. The $T_g$ was taken as the inflection point of the endothermic transition. Limited oxygen index testing was performed using a modified procedure$^{23}$ of ASTM D 2863. A 0.20 g gel polymer electrolyte sample was placed in a glass cup, supported by a clamp in the glass column of the apparatus. Standard inert atmosphere Schlenk techniques or an inert atmosphere glove box (M Braun) were employed throughout this work.
6.2.3 Synthesis of tris(2-(2-methoxyethoxy)ethyl)phosphate (1)

Tris(2-(2-methoxyethoxy)ethyl)phosphate (1) was prepared as described previously. A solution of phosphorous oxychloride (15.3 g, 0.1 mol, 1 equiv.) in THF (60 mL) was added dropwise to a solution of 2-(2-methoxyethoxy)ethanol (50.5 g, 0.42 mol, 4.2 equiv.) and triethylamine (45.5 g, 0.45 mol, 4.5 equiv.) in THF (400 mL) at 0ºC and stirred for 48 h. $^{31}$P NMR spectra were used to confirm the completion of the reaction. The reaction mixture was filtered to remove salts and THF was removed via rotary evaporation. Excess 2-(2-methoxyethoxy)ethanol was removed via vacuum distillation to yield a pure product (32.5 g, 80% yield). $^1$H, $^{13}$C, and $^{31}$P NMR chemical shifts are similar to published values. MS = m/z 405 (MH$^+$).

6.2.4 Preparation of gel polymer electrolyte samples

The GPE samples were prepared by the dissolution of PEO (3), LiTFSI (4), and a specific amount of 1 (5(a-e), 7, 8), propylene carbonate (2) (6(a-e)), tri(ethyl)phosphate (TEP) (9), or bis(2-methoxyethyl) ether (DG) (10) in freshly distilled THF, followed by slow evaporation and subsequent vacuum drying (50ºC at 0.1 mm Hg) for two days. The reagent quantities for all GPE samples are shown Table 6-1.
Table 6-1: Component quantities for GPE samples.

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6.3 Results and discussion

6.3.1 Ionic conductivity analysis

The results of the complex impedance analyses of the gels are shown in Figure 6-2 and Figure 6-3 and are summarized in Table 6-2. As in the polyphosphazene-based system studied earlier\footnote{18}, at low concentrations of 1 in PEO(< 7.0 mol %), the phosphate-based gels 5(a-b) were more conductive than their propylene carbonate counterparts, 6(a-b). This is attributed to the multiple coordination sites on the oligoethyleneoxy side units of phosphate 1, which can facilitate the transport of lithium cations. In addition, the long oligoethyleneoxy side units are able inhibit efficient packing and crystallization of the PEO chains.\footnote{14} However, at high concentrations of 2 (7.0 - 14.9 mol %), the propylene carbonate gels 6(c-e) were more conductive than 5(c-e). This is attributed to micro-phase separation in the phosphate-based systems 5(c-e), which limits efficient transport of lithium cations through the amorphous component of the GPEs. Evidence of micro-phase separation was found from the thermal transition analysis of 5(c-e), which is explained in the next section. The conductivity plots were also non-linear due to the semi-crystalline nature of PEO-LiTFSI complex at lower temperatures, which impeded lithium cation transport in the GPE.\footnote{4,24} Moreover, a sudden increase in the conductivity around 40ºC, which coincided with the melting transitions detected in the thermal analyses of these samples.

