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NOVEL ION-CONDUCTIVE POLYMERIC MATERIALS FOR
FUEL CELL APPLICATIONS

A Thesis in
Chemistry

by
Richard Martin Wood

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The thesis of Richard Martin Wood was reviewed and approved* by the following:

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

Alan J. Benesi  
Lecturer in Chemistry

Karl T. Mueller  
Associate Professor of Chemistry

Ian R. Harrison  
Emeritus Professor of Polymer Science

Ayusman Sen  
Professor of Chemistry  
Head of the Department of Chemistry

*Signatures are on file in the Graduate School
ABSTRACT

The work described in this thesis deals with the design, synthesis, and characterization of ionically conductive polyphosphazenes for fuel cell applications, specifically as polymer electrolyte membranes. In addition, the thermal decomposition of a monomeric polyphosphazene precursor was examined. Chapter 5 of this thesis describes the control of the water uptake of sulfonimide substituted polyphosphazenes by the introduction of a silicate network. Chapter 6 describes the synthesis and characterization of pendant cyclic polyphosphazenes for use as proton exchange membranes. Chapter 7 describes the synthesis and characterization of anion-conductive polyphosphazenes for use as anionically conductive membranes. Chapter 8 outlines the investigation of the state of water in hydrated proton exchange membranes by use of solid-state NMR techniques. A study of the thermal decomposition of trichloro-\(N\)-trimethylsilylphosphoranimine is described in the appendix.

Chapter 5 details the synthesis and characterization of composite materials composed of a sulfonimide substituted polyphosphazene and silicate networks prepared through the sol-gel technique. Substituted, hydrophobic, non-covalently attached silicate networks were prepared by the in-situ sol-gel condensation of trifluoropropyl trimethoxysilane, and the incorporation of the silicate network ranged from 5 to 20 weight percent. Samples of the composites were also exposed to between 5 and 20 MRad of gamma radiation to crosslink the polyphosphazene, and form inter-penetrating networks. Large decreases in the water uptake were observed in these materials.
Composite materials that incorporated an unsubstituted silicate network were likewise prepared from tetraethyl orthosilicate, and were found to increase the water uptake.

Chapter 6 discusses the synthesis of proton conductive membranes based upon organic polymers with pendant cyclic phosphazenes. A 5-norbornene-2-methoxy substituent was introduced into the cyclic phosphazene, which was then polymerized via ring-opening metathesis polymerization. Hydrogenated polymers were substituted with 3-methylphenoxy groups, which were subsequently sulfonated to yield sulfonic acid functionalized polymers. The proton conductivity and methanol permeability of these materials were assessed. A maximum proton conductivity of $4.81 \times 10^{-4}$ S cm$^{-1}$ was measured, which is relatively low. However the minimum methanol permeability was $1.47 \times 10^{-7}$ g cm$^{-2}$ min$^{-1}$, which is very low, thus making these materials candidates for direct methanol fuel cell membranes.

Chapter 7 describes the synthesis of anion conductive membranes. Polymers substituted with arylphosphonium ions were synthesized, and their water uptakes and ionic conductivities were measured. Although the ionic conductivities of these materials were low, they had low water uptake values, and thus may be useful in fuel cell applications.

Chapter 8 outlines the use of solid state NMR techniques to evaluate the state of water in proton exchange membranes. Samples of a sulfonimide substituted polyphosphazene and the commercial proton exchange membrane Nafion were hydrated with deuterium oxide, and the $^2$H T$_1$ relaxation times were measured. These data indicated that solid, ice-like water is present in small quantities in these materials and, although the polyphosphazene absorbed much more water than Nafion, the amounts of
ice-like water were similar. Consequently, it is concluded that the role of water in these two polymers is similar.

The appendix is a study of the thermal decomposition of trichloro-N-trimethylsilylphosphoranimine. The stability of this phosphoranimine in several solvents at room temperature and at -3 °C was examined through the use of phosphorus NMR, and preliminary experiments indicate that suitable medium term storage conditions are in diethyl ether at -3 °C.
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PREFACE

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"... The purpose of knowledge is to appreciate the wonders even more...
Knowledge is just to put into correct framework the wonder that nature is."

Richard P. Feynman (1918-1988), Nobel Laureate (1965)
Chapter 1
Introduction to polymer chemistry

1.1 Introduction

Polymers are ubiquitous in the modern world, and are found in applications as diverse as household items, sports equipment, automobiles, medical devices, and the aerospace industry. The reasons that polymers have become so widespread are that they are - in general - low cost, light weight, easy to process, and have good physical properties. However, in spite of their prevalence, polymers tend to be poorly understood by those outside of the scientific community.

The question of what a polymer is can be answered by examination of the etymology of the word polymer - it is derived from the Greek *polumeros* from polu-"many" and meros "part". Thus a polymer can be defined as a substance whose molecular structure is formed from many identical small molecules (monomers) that are bonded together. Because a polymer is typically a large molecule, the synonym macromolecule is often used.

1.2 History

Polymers have been used by mankind since antiquity, although they were not known to be polymers until relatively recently. Historically significant polymers were, unsurprisingly, obtained from natural sources, typically plants. Examples of such
polymers include polysaccharides such as cellulose - which is the principal constituent of plant matter - that can be used to make, amongst other things, paper. Other examples of polysaccharides include cotton and flax (used to make linen), which remain important in the textile industry today; and starch, found in a variety of foodstuffs. Another class of natural polymers that was employed in the ancient world is polypeptides (polymers formed from amino acid monomers), examples of which include wool and silk. Proteins are also an example of polypeptides.

Little changed in the way that humans utilized polymers until the 19th century. Perhaps the first example of polymer chemistry was the discovery by Henri Braconnot in 1832 that starch could be nitrated with nitric acid. This led to the development of nitrocellulose by Christian Friedrich Schönbein in 1846, who discovered that cotton could be nitrated with a mixture of nitric and sulfuric acids. The interest in these materials was not purely academic – nitrocellulose is powerful explosive, and is still used today as smokeless gunpowder. Nitrocellulose was also processed into films, and became an early medium for the emerging art of cinema. However, its extreme flammability necessitated an alternative material. In 1856 Alexander Parkes discovered the first celluloid material through the reaction of nitrocellulose with camphor. He named his discovery Parkesine.

Another early example of polymer chemistry was the development of vulcanized rubber. Hancock, and later Goodyear\(^1\), discovered that the properties of latex could be dramatically improved by the addition of sulfur – a reaction that would later be understood as crosslinking.
These early polymers were all derived from naturally occurring polymers. The first example of a truly synthetic polymer was Bakelite – a phenol formaldehyde resin developed by Leo Baekeland\textsuperscript{2,3}. This polymer was a highly crosslinked network, and consequently was a hard, durable material that found use in many applications including, importantly, consumer items such as cookware and telephones.

However, at this time in history, the concept of a polymer was not well understood. High molecular weight compounds were possible to synthesize, but the prevailing theory was that polymers were in fact colloids, and this poor understanding of polymers probably contributed to the relatively slow progress in the field.

Perhaps the greatest development in the field of polymer chemistry came in 1920 when Staudinger\textsuperscript{4} postulated that polymers were in fact long chain molecules that consisted of many covalently linked small molecules. This idea met with resistance at first, and it took over a decade for this idea to gain widespread acceptance, partly due to the paucity of good instrumental methods available at the time. Staudinger used the term \textit{macromolecule} to describe these linear polymers – a term that has become commonplace today. In 1953 he was awarded the Nobel Prize in chemistry.

It was only after Staudinger’s macromolecular hypothesis became accepted that the field of polymer chemistry began to expand, although Staudinger himself reported the synthesis of several polymeric materials including cyclopentadiene rubber\textsuperscript{5}. A pioneer of polymer chemistry was Wallace Carothers. In 1929\textsuperscript{6} he proposed that certain polymers could be synthesized through the reaction of di-functional monomers with the elimination of a small molecule (such as \( \text{H}_2\text{O} \), \( \text{NH}_3 \), or \( \text{HCl} \)). He called these polymers condensation polymers, and distinguished them from other known polymers in which the repeat unit
was identical to the monomer, which he called addition polymers. Soon after, he
described the synthesis of several polyester condensation polymers as well as the
synthesis of a polyamide through the ring-opening of \( \varepsilon \)-aminocaproic acid. Another of
Carothers’ discoveries was Neoprene – the first mass-produced rubber substitute
material.

The polymer that Carothers is most famous for (although it was his DuPont
coworker Gerard Berchet who actually first synthesized it) is Nylon. Formed from the
reaction of hexamethylene diamine and adipic acid, Nylon is a polyamide, and has
excellent film and fiber forming properties. It was, and still is, used as a replacement for
silk parachutes and hemp ropes, and is currently used in numerous applications.

In the time since the discovery of Nylon, many synthetic polymers have been
developed and have become almost essential to modern life, including polyethylene (PE),
polypropylene (PP), polystyrene (PS), poly(tetrafluoroethylene) (PTFE, Teflon),
poly(methyl methacrylate) (PMMA, Plexiglas/Perspex), and poly(dimethyl siloxane)
(silicone) to name just a few. The chemical structures of some common polymers are
shown in Figure 1.

The majority of polymers that have been developed so far are organic, that is to
say that they are chiefly composed of carbon. There is however an important class of
polymers called inorganic polymers, which are composed of inorganic elements.
Examples include silicones (comprised of silicon and oxygen) and phosphazenes
(comprised of phosphorus and nitrogen). These materials often have useful properties
that cannot be achieved with organic polymers. However, only the silicones have
achieved widespread commercial success so far.
Figure 1-1: Chemical structures of some common polymers
1.3 Polymer nomenclature and architecture

Polymers can be considered to have two main features – a backbone and pendant groups. When monomers are reacted to form a polymer, a long sequence of atoms forms. This is the polymer backbone. Pendant groups are bonded to atoms in the backbone, but are not part of the backbone themselves. Along the backbone, the sequence of atoms periodically repeats (a consequence of the fact that identical monomers bond together to give the polymer structure), and this is called the repeat unit. It is convention to name polymers based upon the structure of their respective monomers, not the structure of the repeat unit (Figure 1-2).

There are several polymer structures that are possible (Figure 1-3). The simplest of these is a linear polymer, in which monomers are joined together to form a long chain. Related architectures are the macrocycle, in which the ends of a linear chain are attached to each other, and the cyclolinear polymer, in which a cyclic species is incorporated into the backbone of the polymer.

Branched structures are ones where small segments of polymer are pendant to the polymer backbone. These branched segments may be short or long, and the presence of branching often has a large effect on the physical properties of the polymer. An example of this is the difference in properties between low density polyethylene (LDPE), which is branched and high density polyethylene (HDPE), which is linear. LDPE is a flexible and somewhat rubber-like material and is frequently used in low cost household articles such
as trash bags. HDPE is more rigid, tougher, and is semi-crystalline, and is often used in applications where a tougher polymer is required, such as bleach bottles.

Crosslinking is similar to branching – a pendant group can link two polymer chains together, although the crosslinker is usually deliberately introduced and chemically dissimilar to the polymer. Crosslinking can be used to improve the physical properties of a polymer – latex is crosslinked to make useful rubber materials such as car tires – but also results in insoluble materials.

An extreme case of a branched polymer is a star polymer. This architecture is the result of a highly branched polymer in which the lengths of the branched chains are similar to the length of the backbone of the polymer. A special case of highly branched polymer is the dendrimer. These polymers are unique because they are essentially unimolecular – every molecule of a dendrimer is identical. Synthesis of dendrimers is typically quite complicated, but there is a lot of interest in these polymers because they have some unique properties.
Figure 1-2: Polymer features and nomenclature
Figure 1-3: Examples of polymer architecture
1.4 Polymer synthesis

There are numerous factors that make polymer synthesis a challenge. A primary consideration is the type of chemistry used. The formation of a polymer results in a large decrease in entropy. The Gibbs free energy equation (Eq. 1.1) indicates that if there is a large decrease in entropy, for a spontaneous reaction to occur (ΔG is negative), ΔH must be very negative. This means that most polymerization reactions must be highly exothermic, and therefore the chemistry of polymerization must be carefully selected.

\[ ΔG = ΔH - TΔS \]  \hspace{1cm} 1.1

A further consideration is that the reactivity of the end of a polymer chain must be the same as, or very similar to the monomer. Also, as polymerization reactions proceed, the viscosity of the polymer or polymer solution increases, and this also affects the rate of reaction. Another factor is that the purity of the monomers typically has to be very high. However, in spite of these complications, there are thousands of monomers that have been successfully polymerized, and there are several different chemistries that have been employed.

Polymer synthesis can be broadly divided into two types of polymerization: step-growth polymerization, and chain-growth polymerization:
1.4.1 Step-growth polymerization

Step growth polymerizations involve the step-by-step growth of polymer chains (Figure 1-4). Monomers can react to form dimers, dimers may react with more monomer to form trimers or may react with themselves to form tetramers and so on until polymer is formed. Some of the features of step-growth polymerizations are that high molecular weight polymers are not formed until the reactions are almost complete, and that the molecular weight distributions are typically quite broad.

Condensation polymers are formed through step-growth polymerization (indeed the two terms are often used synonymously), common examples of which are polyesters and polyamides, in which a di-functional monomer is used (Figure 1-5). The molecular weight of these types of polymers can be controlled through the introduction of monofunctional reagents, which serve to end-cap a polymer chain and thus prevent further reactions. A corollary of this is that the monomers used must be extremely pure in order to obtain high molecular weight polymers. Furthermore, an exact 1:1 stoichiometry of monomers must be used to obtain high molecular weight polymers. It is also possible to crosslink these polymers via the introduction of a trifunctional monomer.
Figure 1-4: Step growth polymerization
Figure 1-5: Chemistry of step-growth polymerization
1.4.2 Chain-growth polymerization

Chain growth polymerizations involve first the initiation of a monomer, followed by addition of monomers to the activated species. Monomers only ever add to the active end of a polymer chain. In contrast to step-growth polymerizations, molecules of various molecular weights do not combine to generate high molecular weight polymers. Instead, individual polymer chains are grown, and the molecular weight increases by addition of monomer to the end of these polymeric species (Figure 1-6). A consequence of this is that chain-growth polymerizations do not need to proceed to a high percentage of conversion in order to obtain high molecular weight material.

There are several different types of chain growth polymerization (Figure 1-7), each of which has particular features. Radical polymerization involves the initiation of a monomer using a radical species. Monomers add to the active chain end and the radical species is regenerated. Radicals are very reactive, and there are several ways in which radical polymerizations can terminate, such as reaction with another radical chain end, reaction with the middle of a chain, and so on. Consequently, molecular weight distributions tend to be broad for radical polymerizations.
Figure 1-6: Chain-growth polymerization
In ionic polymerizations, monomers are initiated with the addition of a reactive species that generates either a cation or an anion. Monomers then add to the active chain end and regenerate the ionic species. Ionic polymerizations are more controllable than radical polymerizations because there are far fewer ways that an ionic polymerization can terminate. Indeed, in the absence of a deliberately added terminator, the active chain end often may persist indefinitely, a situation that is known as a living polymerization. An advantage of ionic polymerizations is that molecular weight distributions are often narrow.

Ring-opening polymerization involves the use of a cyclic monomer. This monomer may be ring-opened either chemically or thermally to generate a linear species with an active chain end. This active chain end may then reactive with another cyclic monomer, which ring opens and adds to the active chain end. One of the advantages of ring-opening polymerization is that there is a smaller decrease in entropy upon polymerization of the monomer (the entropy first increases upon ring-opening). The result of this is that these polymerizations do not have to be as exothermic as other types of polymerizations, and there are even some examples of ring opening polymerizations that are endothermic.
Figure 1-7: Examples of chain-growth polymerization

radical polymerization of vinyl chloride

anionic polymerization of methyl methacrylate

ring-opening polymerization of ethylene oxide
The molecular weight of chain-growth polymerizations can be controlled by a number of means. The molecular weight depends upon the monomer:initiator ratio – if a greater amount of initiator is used, more polymer chains are grown and therefore (for a fixed amount of monomer) the molecular weight of each chain will be lower. A similar effect can be achieved by the use of a chain transfer agent, which terminates one growing polymer chain but can act as an initiator from which another polymer chain can be grown.

1.4.3 Copolymerization

Polymerizations do not necessarily have to involve only one monomer. Two or more monomers may polymerize to form a copolymer. Some common examples of copolymers include poly(styrene-butadiene), which is an elastomer, and poly(acrylonitrile-butadiene-styrene), which is a tough thermoplastic. DNA can also be considered to be a copolymer.

There are several different kinds of copolymers that can exist (Figure 1-8). Random copolymers are ones in which the sequence of monomers along the backbone is random. Alternating polymers are similar to random copolymers except that the monomers form a consistent pattern along the length of the polymer backbone. A block copolymer consists of segments of individual polymers that are covalently linked together. A graft (sometimes called a comb) copolymer is a type of branched polymer in which the branches are composed of a different monomer.
Figure 1-8: Copolymer architectures

- Homopolymer
- Random copolymer
- Alternating copolymer
- Block copolymer
- Graft copolymer
The properties of copolymers can be different from the properties of homopolymers made from the constituent monomers. Random and alternating copolymers often have properties that are intermediate between the two individual homopolymers. The individual blocks in block copolymers and the grafts in graft copolymers often retain the properties of the individual homopolymers. A simple example of this is the solution behavior of block copolymers – a block copolymer composed of a block of water soluble polymer and a block of a water insoluble polymer will, if placed in water, tend to form a micelle with the water insoluble polymer on the interior of the micelle.

1.5 Molecular weight

In all but the rarest of cases, the individual chains of a polymer are of different lengths and therefore of different molecular weights, and there is a distribution of these molecular weights. The molecular weight of a polymer has an effect on a number of its properties, particularly its mechanical and thermal properties.

There are a number of ways to define and measure the molecular weight of a polymer. Perhaps the simplest measure is the number average molecular weight, $M_n$. The number average molecular weight is defined in Eq. 1.2, where $n$ is the number of polymer chains of a given molecular weight, and $M$ is the molecular weight of a particular polymer chain (which is calculated as the product of the number of repeat units in a polymer chain and the molecular weight of each repeat unit).

$$M_n = \frac{\sum nM}{\sum n} \quad 1.2$$
The weight average molecular weight $M_w$ is similarly defined in Eq. 1.3.

$$M_w = \frac{\sum nM^2}{\sum nM} \tag{1.3}$$

The difference between the molecular weight averages is that $M_n$ is an average by the number of polymer chains, and $M_w$ is an average by the weight of the chains. These two averages are often used in different circumstances because certain polymer properties are dependant upon $M_n$, and others are dependant upon $M_w$.

A measure of the breadth of the distribution of molecular weights, called the polydispersity index, can be obtained by use of Eq. 1.4.

$$PDI = \frac{M_w}{M_n} \tag{1.4}$$

Most polymerizations give rise to a distribution of molecular weights. If the PDI is equal to 1, then every polymer chain is exactly the same molecular weight. This is extremely rare, although this can be achieved with dendrimers. A higher PDI indicates a broader distribution of the molecular weights.

### 1.6 Polymer morphology

Due to the molecular size and weight of polymers, they have some unique properties. Polymers can be rigid and semi-crystalline, rigid and amorphous (glassy), and soft and elastic (rubbery).

The extent to which a polymer is crystalline depends upon its structure, and in general it must be linear with a regular structure to be able to crystallize. Crystalline
polymers are actually best described as semi-crystalline – they possess small regions called crystallites, which are lamellar structures, within an amorphous matrix. Like normal crystalline materials, they possess a crystalline melting temperature, $T_m$, above which the polymer becomes liquid-like.

Glassy polymers are amorphous materials (they have no long range order) in which the polymer chains are essentially frozen in place. Consequently these materials tend to be brittle, and are often optically transparent. Like the crystalline materials, there is a temperature above which the material is no longer glassy. This is called the glass transition temperature, $T_g$. Polymers above their $T_g$ are rubbery, and can flow. Polymers below their $T_g$ are glassy.

The $T_g$ of a polymer is often an important consideration because several properties depend upon the $T_g$ of a polymer. For example, polymers at a temperature below their $T_g$ have higher tensile strengths than polymers at temperatures above their $T_g$. Also, phenomena like ion-transport occur much more readily when the polymer is in a more liquid-like state (above the $T_g$). Consequently, the $T_g$ often defines the useful temperature range of a polymer.

There is a close relationship between the flexibility of a polymer and its $T_g$. Two main factors influence how flexible a polymer is – steric hindrance and the barrier to bond torsion. Polymers that have a low barrier to torsion of the backbone bonds typically have low $T_g$s. Polymers that have large, rigid side groups tend to have high $T_g$s. The $T_g$ is also influenced by the molecular weight of the polymer – the higher the molecular weight, the higher the $T_g$ is, although there is an asymptotic relationship\textsuperscript{13}. 
1.7 Summary

Polymers are materials that consist of many small molecules (monomers) that are covalently attached to form large, high molecular weight molecules. These macromolecules can exist in a number of architectures, and can be synthesized in a variety of ways. Because of their large size and weight, polymers often have some unique properties.
1.8 References

Chapter 2

Introduction to polyphosphazenes

2.1 Introduction

Polyphosphazenes are a class of inorganic polymers that possess a backbone of alternating nitrogen and phosphorus atoms. To each phosphorus atom is bonded two functional groups, which may be organic, inorganic, or organometallic. There is a huge range of groups that may be attached to the polymer backbone, and careful choice of these groups leads to a wide variety of possible polymer structures, with a wide variety of properties. Indeed, one of the assets of the phosphazene platform is the unique ease with which the properties of the polymers can be controlled through judicious choice of the pendant groups.

Polyphosphazenes have many advantages over organic polymers, including high thermal and chemical stability and good solubilities in organic solvents. Polyphosphazenes frequently have low glass transition temperatures (T_g's) due to the high flexibility of the polymer backbone, and this is advantageous for a number of applications.

2.2 History

Phosphazenes have been known since the early 1830s, when Rose¹ and Liebig and Wohler² isolated phosphonitrilic chloride trimer (2.1) (also known as
hexachlorocyclotriphosphazene) from the reaction of phosphorus pentachloride and ammonia. The structure of this compound was not confirmed until some 30 years later by Gladstone and coworkers\(^3\) who – after it had been demonstrated by Gerhardt\(^4\) that the empirical formula of the compound was NPCl\(_2\) – showed via accurate vapor density measurements that the molecular formula was N\(_3\)P\(_3\)Cl\(_6\), or (NPCl\(_2\))\(_3\). An improved synthesis of phosphonitrilic chloride trimer was later developed by Schenck and Romer, which involved the use of tetrachloroethane as a solvent\(^5\).

It was discovered by Stokes in 1897 that upon heating \(2.1\) to between 250 \(^\circ\)C and 350 \(^\circ\)C, a rubber-like material was formed\(^6\). Stokes called this material polyphosphonitrilic chloride (a prophetic name given that the macromolecular nature of polymers was not accepted until the 1920s) and observed that it was of very high molecular weight, highly elastic, and insoluble, although it was observed to swell to a large extent in benzene. Stokes also observed that this material was more susceptible to hydrolysis than the low molecular weight phosphonitrilic chlorides.

Prior to the 1960s, there was relatively little interest in “polyphosphonitrilic chloride” due to its insolubility and hydrolytic instability, although there were some academic studies of the material. In one study it was shown that the polymer under tension yielded an X-ray fiber diffraction pattern with a fiber period of 5.17 Å and was also shown to have almost identical stress-strain behavior as natural rubber\(^7\). There were also a number of studies of the polymerization of phosphonitrilic chloride trimer and depolymerization of the subsequent polymer\(^8-13\). It was also shown by Manley\(^14\) that irradiation of phosphonitrilic chloride trimer with large doses of gamma radiation did not
initiate polymerization, and thus it was concluded that polymerization did not occur through a free radical mechanism.

In the same period there were, by contrast, several reports on the subject of the cyclic trimer and tetramer species\textsuperscript{15} including spectroscopic studies\textsuperscript{16,17}, crystal structure determination\textsuperscript{18-20}, NMR studies\textsuperscript{21-25}, and various reactions\textsuperscript{26-32}. It was also during this period of time that these materials started to become referred to as phosphazenes.

The first report of soluble poly(dichlorophosphazene) (2.2) (Figure 2-1) came in 1959, and was the subject of several patents\textsuperscript{33-35}. The reported polymers, although rubber-like, were of low molecular weight, and were likely hydrolyzed due to the fact that water was used in the synthesis.