For propylene carbonate-based gels 6(a-e), shown in Figure 6-3, the conductivity values increased and the plots approached a linear fit as larger amounts of propylene
carbonate (2) were added to the GPEs. At lower concentrations of 2 (6(a-b)) a sudden rise in conductivity occurred around 50°C, despite the absence of any melting transitions in these samples. This is attributed to a change in the interactions between the PEO, LiTFSI, and 2. At temperatures below 50°C the predominate interaction occurs between PEO and 2, which resulted in poor solvation of LiTFSI and a resultant lower number of lithium cations available for transport. Above 50°C, 2 is better able to solvate LiTFSI as well as PEO, which resulted in a larger number of lithium cations available for transport and increased conductivity.25 Propylene carbonate systems 6(c-e) contained higher concentrations of 2 and, therefore, provided more efficient solvation of LiTFSI as indicated by the near linear conductivity plots and increased conductivities.
Figure 6-2: Temperature dependent ionic conductivity behavior for 5(a-e).
Figure 6-3: Temperature dependent ionic conductivity behavior for 6(a-e).
Table 6-2: Ionic conductivity values for 5(a-e) and 6(a-e).

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<tr>
<td>6a</td>
<td>0.2</td>
<td>1.9</td>
<td>12.7</td>
<td></td>
</tr>
<tr>
<td>6b</td>
<td>0.5</td>
<td>3.5</td>
<td>15.6</td>
<td></td>
</tr>
<tr>
<td>6c</td>
<td>1.5</td>
<td>7.6</td>
<td>26.8</td>
<td></td>
</tr>
<tr>
<td>6d</td>
<td>3.4</td>
<td>13.2</td>
<td>42.4</td>
<td></td>
</tr>
<tr>
<td>6e</td>
<td>7.3</td>
<td>24.2</td>
<td>63.2</td>
<td></td>
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6.3.2 Thermal transition analysis

Differential scanning calorimetry (DSC) results of phosphate systems 5(a-e) and propylene carbonate systems 6(a-e) are summarized in Table 6-3. The glass transition temperature ($T_g$) values of the PEO-LiTFSI complex (no additive present) (7), is relatively low (-45°C), which is attributed to the plasticization effect of the large TFSI anion. The $T_g$ values of 5(a-e) (-50 to -75°C) and 6(a-e) (-45 to -75°C) decreased with increased amounts of 1 or 2, which indicated that both additives serve to plasticize the PEO-LiTFSI complex. Moreover, no other thermal transitions were detected in 6(a-e), which is indicative of their homogenous and amorphous character. The appearance of melting transition ($T_m$) values in 5(c-e) indicated the existence of microcrystalline domains within the GPE matrix at concentrations above 4.9 mol % of phosphate 1. It is proposed that as the concentration of 1 increased, the interactions between the phosphate moiety and LiTFSI became more prevalent and generated agglomerates of 1 cross-linked by lithium cations. This facilitated the formation of amorphous plasticized PEO-LiTFSI domains rich in 1. This is indicated by the progressive decrease in the $T_g$ values of 5(a-e) as the phosphate content is increased. Concurrently, microcrystalline PEO-LiTFSI domains deficient in phosphate were formed, as indicted by the appearance of a $T_m$ and its progressive increase toward that of pure PEO-LiTFSI (50°C), 7, as more additive was introduced into the GPE. This behavior is similar to a previously reported phenomena observed in GPEs that contain poly(bis(2,3-bis(2-methoxyethoxy)propoxy)phosphazene, LiTFSI, and phosphate 1.\textsuperscript{18}
Additional DSC experiments were performed to ascertain if the PEO-LiTFSI microcrystalline domains in 5(c-e) could be eliminated by annealing before evaluation. The results are summarized in Table 6-3 (8-10). GPEs 8-10 were prepared with identical molar proportions of PEO, LiTFSI, and additive to those used in the fabrication of 5d. The annealing experiments first involved conducting a typical DSC experiment as a control and then heating the GPE samples to 100°C for 10 min. before quench-cooling to -100°C. Once cooled, a typical DSC experiment was again performed. GPE 8, which utilized phosphate 1 as the additive, showed a $T_m$ at 42°C. After annealing, the $T_m$ remained similar at 38°C with no reduction in intensity. A $T_g$ at -66°C was detected for both experiments. GPE 9 was prepared with tri(ethyl)phosphate (TEP) as a control to ascertain if the methoxyethoxyethoxy side units of 1 (which should be compatible with PEO) influenced its ability to disrupt the PEO-LiTFSI microcrystalline domains. DSC experiments before and after annealing revealed identical intensity $T_m$ values at 42°C and $T_g$ values at -28°C for the two systems. These results suggest that both 1 and TEP are incompatible with PEO at the concentration utilized and did not disrupt the microcrystalline domains in the PEO-LiTFSI complex. GPE 10 was prepared using bis(2-methoxyethyl) ether (DG) as the additive. This compound should mimic the side units present in 1, but without the phosphate component. This experiment revealed only a $T_g$ at -45°C, which indicated homogeneity within the GPE matrix. Here, the linear DG structure was able to disrupt the microcrystalline domains of the PEO-LiTFSI complex. Thus, this evidence further supports the view that it is the phosphate moiety in 1 and the pseudo-star structure that plays a central role in the micro-phase separation behavior in 5(c-e).
Table 6-3: Thermal transition values for GPE samples.