A breakthrough came in 1965 when Alcock and Kugel synthesized the first soluble high molecular weight polyphosphazenes\textsuperscript{36}. It was discovered that a crosslinked material could be avoided if the polymerization reaction was terminated before 70\% of the trimer had been consumed. A further discovery was that hydrolytically stable materials could be prepared by substitution of the reactive phosphorus-chlorine bonds with stable trifluoroethoxy and phenoxy groups. These two discoveries spawned the field of polyphosphazene chemistry – a field that has, to date, generated over 700 different polyphosphazenes\textsuperscript{37}. 
Figure 2.1: Structures of phosphonitrilic chloride trimer (hexachlorocyclotriphosphazene) (2.1) and poly(dichlorophosphazene) (2.2).
2.3 Chemistry of phosphazenes

Polyphosphazenes are unusual inasmuch as they are synthesized through macromolecular substitution, in which a reactive high molecular weight species – poly(dichlorophosphazene) – is formed first, and reactions are then performed on this polymer to yield useful polymeric materials. This is in contrast to the more usual approach, which is to prepare a functional monomer that is then polymerized to give the desired polymer. One of the advantages of the macromolecular substitution route is that complicated monomer chemistry is not required. However, because poly(dichlorophosphazene) is very sensitive towards hydrolysis, it must be manipulated under inert atmosphere conditions, and long-term storage can be problematic.

2.3.1 Synthesis of poly(dichlorophosphazene)

The main synthetic route to poly(dichlorophosphazene), whether soluble or crosslinked and insoluble, is the thermal ring opening polymerization of 2.1. The mechanism of this reaction was elucidated by Allcock and Best\(^3^8\), who measured the conductance and capacitance of molten samples of 2.1 and showed that there was an increase in conductivity and capacitance above 250 °C - the temperature at which Stokes observed that polymerization occurs. Radical species were not detected, therefore it was postulated that the polymerization was ionic in nature, with the ionization of a phosphorus-chlorine bond in 2.1 as the initiation step of polymerization (Figure 2-2).
Figure 2-2: Polymerization of hexachlorocyclotriphosphazene to poly(dichlorophosphazene)
Poly(dichlorophosphazene) synthesized via thermal ring opening polymerization typically has a high molecular weight, with number average molecular weights of up to $10^6$ Da obtainable. However, polymers prepared by this route often have broad molecular weight distributions (PDI $> 2$), and there is a limited ability to control either the molecular weight or the PDI of these polymers. However, the molecular weight can be controlled via the addition of a strong Lewis acid catalyst to molten $2.1^{39-42}$. Methods to prepare poly(dichlorophosphazene) via a catalyzed solution polymerization of $2.1$ have also been investigated$^{43-46}$.

Alternative synthetic pathways to poly(dichlorophosphazene) have also been investigated. The thermal condensation of phosphoryl compounds yields $2.2$, but low molecular weights are realized, and this route affords little control over molecular weight$^{47-51}$. Another route utilizes the thermal condensation of phosphoranimines$^{52-57}$. Although isolation of these phosphoranimine monomers is a challenge, it is one of the few routes available that results in polyphosphazenes with direct phosphorus-carbon bonds.

A significant advancement in polyphosphazene chemistry came with the development of a living cationic polymerization route to $2.2$ by Manners, Allcock, and coworkers$^{58,59}$. Poly(dichlorophosphazene) can be synthesized in solution by the cationic initiation of trichloro-$N$-trimethylsilylphosphoranimine ($2.3$) with PCl$_5$ (Figure $2-3$). This chemistry produces linear, living polyphosphazenes with narrow polydispersities and excellent control of the molecular weight through careful control of the initiator:monomer ratio. Moreover, through this chemistry it is possible to synthesize
polyphosphazenes with alternative architectures, such as block copolymers and graft copolymers\cite{60-62}.

### 2.3.2 Substitution reactions

The usefulness of poly(dichlorophosphazene) is as a reactive macromolecular intermediate. Useful polyphosphazenes are made by replacement of the reactive phosphorus-chlorine bonds in 2.2 by functional groups. Because the phosphorus-chlorine bonds in 2.2 are susceptible to nucleophilic attack, functional groups may be attached to the polymer backbone through the use of suitable nucleophiles.

There is a wide range of nucleophiles that can be used to prepare polyphosphazene materials, which includes alkali metal (usually sodium) alkoxides\textsuperscript{63-71}, fluoroalkoxides\textsuperscript{72-77}, and aryloxides\textsuperscript{78-84} as well as alkyamines\textsuperscript{85-90}, and arylamines\textsuperscript{91-95} (Figure 2-4). Other good nucleophiles such as alkyllithium reagents and Grignard reagents are rarely used because these reagents often interact with the nitrogen atoms in the phosphazene backbone, and can lead to chain scission.

Macromolecular substitution provides a facile means for tuning the physical and chemical properties of polyphosphazenes. Mixed substituent polymers are readily synthesized through the simultaneous or sequential addition of two or more nucleophiles. Moreover, small or large changes in side group ratios can be obtained, which assists the tuning of structure-property relationships. Indeed, there is a huge number of polyphosphazenes that can be synthesized via this route.
Figure 2-3: Synthesis of 2.2 via living cationic polymerization
Figure 2-4: Macromolecular substitution of poly(dichlorophosphazene)
2.4 Structure, bonding, and properties

Many of the properties of polyphosphazenes are a result of their phosphorus-nitrogen backbone, including high thermal stability, radiation stability, and typically low $T_g$s. This is a consequence of the bonding arrangement in phosphazenes.

The bonding in phosphazenes has been described quite extensively\textsuperscript{96-103}, and involves both $\sigma$ bonds (from the overlap of nitrogen 2sp\textsuperscript{2} hybrid orbitals with phosphorus 3sp\textsuperscript{3} hybrid orbitals) and $\pi$ bonds (from the overlap of a nitrogen p\textsubscript{z} orbital with a phosphorus 3d orbital into which an electron is promoted). In this arrangement, each nitrogen atom is divalent and possesses a lone pair of electrons; phosphorus is tetravalent.

Although 2.1 is represented with alternating single and double bonds and fulfils the Hückel 4n+2 rule with 6 $\pi$ electrons, it is not aromatic. This is a consequence of a mismatch of orbital symmetry (Figure 2-5). However, X-ray crystallography studies have shown that there is a single P-N bond length of 1.58 Å. Similarly, polyphosphazenes do not possess any long-range delocalization. An explanation of this is that there are three-atom “islands” of electron density centered on each nitrogen atom, with nodes at each phosphorus atom. A consequence of this is that polyphosphazenes are not electronically conductive in the same manner as organic polymers such as polyacetylene.
Figure 2-5: Arrangement of orbitals in A: cyclic phosphazenes and B: polyphosphazenes
A further difference between organic polymers and polyphosphazenes is that even though there are $\pi$ bonds along the backbone, there is free rotation about those bonds. An explanation for this is that regardless of the torsional angle between adjacent nitrogen and phosphorus atoms, there is always $\pi$-$d\pi$ overlap because there are two orthogonal phosphorus 3d orbitals that can be used for bonding ($d_{xz}$ and $d_{yz}$) (Figure 2-6). A consequence of this is that polyphosphazenes typically have very low $T_g$s, although this is also dependant upon the nature of the side group. Another factor that results in low $T_g$s is the fact that side groups are not attached to adjacent atoms in the backbone, but every other atom. This results in less steric hindrance to rotation.

The thermal stability of polyphosphazenes can also, in part, be attributed to the bonding arrangement in the phosphorus-nitrogen backbone. Skeletal phosphorus atoms are in the +5 oxidation state – the highest oxidation state for phosphorus. Consequently, oxidation reactions are difficult. Furthermore, a synergistic effect in compounds containing a 1:1 atomic ratio of phosphorus and nitrogen has been reported\textsuperscript{104}. Further stability arises from the fact that the phosphorus-nitrogen backbone is polar, and consequently is resistant to homolytic cleavage and attack by radical species. This is borne out by the fact that the phosphazene backbone is stable towards gamma and ultraviolet radiation\textsuperscript{95,105,106}.
Figure 2-6: Free rotation in polyphosphazenes – rotation about the N-P bond (z-axis) always results in orbital overlap.
A further consequence of the structure of polyphosphazenes is that they possess a degree of biocompatibility. With appropriate side groups, the phosphazene backbone can decompose into phosphates and ammonia, both of which are relatively benign in the human body.

2.5 Applications of polyphosphazenes

Although many of the properties of polyphosphazenes are a result of the polymer backbone, their properties are also determined, to a large extent, by the nature of the side groups. With careful choice of the side group or side groups, materials can be made that are elastomeric, water repellent or water soluble, flame retardant, ion-conductive, or biologically compatible. Furthermore, $T_g$s, solubilities, and hydrolytic stabilities are affected by the nature of the side group. Examples of side groups and the properties they impart are shown in Figure 2-7.

2.5.1 Hydrophobic polyphosphazenes

The earliest examples of polyphosphazenes were poly[bis(trifluoroethoxy)phosphazene] and poly[bis(phenoxy)phosphazene]$^{36}$. These materials are semicrystalline thermoplastic materials, and repel water. The water contact angle of poly[bis(phenoxy)phosphazene] is reported to be 90°; the water contact angle for poly[bis(trifluoroethoxy)phosphazene] is 109°. This water contact angle is almost as high as for Teflon (110°), however poly[bis(trifluoroethoxy)phosphazene] is soluble in
common organic solvents, which means that the polymer can be manipulated in and cast from solution, whereas Teflon is insoluble. This makes the use of poly[bis(trifluoroethoxy)phosphazene in the paints and coatings industry attractive.

Applications of these materials include as fibers, gas separation membranes\textsuperscript{107-109}, and as UV stable coatings.

2.5.2 Elastomers

One of the few commercial applications of polyphosphazenes has been as high-performance elastomers. One of the reasons for this is that, due to the low $T_g$s of polyphosphazenes, they can remain elastomeric at low temperatures. Two types of phosphazene elastomers were commercialized under the trade names PN-F or Eypel-F (2.4) and PN-A or Eypel-A (2.5). PN-F is a mixed-substituent polymer with both trifluoroethoxy and octafluoropentoxy side units. The highly fluorinated groups impart a high degree of water repellency, good thermal stability, and excellent chemical resistance, and this polymer has been used as fuel lines, and o-rings and gaskets for hydraulic systems.
Figure 2-7: Examples of properties generated by different side groups

2.4 elastomer

2.5 elastomer flame retardant

2.6 hydrophobic microcrystalline film and fiber former

2.7 water soluble

2.8 water soluble biocompatible solid polymer electrolyte

2.9 bioerodible
2.5.3 Flame retardants

The thermal stability and non-flammability of polyphosphazenes make them ideal candidates for flame retardant materials for use in, for example, aircraft seat cushions, building ceiling tiles, or even fireproof clothing for firefighters.

Poly(aryloxyphosphazenes) such as 2.5 are particularly suitable flame retardant materials, and there have been several studies\textsuperscript{110-112} of this material which have demonstrated high limiting oxygen indices, high char yields and resistance to flow, low smoke formation, and low toxic emissions. Incorporation of a crosslinkable group such as an allylphenoxy side group provides a means to improve mechanical properties, and the flame retardancy can be improved by the incorporation of ceramic fillers such as expanded graphite.

2.5.4 Ion conductors

Solid polymer electrolytes for lithium ion batteries are attractive alternatives to flammable liquid electrolytes. The polymer that has been studied most widely for this application is poly(ethylene oxide) (PEO), the etheric oxygens in which can solvate lithium ions and consequently allow for their transport. However, PEO is a semi-crystalline material with a $T_m$ of around 60 °C – conduction of lithium ions can only occur through the amorphous regions of the polymer, thus the conductivity of PEO below its $T_m$ is poor.
Polyphosphazenes are excellent candidates for battery electrolytes because it is possible to make polyphosphazenes that are completely amorphous materials with low $T_g$s. The first polyphosphazene that was examined for use as a battery electrolyte was poly[bis(methoxyethoxyethoxy)phosphazene] (MEEP) (2.8), which has a low $T_g$ (-80 °C) and is completely amorphous over a very wide temperature range. Consequently, excellent lithium ion conductivities are realized. Many high polymer and small molecule analogs of MEEP have been investigated.

Proton conductive polyphosphazenes for fuel cell applications have also been studied, and these are discussed in Chapter 4.

2.5.5 Biomedical materials

One of the most promising applications for polyphosphazenes is in the field of biomedical materials. With careful selection of the side groups it is possible to synthesize polyphosphazenes that are biostable, bioerodible, blood compatible, or that encourage the growth of cells.

Early experiments led to the synthesis of amino acid substituted polyphosphazenes, which were bioerodible and decomposed into the amino acid, phosphate, ammonia, and an alcohol. Numerous other polymers have been developed for controlled drug release artificial bone materials, biocompatible hydrogels, and even dental applications. The strength of the phosphazene platform is that properties such as the rate of degradation or the pH behavior can be minutely controlled through the selection of the side group ratios.
2.6 Summary

Polyphosphazenes are a unique class of inorganic polymers, with a backbone of alternating phosphorus and nitrogen atoms. Polymers are synthesized via the macromolecular substitution of the reactive polymer poly(dichlorophosphazene). Through reaction with nucleophiles, a wide range of properties can be realized, which leads to a wide range of properties and applications.
2.7 References


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Chapter 3

Review of fuel cell technology

3.1 Introduction

Fuel cells are electrochemical devices that convert chemical energy into electrical energy. A fuel cell is an example of an open electrochemical device, which will continue to output electrical energy as long as the requisite chemical fuels and oxidants are supplied to the device. This is in contrast to a battery, which is a closed electrochemical device that ceases the output of electrical energy once all of the chemicals contained within it are consumed.

Fuel cells have many advantages over other power systems, such as the internal combustion engine. Because fuel cells directly convert chemical energy into electrical energy, they are typically more efficient than other systems. Furthermore, because electricity generation in a fuel cell is a non-combustive process, a fuel cell has low emissions, specifically of nitrogen oxides and sulfur oxides. Also, there are few moving parts in a fuel cell device, which results in simpler maintenance, a reduced need for lubrication, and fewer frictional losses.

3.2 Fuel cell systems

There are several types of fuel cell and several fuels that can be employed in fuel cells, but all fuel cells have essentially the same features and the same mode of operation.
A fuel cell consists of three basic parts: an anode (negative electrode), a cathode (positive electrode), and an electrolyte. Electrochemical reactions occur at the electrodes to generate an electric current.

A schematic representation of a simple fuel cell – a hydrogen/oxygen fuel cell – is shown in Figure 3-1. The fuel, the oxidant, the nature of the conductive ion, and the direction of movement of the conductive ion all depend upon the type of fuel cell.

The electrolyte is perhaps the most critical component in a fuel cell because it has to perform several tasks – it must physically separate the two halves of the fuel cell, must be an electron insulator, must be an ion conductor, and – depending upon the type of fuel cell – must be thermally and chemically stable. Perhaps because of these stringent requirements, fuel cells are classified by the electrolyte they employ. Common types include alkaline fuel cells, proton exchange membrane fuel cells, phosphoric acid fuel cells, molten carbonate fuel cells, and solid oxide fuel cells. The general features of these common fuel cells are outlined in Table 3-1.
Figure 3-1: Schematic of a fuel cell
<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>PEMFC</th>
<th>AFC</th>
<th>PAFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hydrated polymeric ion-exchange membrane</td>
<td>Mobilized or immobilized potassium hydroxide in asbestos matrix</td>
<td>Immobilized liquid phosphoric acid in ceramic matrix</td>
<td>Immobilized liquid molten carbonate in LiAlO₂</td>
<td>Perovskite ceramic</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Platinum and Platinum alloys</td>
<td>Platinum</td>
<td>Platinum</td>
<td>Nickel or nickel oxide</td>
<td>Perovskite</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>40 – 80 °C</td>
<td>65 – 220 °C</td>
<td>205 °C</td>
<td>650 °C</td>
<td>600 – 1000 °C</td>
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<tr>
<td>Charge Carrier</td>
<td>H⁺</td>
<td>HO⁻</td>
<td>H⁺</td>
<td>CO₃⁻</td>
<td>O⁻</td>
</tr>
</tbody>
</table>

PEMFC = proton exchange membrane fuel cell  
AFC = alkaline fuel cell  
PAFC = phosphoric acid fuel cell  
MCFC = molten carbonate fuel cell  
SOFC = solid oxide fuel cell
3.3 The proton exchange membrane fuel cell

In a proton exchange membrane fuel cell (PEMFC), the electrolyte is a polymeric material that conducts protons. This polymer also separates the two halves of the cell to prevent fuel and oxidant from directly mixing, which reduces the efficiency of the fuel cell. To operate in a fuel cell, the membrane is prepared into a membrane electrode assembly (MEA) - both sides of the membrane are coated with a catalyst, and the membrane is sandwiched between carbon cloth, which serves as the electrodes.

PEMFCs have a number of advantages over other types of fuel cells, including a low temperature of operation, a high power density and, because the fuel and oxidant are typically gases, corrosion of the fuel cell components is usually minimal. However, there are several issues with PEMFCs. The polymer membranes that are employed as the electrolytes must remain hydrated, which limits the upper temperature of operation of the fuel cell. The catalysts used are very expensive noble metals, such as platinum and platinum/ruthenium alloys. These catalysts are highly susceptible to poisoning by carbon monoxide, thus the purity of the fuel and the oxidant must be carefully controlled. Furthermore, relatively high loadings of catalyst are required at both the anode and cathode.

Nevertheless, PEMFCs are considered to be one of the best technologies for mobile power applications, such as automobiles and portable electronics. There are two main candidates for these applications: the hydrogen fuel cell, and the direct methanol fuel cell (DMFC).
3.3.1 Hydrogen fuel cells

A hydrogen fuel cell, as the name suggests, is one in which the fuel is hydrogen gas. The oxidant is oxygen, which is typically supplied from the air. One of the advantages of using hydrogen as a fuel is that the only by-product of the electrochemical reactions is water and because of this fact, it is considered to be a clean power technology. Another benefit of using hydrogen as the fuel in a PEMFC is that a high power density is available (1 A cm\(^{-2}\) at 0.7 V), which is greater than with other fuels. The electrochemistry of the hydrogen fuel cell is shown in Eq. 3.1.

\[
\text{Anode: } \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \\
\text{Cathode: } \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \\
\text{Overall: } 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{electrical power} + \text{heat}
\]  

3.1

The use of hydrogen as a fuel is relatively straightforward – the fuel is simply fed into the fuel cell device – but the storage and delivery of hydrogen gas are a problem. Compressed hydrogen gas or liquid hydrogen pose potential safety risks, especially in automotive applications where there is a risk of an accident and subsequent conflagration. Other storage technologies, such as metal hydrides and carbon nanotubes are safer, but suffer from a low storage density, and consequently insufficient hydrogen can be stored in these systems. Other drawbacks of hydrogen as a fuel are that the necessary infrastructure for delivery of hydrogen (for example as an automotive fuel) does not yet exist, and the large-scale production of hydrogen currently requires the reformation of
fossil fuels. This process generates large quantities of carbon dioxide, and negates any potential benefits of the use of hydrogen as a fuel.

### 3.3.2 Direct methanol fuel cells

In a direct methanol fuel cell, liquid methanol is the fuel, and oxygen from air is the oxidant. One of the advantages of methanol as a fuel is that it is a liquid, and thus storage and delivery of methanol is much more simple compared to hydrogen. However, the power density of methanol fuel cells is lower than hydrogen fuel cells (400 mA cm$^{-2}$ at 0.5 V). Furthermore, methanol fuel cells tend to be less efficient than hydrogen fuel cells. Another drawback of methanol as a fuel is that carbon dioxide is a waste product.

The electrochemistry of the direct methanol fuel cell is outlined in Eq. 3.2.

\[
\begin{align*}
\text{Anode: } & \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 6\text{H}^+ + 6\text{e}^- \\
\text{Cathode: } & 3/2 \text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O} \\
\text{Overall: } & \text{CH}_3\text{OH} + 3/2 \text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 + \text{electrical power} + \text{heat}
\end{align*}
\]

One of the greatest challenges with the use of methanol as a fuel is the prevention of so-called methanol “crossover”, where methanol permeates through the electrolyte membrane, and then may directly react with the oxidant. This reaction is shown in Eq. 3.3. This reaction is basically the same as the overall reaction in Eq. 3.2. However, no electrons are driven through an external circuit and therefore the overall efficiency of the fuel cell is reduced because fuel is consumed without any useful work being harnessed.
3.3.3 Design criteria

There are several requirements for a polymer electrolyte material to be successful. First and foremost of these is that the polymer electrolyte must conduct ions. In the case of the PEMFC, the electrolyte must conduct protons, and this is usually achieved by the synthesis of a polymer with covalently bound anions. These anionic groups can then be acidified to yield a polymer with acidic functionalities. Commonly, a sulfonate anion is employed to yield a polymer with a sulfonic acid attached to it.

In principle the more acidic functionalities that are contained within the polymer, the greater the conductivity of the polymer will be. A convenient measure of the number of acidic groups within a polymer is the ion exchange capacity (IEC). This is a measure of the number of equivalents of acid per unit weight of the polymer, and is usually reported in milliequivalents per gram (m equivs g\(^{-1}\)). Thus, another criterion for polymer electrolytes is that they have a high IEC.

Another important consideration is the hydrophobicity of the polymer. In PEMs, water is essential to allow for the conduction of protons, and thus the material must be able to absorb water. Excessive water uptake, however, leads to swelling of the material, and a reduction of mechanical integrity. Because the acidic functionalities are hydrophilic, the more of them there are on a polymer (i.e. the higher the IEC of the polymer), the more hydrophilic the polymer will become, and thus the greater the water absorption

\[
\text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 + \text{heat}
\]
uptake will be. Consequently, a fine balance between high IECs and low water uptake must be achieved. PEM materials that are employed in DMFCs must also be impermeable to methanol.

Further criteria are that the polymer must be thermally stable at the temperatures at which the fuel cell will operate, and chemically stable to resist electrochemical reactions within the fuel cell and reactions with hydroperoxy radicals that may form in the fuel cell.

3.4 Overview of PEM materials

Although fuel cells have existed since the late 1830s, it was not until the 1960s that PEM fuel cell systems were developed. The first such system was developed for the Gemini space missions, and the polymer electrolyte membrane utilized was a sulfonated polystyrene crosslinked with divinyl benzene. These materials were not only very expensive, but also rapidly degraded due to their susceptibility towards oxidative degradation.

Shortly thereafter, DuPont developed what is now considered to be the benchmark PEM material, Nafion. Nafion is a copolymer of poly(tetrafluoroethylene) and a perfluorinated alkyl sulfonic acid. This material combines high ionic conductivity with low water uptake and excellent chemical stability. However, Nafion has an upper operational temperature limit of 80°C, above which the material dehydrates and loses mechanical integrity. Furthermore, Nafion is highly permeable to methanol, which prevents its use in direct methanol fuel cells that utilize high
concentrations of methanol in water. Also, Nafion is expensive, and this is a major hindrance to the wider commercialization of fuel cells based on this material. Consequently, there has been a great deal of research into alternative membrane materials.

The majority of alternative membrane materials incorporate a sulfonic acid moiety. Sulfonic acids are a logical choice for PEM materials because they are strongly acidic and have a high degree of thermal stability. However other functionalities have also been used, such as phosphonic acids\textsuperscript{7,8} and sulfonimides\textsuperscript{9,10}.

Several alternative PEM materials based upon poly(styrene) have been examined. Sulfonated, non-fluorinated copolymers of styrene and ethylene were synthesized\textsuperscript{11} and found to give excellent conductivities. However, their instability towards oxidation limits their use to low temperatures of operation. Sulfonated copolymers of poly styrene-block-(ethylene-butylene)-block-styrene were also examined\textsuperscript{12}. These materials exhibited good conductivities, but high methanol permeabilities. Grafts of (polystyrenesulfonic acid) with poly(acrylonitrile), poly(styrene), poly(ethylene-co-tetrafluoroethylene), and poly(vinylidene fluoride) were also examined\textsuperscript{12}. Low water uptake values were achieved, as were high conductivities. However, the partial aliphatic nature of these polymers suggests that they will be susceptible to oxidative degradation.
Figure 3-2: Chemical structure of Nafion
Oxidative stability is an issue crucial to the long-term performance of PEM materials. Consequently, several high-performance polymers have been investigated for use as PEM materials. Poly(arylene ether)s such as poly(arylene ether ether ketone) (PEEK), shown in Figure 3-3 and poly(arylene ether sulfone) are attractive PEM candidates due to their high thermo-oxidative stability. Sulfonated PEEK has been examined as a PEM material\(^\text{13}\), and was shown to have high conductivities, and high thermal stabilities. PEEK also has the advantage of being relatively cheap to synthesize.