<table>
<thead>
<tr>
<th>GPE</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
</tr>
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<tr>
<td>5a</td>
<td>-50</td>
<td>-</td>
</tr>
<tr>
<td>5b</td>
<td>-56</td>
<td>-</td>
</tr>
<tr>
<td>5c</td>
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<td>36</td>
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<td>5d</td>
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<td>5e</td>
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</tr>
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<td>6a</td>
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</tr>
<tr>
<td>8</td>
<td>-66</td>
<td>42 (38)*</td>
</tr>
<tr>
<td>9</td>
<td>-28</td>
<td>42 (42)*</td>
</tr>
<tr>
<td>10</td>
<td>-45</td>
<td>- (-)*</td>
</tr>
</tbody>
</table>

* $T_m$ after annealing
6.3.3 Flammability analysis

The amount of oxygen needed to sustain a flame is termed the limiting oxygen index (LOI). LOI values of 20 or less are associated with materials that are flammable in air. The LOI values for 5(a-e) and 6(a-e) are summarized in Table 6-4. Solvent-free PEO (3), with a LOI of 17.0, burned readily, which reflects its carbon, hydrogen, and oxygen composition. The addition of LiTFSI, to PEO increased the LOI to 18.5, presumably due to the absence of combustible components in LiTFSI. The addition of propylene carbonate (2) progressively lowered the LOI in 6(a-e) which is due to the high flammability of 2. An increase in the LOI of phosphate systems 5(a-e) was detected as the mol % of 1 was increased. However, a significant increase in the LOI is not evident until 7.0 mol % of the phosphate is present, which is, coincidentally, the point at which micro-phase separation begins to occur. Thus, phosphate 1 is useful mainly to enhance the conductivity of PEO at levels below 7.0 mol %, with a maximum room temperature conductivity of $1.1 \times 10^{-4}$ S/cm. By utilizing a mixture of both 1 and 2 as additives it may be possible to balance both the conductivity and the fire retardancy of a gel polymer electrolyte system.
Table 6-4: Limiting oxygen index (LOI) values for 3, 5(a-e), 6(a-e), and 7.

<table>
<thead>
<tr>
<th>GPE</th>
<th>LOI (%)</th>
</tr>
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<tbody>
<tr>
<td>3</td>
<td>17.0</td>
</tr>
<tr>
<td>5a</td>
<td>18.5</td>
</tr>
<tr>
<td>5b</td>
<td>18.5</td>
</tr>
<tr>
<td>5c</td>
<td>20.0</td>
</tr>
<tr>
<td>5d</td>
<td>21.0</td>
</tr>
<tr>
<td>5e</td>
<td>20.5</td>
</tr>
<tr>
<td>6a</td>
<td>18.0</td>
</tr>
<tr>
<td>6b</td>
<td>17.5</td>
</tr>
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<td>6c</td>
<td>17.0</td>
</tr>
<tr>
<td>6d</td>
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<td>6e</td>
<td>16.5</td>
</tr>
<tr>
<td>7</td>
<td>18.5</td>
</tr>
</tbody>
</table>
6.4 Conclusions