Other high performance systems have been investigated. Sulfonated naphthalenic polyimides were investigated\(^\text{14,15}\). These materials had high IECs, high water uptake values, and relatively low room temperature conductivities, although conductivities at 100 °C were high. Sulfonated polybenzimidazole (PBI) (Figure 3-4) has also been examined for use as a PEM material\(^\text{16,17}\). These materials were very thermally stable, and had conductivities that were two orders of magnitude higher than acid-doped materials\(^\text{16}\), although materials with low degrees of sulfonation performed poorly due to interactions of the acidic protons with the basic nitrogen atoms in the polymer backbone\(^\text{17}\).
Figure 3-3: Chemical structures of PEEK and sulfonated PEEK
Figure 3-4: Polybenzimidazole (PBI) and sulfonated PBI
Polymers with inorganic backbones are logical candidates for PEM materials – they have high thermal and oxidative stability, and are resistant to reaction with radicals. Polysiloxanes, which are relatively cheap, highly flexible, and have good thermal stability, are an example of inorganic polymers. However, few examples of the use of polysiloxanes as PEM materials exist. Another example of inorganic polymers are polyphosphazenes. Unlike the polysiloxanes, these polymers have been studied quite extensively for use as PEM materials, and their use as PEM materials is discussed in Chapter 4.

3.5 Summary

Fuel cells are an emergent power generation technology, and offer greater fuel efficiencies than traditional technologies like the internal combustion engine, and greater convenience than energy storage devices such as batteries. The type of fuel cell that is considered most viable for portable power generation is the proton exchange membrane fuel cell due to its high power density and low temperature of operation.

One of the most crucial components of a fuel cell is the electrolyte. There are numerous criteria that a successful PEM material must meet, including high thermal and chemical stability, a high IEC, low water uptake, and a high ionic conductivity. Several types of polymer system have been investigated for use as PEM materials, but to date few have performed better than Nafion.
3.6 References


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*J. Membr. Sci.* **2001**, *188*(1), 71-78.
Chapter 4

Ion-conductive polyphosphazenes for fuel cell applications

4.1 Introduction

One of the most serious obstacles to the advancement of proton exchange membrane fuel cells (PEMFCs) is the current shortage of suitable polymer electrolyte materials. One of the reasons for this is that an electrolyte membrane must perform several tasks within a fuel cell: it must be mechanically stable to physically separate the two halves of the cell, must have a high ionic conductivity, and be an electron insulator. It should also be electrochemically stable, and have good barrier properties to prevent the fuel and oxidant from mixing.

4.2 Current technology

These stringent requirements necessitate the use of specialized high performance polymers as PEM materials. An example of such a material is Nafion®, which is a copolymer of poly(tetrafluoroethylene) and a perfluorinated sulfonic acid. Nafion 117 is the current benchmark PEM material. Much literature exists on the behavior of Nafion®\textsuperscript{1}. Conductivities as high as $10 \times 10^{-2}$ S cm\textsuperscript{-1} at ambient temperatures have been reported\textsuperscript{2}, and higher conductivities are realized at elevated temperatures\textsuperscript{3}. 
However, Nafion has limitations. It has an upper operational temperature limit of 80 °C, above which the material dehydrates and loses mechanical integrity. Furthermore, Nafion is highly permeable to methanol, which prevents its use in direct methanol fuel cells that utilize high concentrations of methanol in water. Also, Nafion is expensive, and this is a major hindrance to the wider commercialization of fuel cells based on this material. Consequently, there has been a great deal of research into alternative membrane materials.

4.3 Other materials

Numerous alternatives to Nafion have been investigated\textsuperscript{4,5}. Many of these materials are high performance, high thermal stability polymers, such as aromatic polybenzimidazoles, poly(phenylene oxides), and poly(aryl ether ketones), which contain aryl rings in the polymer backbone. These polymers are not inherently conductive and must be modified to incorporate acidic functionalities, usually sulfonic acid groups. This can be accomplished by sulfonation with SO\textsubscript{3}.

Some of these membranes have shown considerable promise, specifically polybenzimidazole and sulfonated poly(ether ketones), in which the electro-osmotic drag is lower than in Nafion\textsuperscript{4}. However, questions remain about the long-term stability of these membranes. The ability to fine-tune their chemical compositions and structures is an ongoing challenge\textsuperscript{4}.
4.4 Polyphosphazenes

An alternative experimental class of polymers for PEM materials are polyphosphazenes. Polyphosphazenes are polymers that possess a backbone of alternating phosphorus and nitrogen atoms. Each phosphorus atom bears two organic, inorganic, or organometallic side groups (Figure 4-1).

The properties of polyphosphazenes are largely controlled by the choice of side groups. Polyphosphazenes that are hydrophobic, hydrophilic, ionically conductive, and rigid or elastomeric can be synthesized by careful choice of the side groups.

Polyphosphazenes have numerous advantages over classical hydrocarbon based polymers. One of the principal attributes is the thermal and chemical stability of the polymer backbone – both phosphorus and nitrogen are in their highest oxidation states, which results in a high degree of thermo-oxidative stability. The polar nature of the bonding along the backbone inhibits chemical attack by free radicals. Furthermore, due to the absence of long-range conjugation and the low barrier to skeletal free rotation about each phosphorus-nitrogen bond, the polymer backbone is highly flexible. This results in polymers with low $T_g$s, although this is often dictated by the choice of side group.
Figure 4-1: General polyphosphazene structure
Perhaps the greatest advantage of polyphosphazenes over hydrocarbon polymers is that the properties of the final polymer can be finely tuned through macromolecular substitution reactions carried out on the parent macromolecular intermediate, poly(dichlorophosphazene). The chlorine atoms in this polymer can be replaced by a wide range of different organic groups, and this provides a facile means for tuning the physical and chemical properties (Figure 4-2). Mixed substituent polymers are also readily synthesized through the simultaneous or sequential addition of two or more nucleophiles. Moreover, small or large changes in side group ratios can be obtained, which assists the tuning of structure-property relationships.

Factors affecting the design of a successful PEM material include thermal, mechanical, and chemical stability; barrier properties; and water uptake/hydrophobicity. Polyphosphazenes that yield the best combination of properties are aryloxide substituted. Poly(aryloxyphosphazene)s typically have high thermal, mechanical, and chemical stability, and are hydrophobic.
Figure 4-2: Macromolecular substitution route
Another consideration is the nature of the acidic functionality that is incorporated into the polymer. Different strength acid moieties give rise to different conductivities, but also different degrees of hydrophilicity and barrier properties – a balance between high conductivity and good physical properties must be achieved, and this is often accomplished by careful selection of the side group ratios. A further consideration is the ability to crosslink the polymer so that deficiencies in mechanical and barrier properties can be overcome. For this reason, methyl substituted aryloxy side groups are often employed because crosslinking via the methyl group can be achieved via gamma irradiation.

Polyphosphazenes can be categorized according to the type of acid functionality they possess:

### 4.5 Sulfonic acid functionalized polyphosphazenes

The earliest examples of polyphosphazene based PEM materials were sulfonated polymers. Sulfonic acid functionalized polyphosphazenes are a logical choice for PEM materials because of the strong acidity and high thermal stability associated with the sulfonic acid group. Allcock and co-workers sulfonated a series of aryloxy and arylamino-substituted polymers as well as small molecule model compounds using concentrated sulfuric acid, fuming sulfuric acid, or chlorosulfonic acid. It was found that, for aryl groups with alkyl units in the 3-position and phenyl rings with no alkyl substitution, the favored site of sulfonation was at the 4-position; for aryl groups with alkyl substitution in the 4-position, sulfonation was favored in the 3-position.
These materials underwent some chain cleavage during sulfonation, depending on the time and temperature of the reaction – the largest reduction in molecular weight occurred within the first ten minutes of the reaction. Polymers with high degrees of sulfonation (typically more than 30% of the side groups) were water soluble, but water swelling could be controlled by gamma irradiation crosslinking via the alkyl chains on the aryl rings. Though the utility of the sulfonation reactions was demonstrated, these materials were not examined specifically for fuel cell materials.

Other work in our program illustrated the possibility of sulfonation of poly(aminophosphazenes) with 1,3-propanesultone\textsuperscript{8}. Sulfonation occurred both on the amino side groups and the backbone nitrogen atoms, which yielded zwitterions (Figure 4-3). Low degrees of sulfonation dramatically improved the polymer solubility in polar solvents, and ionic crosslinking with multivalent ions was possible. Sulfonation of poly(aminophosphazenes) in which the amine was separated from the backbone of the polymer by an alkyl spacer were found to react under milder conditions.
Figure 4-3: Sulfonation of poly(aminophosphazenes) with 1,3-propanesultone$^8$. 
Montoneri, Gleria and co-workers demonstrated sulfonation of aryloxyphosphazenes with SO$_3$ in chlorinated solvents$^9$. It was shown that the initial addition of SO$_3$ results in a complex between the ring or backbone nitrogen atoms. At SO$_3$/[NP(OAr)$_2$] ratios higher than 1.0, sulfonation occurred on the aromatic rings. Disruption of the N→SO$_3$ complex was achieved by the addition of water to yield sulfuric acid, by addition of a competing donor solvent, or by drying under vacuum (Figure 4-4).

Pintauro and co-workers have studied the sulfonation of a variety of poly(aryloxyphosphazenes) with SO$_3$ for specific use as PEM membranes$^{10}$. The polymers chosen for this study were a) poly[(3-methylphenoxy)(phenoxy)phosphazene], b) poly[(4-methylphenoxy)(phenoxy)phosphazene], c) poly[(3-ethylphenoxy)(phenoxy)phosphazene] and d) poly[(4-ethylphenoxy)(phenoxy)phosphazene (Figure 4-5). Sulfonation was achieved by addition of SO$_3$ to solutions of the polymers in dichloroethane. After purification, films were cast from either $N,N$-dimethylacetamide or 1-methyl-2-pyrrolidinone. The methylphenoxy substituted polymers were sulfonated, but the ethylphenoxy substituted polymers were found to degrade.
Figure 4-4: Sulfonation of poly(aryloxyphosphazenes)\textsuperscript{11}. 
Figure 4-5: Structure of poly(aryloxyphosphazenes).\textsuperscript{10}
The degree of sulfonation, and consequently the ion-exchange capacity (IEC) and water uptake of the polymers, was controlled by variation of the amount of SO$_3$ added. The IECs ranged from 0-2.3 m equivs g$^{-1}$ for the methylphenoxy derivatives, and 0-7.0 m equivs g$^{-1}$ for the ethylphenoxy derivatives. The methylphenoxy derivatives were water insoluble for IECs less than 2.1 m equivs g$^{-1}$. The 3-methyl substituted polymer (IEC=1.5) and the 4-methyl substituted polymer (IEC=0.8) had water uptake values of 58% and 28% respectively (weight percent based upon the dry weight of the polymer); the ethylphenoxy derivatives were water soluble. The best material in terms of IEC and water uptake was identified as sulfonated poly[(3-methylphenoxy)(phenoxy)phosphazene].

Solid state characterization of poly[(3-methylphenoxy)(phenoxy)phosphazene]$^{11}$ confirmed the presence of the N→SO$_3$ complex sites, and indicated that aryl ring sulfonation did not occur until the SO$_3$/[NP(OAr)$_2$] ratio was more than 0.64. The location of SO$_3$ attack on the aromatic rings was found to be in agreement with the earlier work in our laboratory$^6$. The mole percentage of sulfonation was confirmed by elemental analysis, and showed good agreement with the measured IEC values (IECs were greater than 94% of the theoretical value based on mol% sulfonation).

The T$_{gs}$s of the polymers ranged from -28 °C for the parent polymer to -10 °C for a sulfonated polymer with an IEC of 2.1 m equivs g$^{-1}$. Differential scanning calorimetry and wide-angle X-ray diffraction measurements indicated that poly[(3-methylphenoxy)(phenoxy)phosphazene] is semi-crystalline although, following treatment with SO$_3$, this crystallinity disappeared.

Further work by Pintauro et al examined the use of crosslinked sulfonated
polyphosphazenes\textsuperscript{12}. Sulfonated poly[bis(3-methylphenoxy)phosphazene] membranes with a fixed IEC of 1.4 m equivs g\textsuperscript{-1} were crosslinked by dissolution in a solvent in the presence of benzophenone, and the cast films were then exposed to UV light. High proton conductivities were reported (4.0 x 10\textsuperscript{-2} S cm\textsuperscript{-1} at 25 °C and 8.2 x 10\textsuperscript{-2} S cm\textsuperscript{-1} at 65 °C) combined with a low methanol diffusion coefficient (8.5 x 10\textsuperscript{-8} cm\textsuperscript{2} s\textsuperscript{-1} at 45 °C). Good chemical resistance was demonstrated, with <5% weight loss after treatment with 3% aqueous H\textsubscript{2}O\textsubscript{2} for 24 hours. The mechanical stability of the polymers was ascertained by thermomechanical analysis. The uncrosslinked materials softened and deformed at 76 °C, but the crosslinked materials were stable up to 173 °C. However, the tensile strengths of these materials were not measured.

Further studies with sulfonated aryloxy polyphosphazenes have involved the fabrication of blends. Pintauro and co-workers examined blends of sulfonated polyphosphazenes with both polyacrylonitrile\textsuperscript{13} and polybenzimidazole\textsuperscript{14}. Blends of sulfonated poly[bis(3-methylphenoxy)phosphazene] with polyacrylonitrile were examined for direct liquid methanol fuel cell membranes. The sulfonated polyphosphazene was blended with polyacrylonitrile and then UV crosslinked in the presence of benzophenone. Fuel cell power output was reported to be almost as good as Nafion (0.38 V at 0.10 A cm\textsuperscript{-2} current density for the phosphazene vs. 0.40 V for Nafion), but methanol diffusion was reported to be 2.5 times lower than in Nafion (3 x 10\textsuperscript{-6} mol cm\textsuperscript{2} min\textsuperscript{-1} for the phosphazene vs. 8 x 10\textsuperscript{-6} mol cm\textsuperscript{2} min\textsuperscript{-1} for Nafion).

Blends of poly[bis(phenoxy)phosphazene] with polybenzimidazole (PBI) were also examined for direct methanol fuel cell membranes. Because PBI is basic, it serves to crosslink the polyphosphazene. Sulfonated polyphosphazenes with IECs of 1.2 and 1.4
m equivs g⁻¹ were prepared, and these were blended with between 5% and 12% of PBI. Membranes were reported to have room temperature conductivities of between $0.5 \times 10^{-2}$ to $8 \times 10^{-2}$ S cm⁻¹ and equilibrium water swellings of between 18 and 75%, depending on IEC and the amount of PBI present. Reported methanol permeabilities ranged from $1.0 \times 10^{-7}$ to $2.0 \times 10^{-6}$ cm² s⁻¹ (at 60 °C with a 1.0 M aqueous methanol feed).

A milder alternative to sulfonation with SO₃ has been developed by Andrianov and co-workers¹⁵. This method utilizes the non-covalent protection of hydroxybenzenesulfonic acid with dimethyldipalmitylammonium ions. Deprotection of the protective ion was achieved by treatment with potassium hydroxide followed by treatment with hydrochloric acid to yield the sulfonic acid. Homopolymers and copolymers were synthesized via this route, and the authors report that this method affords good synthetic control (Figure 4-6).
Figure 4-6: Synthesis of sulfonated polyphosphazenes via protected sulfonic acid\textsuperscript{15}. 
4.6 Phosphonic acid functionalized polyphosphazenes

Phosphonic acid functionalized polyphosphazenes are a viable alternative to the sulfonic acid polymers, and this possibility has been explored in our program. Phosphonic acid units have two acidic protons at each acid site and, although phosphonic acids are weaker acids than sulfonic acids, they are in principle less hydrophilic, and thus water uptake should be less. Furthermore, it is possible to incorporate phosphonic acids into polyphosphazenes without the harsh sulfonation conditions required to incorporate sulfonic acids.

Initially, phosphonate side groups were incorporated into polyphosphazenes through a phosphorus-oxygen-carbon linkage\textsuperscript{16}. These polymers were susceptible to hydrolysis and thermal cleavage, and could not be used for fuel cell applications. An alternative approach is to use the more stable carbon-phosphorus linkage. Work in our laboratory demonstrated phosphonate incorporation via treatment of bromomethylene phenoxy side groups with a sodium dialkyl phosphite, and by treatment of bromophenoxy groups with butyllithium followed by treatment with a dialkyl chlorophosphate\textsuperscript{17} (Figure 4-7). The first method gave quantitative yields, whereas the second approach gave yields of around 85%.
Figure 4-7: Synthesis of phenylphosphonic acid substituted polyphosphazenes\textsuperscript{17}.
The second method was used to synthesize candidate PEM materials. Copolymers of 4-methylphenoxy and 4-bromophenoxy polyphosphazenes were synthesized where the 4-bromophenoxy side group incorporation ranged from 18.5% to 30%. Following treatment with tert-butyllithium at -75 °C, the bromophenoxy side groups were converted to the corresponding lithiophenoxy derivative. Addition of diphenyl chlorophosphate followed by basic hydrolysis and acidification with hydrochloric acid yielded a mixture of diester, monoester/monoacid and diacid side groups.

Phenylphosphonic acid functionalized polyphosphazenes co-substituted with either 4-methylphenoxy or 3-methylphenoxy side groups were then synthesized and examined for use as PEM materials. The IECs for the 4-methylphenoxy derivatives ranged from 1.17 to 1.43 m equivs g⁻¹. Agreement with theoretical IEC values (based upon NMR and elemental analysis data) ranged from 100% to 82% respectively. Equilibrium water swelling ranged from 19 to 32 weight %. Ionic conductivities ranged from $3.8 \times 10^{-2}$ S cm⁻¹ to $5.4 \times 10^{-2}$ S cm⁻¹; the 3-methylphenoxy derivative had an IEC of 1.35 m equivs g⁻¹ (90% of theoretical), an equilibrium water swelling of 12 weight % and an ionic conductivity of $5.6 \times 10^{-2}$ S cm⁻¹. Gamma radiation crosslinking of the 3-methylphenoxy substituted polymer was examined. Radiation doses of up to 40 Mrad had little effect on water swelling, but brought about an improvement in mechanical stability, although quantification of this mechanical stability has yet to be obtained.

The 3-methylphenoxy substituted polymer was also evaluated for methanol crossover. At 80 °C and 2.8 bar with a 3 M aqueous methanol fuel feed, the phosphonated polymer had roughly 12 times lower methanol crossover than Nafion (0.27
x $10^{-6}$ mol cm$^{-2}$ min$^{-1}$ for the phosphazene vs. $3.39 \times 10^{-6}$ mol cm$^{-2}$ min$^{-1}$ for Nafion), and roughly 6 times lower methanol crossover than a sulfonated, crosslinked polyphosphazene ($1.58 \times 10^{-6}$ mol cm$^{-2}$ min$^{-1}$). Other measurements$^{19}$ with 50% v/v aqueous methanol showed methanol diffusion to be roughly 40 times lower than in Nafion and between 10 and 20 times lower than a sulfonated polyphosphazene.

The high temperature transport properties of the phosphonated material were also examined$^{20}$. At 120 °C, the phosphonated polyphosphazene membranes had roughly a 9 times lower methanol diffusion than Nafion ($9.51 \times 10^{-7}$ cm$^2$ s$^{-1}$ for the phosphazene vs. $8.15 \times 10^{-6}$ cm$^2$ s$^{-1}$ for Nafion). This should allow more efficient operation of DMFCs because a more concentrated methanol fuel feed solution could be utilized.

A difference in activation energies for proton conduction between Nafion, a sulfonated polyphosphazene, and a phosphonated polyphosphazene was detected – the activation energies were 22.4 kJ mol$^{-1}$, 41.4 kJ mol$^{-1}$ and 36.8 kJ mol$^{-1}$ respectively. This indicates differences in the diffusion mechanisms in each polymer. However, it has been reported that the activation energy for Nafion is dependent upon the morphology of the film, and is consequently dependent upon water content, thermal history, and the method by which the film was prepared$^{21}$.

### 4.7 Sulfonimide substituted polyphosphazenes

An alternative to sulfonic and phosphonic acid functionalized polyphosphazenes is to use polymers that incorporate a sulfonimide side group. The high acidity of
sulfonimide groups is known\textsuperscript{22}. Thus sulfonimide functionalized polyphosphazenes have potential advantages as PEM materials.

The behavior of polyphosphazene copolymers with sulfonimide side groups and 4-methylphenoxo groups has been investigated in our program\textsuperscript{23}. The sulfonimide side group was synthesized via the reaction of 4-methoxybenzenesulfonyl chloride with trifluoromethanesulfonamide in the presence of triethylamine. The resultant triethylamine salt was converted to the sodium salt with sodium methoxide. The free phenol was generated by cleavage of the aryl methyl ether with sodium ethanethiolate (Figure 4-8).

Polymers were synthesized initially by replacing 50% of the chlorine atoms in poly(dichlorophosphazene) by 4-methylphenoxy side groups to ensure polymer solubility in tetrahydrofuran for the second step. Reaction of the partially substituted polymer with the sodium sulfonimide salt in refluxing THF was then followed by further addition of sodium 4-methylphenoxide at 150 °C in a sealed pressure reactor (Figure 4-9). The polymers were converted into the acid form by precipitation into concentrated hydrochloric acid.
Figure 4-8: Synthesis of aryl sulfonimide side group\textsuperscript{23}.
Figure 4-9: Synthesis of sulfonimide functionalized polyphosphazenes$^{23}$. 
A mixed substituent polymer with 17% sulfonimide side groups and 83% p-methylphenoxy side groups had an IEC of 0.99 m equivs g\(^{-1}\) (95% of the theoretical maximum of 1.04 m equivs g\(^{-1}\)). The conductivity of this material was 4.9 x 10\(^{-2}\) S cm\(^{-1}\), although a very high water uptake of 119 weight % occurred. Efforts to control the water uptake of this material were made by radiation crosslinking. Gamma radiation doses of 20 Mrad and 40 Mrad crosslinked the material, and the water uptake was reduced to 73 and 42 weight % respectively. Surprisingly, the crosslinking was accompanied by a small increase in conductivity (7.1 x 10\(^{-2}\) S cm\(^{-1}\) and 5.8 x 10\(^{-2}\) S cm\(^{-1}\) respectively). It is possible that crosslinking may reduce the average separation between polymer chains, and thus lower the distance between acidic groups.

The control of water uptake was also achieved by the formation of a blend of the sulfonimide polyphosphazene with poly(vinylidene fluoride) (PVDF). A 75% polyphosphazene/25% PVDF film cast from \(N,N\)-dimethylacetamide showed no phase separation. The water uptake was reduced to 41 weight %, and the measured proton conductivity was 6.0 x 10\(^{-2}\) S cm\(^{-1}\).

The sulfonimide substituted polyphosphazenes have some of the highest conductivities and highest membrane electrode assembly characteristics of any polyphosphazene\(^{24}\). A maximum power density of 0.36 W cm\(^{-2}\) at 0.87 A cm\(^{-2}\) was achieved at 22 °C. At 80 °C, this rose to 0.47 W cm\(^{-2}\) at 1.29 A cm\(^{-2}\). This compares favorably with Nafion. However, their good performance is counteracted by their solubility in methanol. This precludes their use in DMFCs in their uncrosslinked form, although they may be viable following high levels of crosslinking and/or a low methanol
concentration in the aqueous fuel feed. However they are excellent candidates for use in
H₂/O₂ fuel cells.

4.8 Summary

Polyphosphazene-based proton exchange membrane materials have been
developed. Several of the polymers synthesized are comparable to Nafion in their
performance, and significantly surpass Nafion in terms of methanol permeability.
Moreover, they are potentially less expensive. The electrochemical properties of selected
polyphosphazenes are shown in Table 4-1.