We have examined a new additive, tris(2-(2-methoxyethoxy)ethyl)phosphate, in poly(ethylene oxide)-based GPEs and have found that it may be an attractive alternative to the commercially available plasticizer, propylene carbonate in lithium batteries. At low concentrations, GPEs that contained tris(2-(2-methoxyethoxy)ethyl)phosphate showed improved ionic conductivities compared to propylene carbonate-containing GPEs. Despite the micro-phase separation, indicated by the presence of thermal melting transitions at higher concentrations of the tris(2-(2-methoxyethoxy)ethyl)phosphate, the ionic conductivities of the tris(2-(2-methoxyethoxy)ethyl)phosphate GPEs did not increase beyond a certain point as the amount of additive was increased. Limiting oxygen index analyses, demonstrated the fire retardant properties of tris(2-(2-methoxyethoxy)ethyl)phosphate compared to propylene carbonate in GPEs at concentrations above 7.0 mol %.
6.5 References


Appendix A

Preparation of boron-carbide/carbon nanofibers from a poly(norbornenyldecaborane) single-source precursor via electrostatic spinning

A.1 Introduction

Micro- and nanoscale fibers are important materials for structural reinforcements in many applications including microelectronics [for example, see\textsuperscript{1,2}]. The fabrication of such nanostructured materials in well-defined and mono-dispersed forms with controlled length scales has been a major challenge in materials science and engineering. Recently, electrostatic spinning\textsuperscript{3,4} has been shown to be an efficient and facile method to prepare fine fibers, and following the use of pyrolytic techniques have been used to make carbon\textsuperscript{5}, silica\textsuperscript{6}, alumina-borate\textsuperscript{7}, titania\textsuperscript{8,9}, alumina\textsuperscript{10}, niobium oxide\textsuperscript{11}, and some composite fibers such as nickel ferrite\textsuperscript{12}. However, we are unaware of any research dealing with the fabrication of non-oxide ceramics via the electrostatic spinning of polymeric precursors.

One type of non-oxide ceramic, boron carbide, is of great interest for its structural and electronic properties. This refractory material has many advantageous characteristics including its chemical inertness, low density, high thermal stability, hardness, high cross-section for neutron capture, and high temperature thermoelectric properties. These
characteristics favor the use of boron carbide in many applications including abrasive wear-resistant materials, ceramic armor, neutron moderators in nuclear reactors, and potentially for power generation in deep space flight applications.\textsuperscript{13-15}

Boron carbide is normally represented by a $\text{B}_4\text{C}$ ($\text{B}_{12}\text{C}_3$) composition with a structure based on $\text{B}_{11}$ icosahedra and C-B-C intericosahedral chains, but single-phase boron carbide is known with carbon concentrations that range from 8.8 ($\text{B}_{10.5}\text{C}$) to 20 ($\text{B}_4\text{C}$) atom %. This range of concentrations is made possible by the substitution of boron and carbon atoms for one another within both the icosahedra and the three-atom chains.\textsuperscript{13,16}

Nanoscale boron carbide ceramic fibers have previously been generated via plasma-enhanced chemical vapor deposition\textsuperscript{17}, reaction of boron oxide vapor with carbon nanotubes\textsuperscript{18} and by nanoporous alumina templating methods.\textsuperscript{19-21} However, these methods have been limited to small-scale syntheses. Thus, a simple and large-scale preparation method is needed.