Polyphosphazenes have several advantages over conventional organic polymers –
they are thermo-oxidatively stable and typically have low Tₜgs. The unique synthetic
route of macromolecular substitution gives unprecedented versatility to this class of
polymers – fine control of the side group ratios allows for the facile study of structure
property relationships.
Table 4-1: Selected polymer data

<table>
<thead>
<tr>
<th>Polymer</th>
<th>IEC (m equivs g⁻¹)</th>
<th>Crosslinking (Mrad)</th>
<th>Conductivity(^a) (x 10⁻² S cm⁻¹)</th>
<th>Water Swelling (weight %)</th>
<th>MeOH Diffusion(^b) (x 10⁻⁶ cm² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfonated</td>
<td>1.07</td>
<td>20</td>
<td>1.1</td>
<td>38</td>
<td>1.02</td>
</tr>
<tr>
<td>Phosphonated</td>
<td>1.35</td>
<td>20</td>
<td>4.4</td>
<td>13</td>
<td>0.77</td>
</tr>
<tr>
<td>Sulfonimide</td>
<td>0.99</td>
<td>20</td>
<td>7.1</td>
<td>73</td>
<td>-</td>
</tr>
<tr>
<td>Nafion 117</td>
<td>0.91</td>
<td>-</td>
<td>10.0</td>
<td>30</td>
<td>6.22</td>
</tr>
</tbody>
</table>

\(^a\)100% relative humidity, 25 °C

\(^b\)12M MeOH, 80 °C, 2.8 bar
The most promising of the polyphosphazene PEM materials are the aryloxy substituted polymers. These can be sulfonated, phosphonated, or converted to mixed substituent polymers with sulfonimide side groups. The sulfonated materials have been studied in the greatest detail. They have good proton conductivities, low water uptake, and low methanol permeability. However, sulfonation requires the use of aggressive reaction conditions.

Phosphonated polymers can be prepared from either bromomethylene phenoxy side groups or bromophenoxy side groups. Although the overall phosphonation yields are low for the bromophenoxy derivatives, they yield good conductivities, low water uptake, and very low methanol crossover.

Sulfonimide functionalized polyphosphazenes are prepared via the co-substitution with 4-methylphenoxy and sulfonimide side groups. These materials have high conductivities, and excellent performance as MEAs, but high water and methanol uptake are problems. However, these can be controlled through crosslinking or blending with PVDF.
4.9 References


Chapter 5

Control of water uptake of polyphosphazene based fuel cell membranes by silicate inter-penetrating networks

5.1 Introduction

Recent interest in fuel cell technology has led to the development of a wide range of technologies for proton conducting membranes. Of these, the polymer electrolyte membranes (PEMs) show promise as lightweight and inexpensive materials. Many examples of such materials exist, including fluorinated polymers such as Nafion\textsuperscript{1}, aromatic polymer derivatives\textsuperscript{2} such as polybenzimidazoles\textsuperscript{3}, and polysiloxanes\textsuperscript{4}. Numerous requirements exist for such materials to be viable – good mechanical strength and chemical stability; high temperature of operation; low water uptake; and high proton conductivity.

Polyphosphazenes are ideal candidates for PEM materials, due to their high thermo-oxidative stability and the unique ease with which their properties can be customized\textsuperscript{5}. A recent development\textsuperscript{6} has been a $p$-cresoxy substituted polyphosphazene that is co-substituted with an aryl trifluoromethylsulfonimide derivative – a strong acid (Figure 5-1).
Figure 5-1: Structure of sulfonimide substituted polyphosphazenes
Polyphosphazenes with this structure have exhibited high proton conductivities$^6$ of up to $7.1 \times 10^{-2}$ S cm$^{-1}$, but also exhibit a large degree of water uptake, which leads to swelling and a reduction in mechanical stability. These problems have been overcome by gamma radiation induced crosslinking, which is effective but may cause an undesirable increase in $T_g$ and, in the case of high levels of crosslinking, a reduction of conductivity. An alternative method by which the water uptake was controlled was the formation of blends of the sulfonimide substituted polymers with non-conductive polymers such as poly(vinylidene fluoride) and poly(vinylidene fluoride-co-hexafluoropropylene)$^7$. The resultant blended materials showed lower water swelling and improved mechanical stability compared to the parent polymer, but there exists the possibility of macroscopic phase separation over a period of time. Thus, an alternative method by which the water uptake of these materials could be controlled was examined.

Sol-gel chemistry is attractive due to the relative ease with which cross-linked networks can be formed, and the incorporation of silicate networks into polyphosphazenes is known$^8$-$^{12}$. Previous studies have examined the incorporation of a silicate network into poly[bis(methoxyethoxyethoxy)phosphazene] (MEEP) via both non-covalent interactions$^{11}$, where improvements in thermal and mechanical stability were observed, and covalent interactions$^{12}$, where a reduction in water uptake was observed because the material was crosslinked (and there was a presumed increase in $T_g$). A similar motif is herein examined in which partial and full inter-penetrating networks (IPNs) of silicate and polyphosphazene are formed by sol-gel condensation in a solution of the polyphosphazene without covalent attachment of a sol-gel precursor to the polyphosphazene. The rationale behind this approach is that the water uptake could be
modified with limited effect on the $T_g$ of the polyphosphazene, and thus high levels of conductivity can be maintained. Furthermore, an IPN would prevent phase separation over a period of time. The sol-gel precursor tetraethyl orthosilicate (TEOS) and a substituted sol-gel precursor (3,3,3-trifluoropropyl)trimethoxysilane (TFPTMS) were utilized. The resultant materials were characterized via DSC, NMR, SEM, and ionic conductivities were measured. Water uptake was measured by mass increase.

5.2 Experimental

This work was a collaborative effort between Dr. Elena Chalkova from the Energy Institute at the Pennsylvania State University, who was responsible for the measurement of ionic conductivities; Bernie O’Hare from the Department of Chemistry at the Pennsylvania State University, who obtained solid state $^{29}$Si NMR spectra; and myself, who performed all of the synthetic work and collected water uptake, IEC, and differential scanning calorimetry data, and obtained scanning electron micrographs.

5.2.1 Materials

Poly(dichlorophosphazene) was prepared according to literature procedures. Sodium hydride (95%, Aldrich), $p$-cresol (99%, Aldrich), 4-methoxybenzenesulfonyl chloride (99%, Aldrich), tetraethyl orthosilicate (99%, Aldrich), sodium ethanethiolate (80%, Aldrich), trifluoromethane sulfonamide (98 %, TCI), methanol (99.8%, EMD), chloroform (99.8%, EMD), hydrochloric acid (36.5-38.0%, EMD), (3,3,3-
trifluoropropyl)trimethoxy silane (97%, Lancaster), and N,N-dimethylformamide (99.8%, Alfa Aesar) were used as received. Tetrahydrofuran was purchased from EMD Chemicals and distilled from sodium benzophenone ketyl prior to use. Acetone was purchased from EMD and distilled from calcium sulfate prior to use. Triethylamine was purchased from EMD and distilled from calcium hydride prior to use. All reactions were performed under an atmosphere of dry argon.

5.2.2 Instruments

High field $^1$H (360.14 MHz) NMR spectra were recorded using a Bruker AMX-360 NMR spectrometer, and were referenced to external tetramethylsilane. Direct observed $^1$H decoupled solid state $^{29}$Si (59.08 MHz) NMR spectra were recorded on a Chemagnetics CMX-300 spectrometer with a pulse delay of 60s, and were referenced to external tetramethylsilane. Liquid state $^{29}$Si (59.08 MHz) NMR were recorded on a Bruker DPX-300 spectrometer and were referenced to external tetramethylsilane. Thermal data were obtained by use of a TA Instruments Q10 differential scanning calorimeter (DSC), calibrated with indium, water, and cyclohexane standards. Scanning electron micrographs were obtained with a FEI-Philips XL-20 scanning electron microscope. Masses were recorded from an Ohaus Explorer E10640 balance. Ionic conductivities were measured with a Gamry Instrument Inc. four point probe.
5.2.3 Synthesis of sulfonimide substituted polymer

The synthesis of sulfonimide substituted polymers is described elsewhere\(^6\). The reagent quantities used to synthesize a 15% sulfonimide/85% p-cresoxy polyphosphazene (5.1) are listed in Table 5-1. The polymer was purified by dialysis against methanol in 12-14,000 molecular weight cut-off dialysis membrane, followed by precipitation into hexane. The ratio of side groups and the purity of the polymer were confirmed by \(^1\)H NMR.

5.2.4 Preparation of silicate IPNs

Samples of polymer 5.1 (1 g) were dissolved in DMF (5 ml) under argon. To each solution was added a different weight percent of either tetraethyl orthosilicate or (3,3,3-trifluoropropyl) trimethoxysilane, shown in Tables 5-2 and 5-3 respectively. Sol-gel condensation was initiated by the addition of 0.1 M HCl (aq) solution (1 ml), and the solutions were heated at 60 °C for 3 hours, after which time they were cooled and poured into Teflon trays to form films. The films were dried in a vacuum oven at ambient temperature for 24 hours and at 60 °C for a further 48 hours. After 48 hours, the films were removed from the trays, and their masses were recorded.
Table 5-1: Synthesis of 15% sulfonimide/85% p-cresoxy polymer: amounts of reagents used.

<table>
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<tr>
<th></th>
<th>50% sodium p-cresoxide salt</th>
<th>15% sodium sulfonimide salt</th>
<th>50% sodium p-cresoxide salt</th>
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<tr>
<td>(NPCl₂)ₙ</td>
<td>(NPCl₂)ₙ</td>
<td>(NPCl₂)ₙ</td>
<td>(NPCl₂)ₙ</td>
</tr>
<tr>
<td>Mass(g)</td>
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<td>3.10</td>
<td>0.93</td>
</tr>
<tr>
<td>Mmol</td>
<td>129</td>
<td>129</td>
<td>39</td>
</tr>
<tr>
<td>p-cresol</td>
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</tr>
<tr>
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<td>39</td>
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<tr>
<td>p-cresol</td>
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Table 5-2: Preparation of silicate/phosphazene composites with TEOS

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<thead>
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<th>Sample</th>
<th>Mass polymer (g)</th>
<th>Mass TEOS (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>1.0</td>
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</tr>
<tr>
<td>5.2</td>
<td>0.9</td>
<td>0.1</td>
</tr>
<tr>
<td>5.3</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>5.4</td>
<td>0.7</td>
<td>0.3</td>
</tr>
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<td>5.6</td>
<td>0.5</td>
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</tr>
</tbody>
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Table 5-3: Preparation of silicate/phosphazene composites with TFPTMS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass polymer (g)</th>
<th>Mass TFPTMS (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.7</td>
<td>1.00</td>
<td>0.06</td>
</tr>
<tr>
<td>5.8</td>
<td>1.00</td>
<td>0.11</td>
</tr>
<tr>
<td>5.9</td>
<td>1.00</td>
<td>0.25</td>
</tr>
</tbody>
</table>
The samples that contained (3,3,3-trifluoropropyl) trimethoxysilane were exposed to 0 – 20 Mrad dosages of gamma radiation to form full IPNs. SEM micrographs and $^{29}$Si solid state NMR spectra were recorded. The films were then soaked in de-ionized water for 7 days. After removal of surface water, the weights of the films were measured. Percentage of water uptake by mass was calculated via equation (Eq. 5.1). The ionic conductivities of the fully hydrated films were then measured.

\[
\varphi_{\text{w}} = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \times 100
\]

5.3 Results and discussion

The IEC of the parent polymer was ascertained by titrimetry to be 0.79 m equivs g$^{-1}$. This value, although rather low with respect to the theoretical maximum IEC of 0.94 m equivs g$^{-1}$, was adequate. The percent water uptake of the trifluoropropyl silicate containing films is reported in Figure 5-2. The water uptake of these films decreases as the incorporation of the silicate increases, and also decreases as the gamma irradiation dose increases. These observations can be attributed to the partial hydrophobicity of the trifluoropropyl substituted silicate and the fact that the polymer crosslinks upon exposure to gamma radiation. It is interesting to note that the water swelling for the 5% silicate containing composites at 5 MRad and 10 MRad gamma irradiation dose appears to be lower than expected. This is attributed to the fact that the 5% silicate containing composites are homogeneous, as evidenced by the SEM micrographs (vide infra), and thus the hydrophobicity/hydrophilicity of the composites is more uniform. The fact that
this phenomenon is not observed at higher gamma irradiation doses is attributed to this effect being masked by the gamma irradiation induced crosslinking.