Here we report the efficient fabrication of boron-carbide/carbon nanofibers via the electrostatic spinning of a single-source polymeric ceramic precursor, poly(norborenyldecaborane) (PND), followed by pyrolytic ceramic conversion.
Figure A-1: Ruthenium catalyzed ROMP synthesis of poly(norbornenyldecaborane) (PND).
A.2 Experimental

Pyrolysis was performed with a Lindberg Model 54434 1700°C tube furnace under high purity argon. The fibers were placed in a boron nitride boat which was put in the center of a 1 1/8’ alumina tube. The sample was subjected to a cycle of ramping up at 10°C/min to the desired temperature, then dwelled for 1 h and cooled down at 10°C/min. Diffuse reflectance infrared Fourier transform (DRIFT) spectra were obtained with a Mattson Galaxy FT-IR spectrometer. The samples were prepared in a 6 to 1 potassium bromide to ceramic ratio at a resolution of 4 cm⁻¹ for 64 scans. Thermogravimetric analysis (TGA) traces were obtained on a Texas Instruments SDT 2960 Simultaneous DTA-TGA with a ramping rate of 10°C/min to 1200°C and under argon gas with a purge rate of 80 mL/min. The x-ray diffraction (XRD) patterns in Figure 1 were obtained with a Rigaku Geigerflex automated x-ray powder diffractometer using Cu Kα radiation and a graphite monochromator. Scanning electron microscopy (SEM) images in Figures 2 and 3 were obtained with a FEI-Phillips XL-20 scanning electron microscope. The samples were gold coated. A working distance of approximately 10 mm and accelerating voltage of 20.0 kV were used.

A.3 Results and discussion

PND polymers (Figure A-1) were prepared via ring opening metathesis polymerization (ROMP) of 6-norbornenyldecaborane with Grubbs’ first generation...
catalyst $\text{Cl}_2(\text{PCy}_3)_2\text{Ru}(=\text{CHPh})$.\textsuperscript{23} The polymers are air stable white solids readily soluble in organic solvents. Molecular weight analysis yielded number average molecular weights ($M_n$'s) in excess of 30 kDa and polydispersity indices between 1.1 and 1.7.

Thermogravimetric analysis (TGA) of the ceramic conversion of PND with a $M_n$ of 32 kDa indicated that weight loss began near 150°C and was complete by 600°C.\textsuperscript{21} The observed TGA (72%) and bulk ceramic (58% at 1650°C) yields were in the range of the theoretical ceramic yield (65%) predicted by the reaction in Figure A-3. Elemental analysis of the grey/black 1650°C residue (B, 67.9%; C, 32.2%) corresponded to a $\text{B}_4\text{C}\cdot0.74\text{C}$ composition.

Powder x-ray diffraction (XRD) analysis (Figure A-4) of the bulk ceramic residues indicated that up to 1200°C the materials were amorphous. PND samples pyrolyzed at 1300°C and 1650°C showed both boron carbide\textsuperscript{24} and graphite diffraction peaks, indicating that crystallization began between 1200°C and 1300°C. In addition, as indicated by various broad diffraction peaks in the XRD, the 1300°C and 1650°C bulk ceramic residues retained a substantial amorphous component. There was a corresponding increase in density as the pyrolysis temperature was increased from 1000°C (2.0 g/cm$^3$) to 1650°C (2.2 g/cm$^3$) as measured by floatation. Compared to the theoretical density of $\text{B}_4\text{C}$ (2.54 g/cm$^3$)\textsuperscript{13}, the presence of excess carbon in these materials undoubtedly retarded the boron carbide crystallization process. Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy showed the characteristic boron carbide absorptions at 1587 cm$^{-1}$ and 1120 cm$^{-1}$ in all samples\textsuperscript{25}, including the amorphous 1000°C material.
A solution of 32 kDa PND in dry THF was electrostatically spun (potential, 18-20 kV; flow rate, 2.5 mL/h) to give a non-woven mat of fine fibers which were collected on a carbonized Teflon® target at a distance of 15 cm. The electrostatic spinning set-up is shown in Figure A-2. The PND fibers could be readily dissolved in THF and the $^{11}$B NMR spectrum of the resulting solution showed the characteristic PND pattern. The absence of a B(OH)$_3$ resonance in this solution indicated that oxidation did not occur during the electrostatic spinning process.
Figure A-2: Experimental set-up for electrostatic spinning
Figure A-3: Ceramic conversion reaction of PND to boron carbide.
Figure A-4: XRD patterns of the bulk ceramic residues obtained from pyrolyses of PND at different temperatures. (●) boron carbide; (■) graphite.
As illustrated in the scanning electron microscopy (SEM) images (Figure A-5), fibers derived from different concentrations showed different morphologies. Those spun from a 20 wt. % (w/w) PND solution gave round cylindrical fibers with diameters in the microscale domain (Figure A-4a). At a concentration of 10 wt. % (w/w) PND, nanoscale fibers with polymer beads were evident (Figure A-4b). Uniform cylindrical fibers with diameters from 500 to 650 nm were obtained from a 13 wt. % (w/w) PND solution (Figure A-5a). The dependence of fiber diameter and morphology on polymer concentrations agrees with other systems which have been studied both experimentally and theoretically.\textsuperscript{26,27}

Due to the narrow diameter and size distribution, the fibers spun from the 13 wt. % (w/w) PND solution were used for further ceramic conversion studies. The nanofibers mats were pyrolyzed at different temperatures and the obtained ceramic fiber residues were studied by SEM, XRD, and DRIFT spectroscopy. The SEM images of the ceramic fiber residues at different temperatures derived from the spun polymer fibers (Figure A-6) confirmed that the nanoscale fibrous network was retained post-pyrolysis. This retention of the nanostructure is important in the fabrication of ceramic nanofibers. Consistent with the weight loss (>35\%) and large change in density (>1 g/cm\(^3\)) that occurs in the conversion of PND to the ceramic, significant fiber shrinkage occurred as pyrolysis progressed. The apparent fiber diameter at 1000°C ranged from 400 to 600 nm (Figure A-5b). Fiber shrinkage was essentially complete by 1300°C, which was in agreement with the small density change that was observed between the 1300°C and 1650°C bulk ceramic residues. As illustrated in the SEM images (Figure A-5c, A-5d) of the 1300°C
and 1650°C pyrolyzed PND samples, the fiber diameters were similar and varied between 350 to 500 nm.

The same patterns evident in the XRD pattern of the bulk ceramic residues at different temperatures were observed in the pyrolyzed fibers, indicating that the pyrolysis of the nanofibers followed the same process as in the bulk studies. Even though XRD analyses showed significant crystallization of the high temperature ceramic fiber residues, isolated crystals were not observed in SEM images. This indicated that the crystals were in a smaller length scale than the size of the fibers, which helped to retain the fibrous structure at high temperatures. DRIFT spectroscopy showed a change in composition as pyrolysis was performed on the PND fibers. In agreement with the bulk ceramic studies, characteristic boron carbide absorptions at 1593 and 1105 cm\(^{-1}\) were clearly apparent in the PND fibers pyrolyzed at or above 1200°C.

A.4 Conclusions

We have developed methods for the fabrication of nanoscale, freestanding, porous boron-carbide/carbon ceramic fiber matrices through electrostatic spinning and pyrolysis of poly(norbornenyldecaborane). Due to the versatility of electrostatic spinning with various polymer and molecular systems, this approach should be useful with polymer blends to fabricate composite ceramic fibers with various compositions. This would allow the fabrication of ceramics tailored for specific applications.
Figure A-5: SEM images of PND electrostatically spun fibers derived from different concentrations (a) 20 wt. % (w/w) (b) 10 wt. % (w/w).
Figure A-6: a) SEM images of PND fibers obtained from 13 wt. % (w/w) PND/THF solution via electrostatic spinning at a potential of 19 kV onto a carbonized Teflon® collector at 15 cm screen distance with a flow rate of 2.5 mL/h. B-D) SEM images of the PND fibers pyrolyzed in high purity argon with a temperature ramp of 10°C/min to (b) 1000°C, (c) 1300°C, (d) 1650°C followed by a 1 h dwell and cooling to room temperature at 10°C/min. The scale bars are 2 µm in length.
A.5 References


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VITA

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