To assess the extent of the sol-gel condensation reaction, solid state $^{29}$Si NMR spectra were obtained. For all the composite materials, a major resonance was observed between $\delta = -68.8$ and $\delta = -70.8$ ppm. These chemical shifts are consistent with an alkyl-substituted T$_3$ silicon\textsuperscript{14}, which indicates that the condensation reactions were largely complete. However, the NMR spectra contained a lot of noise due to the relatively low silicon contents of the composite materials. Consequently, other peaks may have been present but were not observed.

The thermal transitions of the composite films were examined by DSC, and the DSC thermograms are shown in Figure 5-3. These data indicate that the $T_g$ of the polymer is 17 °C, and that the position of the $T_g$ of the polymer in the composite remains unchanged regardless of the amount of silicate incorporation.

An interesting feature of the $T_g$ of the parent polymer is the hysteresis peak at 30 °C. This is attributed to a slow relaxation caused by coulombic interactions of the highly ionic acidic group with other parts of the polymer. This peak disappears upon incorporation of the silicate, which implies that there is a weak interaction between the polymer and the silicate.
Figure 5-2: Water swelling data for TFP silicate composites.
Figure 5-3: DSC thermograms of TFP silicate composite materials
SEM micrographs of the composite films were obtained, and are shown in Figure 5-4. These micrographs indicate that the 5% silicate composite was homogeneous, but the composites with higher silicate contents became micro-phase separated. This is probably because, during film casting from solution, the concentration of TFPTMS was sufficient to allow for agglomeration of the hydrophobic trifluoropropyl units.

Conductivites of the hydrated composite films were measured, and are reported in Table 5-4. These conductivities are low – about 2 orders of magnitude lower than expected given the IEC of the parent polymer. However, the conductivities of the composite films are very high in comparison to the parent polymer, and the 10% and 20% silicate containing composites show essentially the same conductivity as the polyphosphazene. It can therefore be concluded that, upon incorporation of the silicate into the polymer, the conductivities are invariant.

To compare the effect of the incorporation of a hydrophobic, substituted silicate, phosphazene/silicate composites were prepared from tetraethyl orthosilicate. Water uptake of these materials is shown in Figure 5-5. These data indicate a large amount of water uptake, which can be attributed to both the hydrophilicity of the polymer and the hydrophilicity of the silicate network. It is interesting to note that the water uptake starts to drop with silicate incorporations above 30 %. A possible explanation for this is the increased barrier properties of the composites with higher incorporations of the silicate – the materials became more glassy as the silicate content increases.
Figure 5-4: SEM micrographs of TFP silicate composites. A: 5%, B: 10%, C: 20%.
Figure 5-5: Water uptake of silicate composites formed from TEOS
Figure 5-6: DSC thermograms of silicate composites formed from TEOS.
Table 5-4: Ionic conductivities of TFPTMS containing composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ionic conductivity (x 10^{-4} S cm^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>8.9</td>
</tr>
<tr>
<td>5.7</td>
<td>7.8</td>
</tr>
<tr>
<td>5.8</td>
<td>9.0</td>
</tr>
<tr>
<td>5.9</td>
<td>9.0</td>
</tr>
</tbody>
</table>
The composites prepared from TEOS were also examined by DSC, and the DSC thermograms are shown in Figure 5-6. These data show that the $T_g$ of the polymer remains unchanged as the silicate incorporation increases. However, there appears to be some quenching of the coulombic relaxation peak. This indicates that there is some interaction between the acidic moiety in the polymer and the silicate network.

5.4 Conclusions

Composite materials formed from a sulfonimide substituted polyphosphazene and a silicate were prepared via the sol-gel technique. A silicate substituted with a hydrophobic trifluoropropyl moiety was utilized, and a silicate network was formed in-situ. Complete network formation was confirmed by $^{29}$Si solid state NMR. These materials were found to have significantly lower degrees of water uptake compared to the parent polymer, and even lower levels of water swelling were achieved after crosslinking of the polymer via gamma irradiation to form full IPNs. Composite materials that were formed from the silicate precursor TEOS were significantly more hydrophilic, and had much higher water uptake values.

DSC data showed that there was little effect on the $T_g$ of the polymer upon incorporation of the silicate, which suggests that the interactions between the polymer and the silicate network are weak.

SEM micrographs indicated that, for high amounts of silicate incorporation, the composite materials are phase separated. However, at 5% incorporation, the composites was homogeneous.
Ionic conductivities measurements indicated that, although the conductivities were low, there is no change in conductivity upon incorporation of the silicate. This suggests that sulfonimide polyphosphazene/trifluoropropyl silicate composite materials are promising candidates for use as PEMs.
5.5 References


Chapter 6

Organic polymers with pendant cyclic phosphazene side groups as proton conductive direct methanol fuel cell membranes

6.1 Introduction

The rapid growth in popularity of portable electronic devices, such as laptop computers and mobile telephones, has necessitated the development of better, higher performance energy systems to power these devices. Specifically, energy systems that are small, lightweight, and can power a device for an extended period of time are required.

Current portable energy technology is based upon secondary (rechargeable) batteries. Secondary batteries are a convenient technology, however they are limited, in general, by the fact that they are energy storage devices – closed electrochemical devices. Once all the useful energy from a secondary battery has been harnessed it must be recharged, which can often be a lengthy process. Furthermore, there is a finite amount of energy that can be stored in a battery, which limits the length of a time an electronic device can be operated for.

An open electrochemical device, or energy conversion device, is a practical solution to these problems. An energy conversion device can output electricity for as long as a fuel is added to the system. Also, as an energy conversion device is an open system, it typically will require less containment material.
The most common type of electrochemical energy conversion device is the fuel cell. There are several types of fuel cell technology\(^1\), including phosphoric acid fuel cells, molten carbonate fuel cells and solid oxide fuels cells, but the type that is considered the most applicable to portable electronic devices is the proton exchange membrane (PEM) fuel cell. In this type of fuel cell, a proton conductive polymer electrolyte is used. PEM fuel cells typically operate at low temperatures (less than 80 °C) and have a high power density.

The fuel that a PEM fuel cell utilizes is a critical consideration. Hydrogen would appear to be the logical choice because of the high power density (1 A cm\(^{-2}\) at 0.7 V)\(^1\) and low emissions (water vapor is the only by-product). However, for portable electronic devices, storage and safe usage of hydrogen gas would necessitate extra bulk and weight. An alternative fuel is methanol. Reformation of methanol to yield hydrogen is not practical, as a reformer would add extra bulk, weight, and complexity to the system. A direct methanol fuel cell, however, can utilize methanol directly as the fuel, without need for reformation.

Current direct methanol fuel cells (DMFCs) are inefficient for a number of reasons. Power density is lower than for hydrogen fuel cells (400 mA cm\(^{-2}\) at 0.5 V); carbon dioxide is a waste product; there are currently no good membrane materials that resist methanol permeation.

The low power density is offset by the advantages of a smaller, lighter fuel cell device. Carbon dioxide output is not a great concern as the volumes involved are comparatively small. However, the issue of methanol permeation is critical – methanol permeation (so called “methanol crossover”) results in a loss of efficiency because
methanol can be oxidized directly at the cathode without producing any useful work. Consequently, there is a need to develop high performance PEM materials that have low methanol permeabilities.

Polyphosphazenes have been investigated previously for direct methanol fuel cell applications. Although high conductivities and methanol permeabilities lower than Nafion were achieved, the methanol permeabilities were still unacceptably high. Consequently, there is a need to develop new materials that can combine the high thermo-oxidative stability of the phosphazenes with greater resistance to methanol permeability.

Potential candidates for this application are organic polymers with pendant cyclic phosphazene molecules. These polymers combine the low $T_g$s and hydrophobicity of organic polymers with the tailorability of the phosphazene units. Furthermore, because each repeat-unit contains a phosphazene ring with five available bonding sites, there is a possibility for higher incorporations of functional groups than would be possible with a linear organic or phosphazene polymer. Organic/pendant cyclic phosphazene polymers are known, and have been investigated previously for use as battery electrolyte materials. Consequently, they should also be viable candidates for PEM applications.

Aryl sulfonic acid containing polymers are known PEM materials, and are utilized because of the large basicity of the sulfonate anion coupled with the low methanol solubility of the aryloxy groups. Therefore attempts to synthesize aryl sulfonic acid containing pendant polymers by the use of $\text{SO}_3$ were explored.
6.2 Experimental

This work was a collaborative effort between David Stone from the Department of Chemistry at the Pennsylvania State University, who synthesized the 5-norbornene-2-methoxy-pentakis(chloro)cyclotriphosphazene monomer and assisted with the collection of infrared spectra; Shih-To Fei from the Department of Chemistry at the Pennsylvania State University, who measured water uptake values and methanol diffusion coefficients, and was responsible for the gamma irradiation of samples; and myself, who performed all the other synthetic work, measured IECs, obtained differential scanning calorimetry and molecular weight data, and measured ionic conductivities.

6.2.1 Materials

Hexachlorocyclotriphosphazene was obtained from Ethyl Corp./Nippon Fine Chemical and was recrystallized from heptane and sublimed at 30 °C at 0.01 mm Hg before use. Sodium (ACS reagent grade, Aldrich), potassium tert-butoxide (98%, Acros), Ethyl vinyl ether (99%, Aldrich), bis(tricyclohexylphosphine)benzylidene ruthenium (IV) chloride (97%, Aldrich), p-toluenesulfonylhydrazide (97%, Aldrich), p-xylene (anhydrous, 99+%, Aldrich), 1,2-dichloroethane (99%, Aldrich), sulfur trioxide (99%, Aldrich) and methanol (99.8%, EMD) were used as received. 3-Methylphenol (97%, Aldrich) was distilled from calcium chloride under reduced pressure before use. Tetrahydrofuran (99.99%, EMD), dichloromethane (99.8%, EMD), and dioxane (99.0%, EMD) were dried by passage through Glass Contour alumina columns before use. De-ionized water was
obtained from a Barnstead Nanopure Diamond water purification system. All reactions were carried out under an inert atmosphere of nitrogen.

6.2.2 Instruments

High field $^1$H (360.14 MHz) and $^{31}$P (145.79 MHz) NMR spectra were recorded by use of a Bruker Avance-360 NMR spectrometer. $^1$H NMR spectra were referenced to external tetramethylsilane; $^{31}$P NMR spectra were referenced to external 85% aqueous phosphoric acid. Thermal data were obtained by use of a TA Instruments Q10 differential scanning calorimeter (DSC), calibrated with indium, water, and cyclohexane standards. Molecular weights and polydispersity indices were estimated by use of a Hewlett-Packard 1090 gel permeation chromatograph equipped with a HP-1047A refractive index detector, and Phenomenex Phenogel 10 µm linear columns calibrated with polystyrene standards. All samples were eluted at a flow rate of 1.0 mL min$^{-1}$ at 40 °C in a 0.3 wt % solution of tetra-n-butylammonium nitrate in stabilized THF (EMD).

Methanol permeabilities were measured by use of the apparatus shown in Figure 6-1. A film of polymer was sandwiched between the two halves of the apparatus, and the screws carefully tightened to give a tight seal. One chamber of the apparatus was filled with de-ionized water; the other was filled with a 5% methanol in water solution. After 24 hours, the methanol content of the de-ionized water was evaluated by $^1$H NMR, and the methanol concentration of the water was determined by comparison of the integral of the methanol CH$_3$ resonance with a series of standard solutions of known concentration.
Room temperature ionic conductivities were measured using a Hewlett Packard 4192A LF impedance analyzer at a potential of 0.1 V and an alternating current frequency range of 5 Hz to 1 MHz. The instrument set-up is described elsewhere.

6.2.3 Synthesis of poly[5-norbornene-2-methoxy-pentakis(chloro) cyclotriphosphazene] \([N_3P_3Cl_5(OC\text{H}_2\text{C}_7\text{H}_{10})]_n\) (6.2)

Synthesis of 5-norbornene-2-methoxy-pentakis(chloro)cyclotriphosphazene (6.1) was carried out according to a literature procedure\(^{17}\). The complete synthetic scheme is shown in Figure 6-2. 50 g (114.8 mmol) of 6.1 was dissolved in 500 mL dry dichloromethane. Polymerization was accomplished by the rapid addition of 0.472 g (574 µmol) bis(tricyclohexylphosphine)benzylidene ruthenium (IV) chloride (Grubbs 1\(^{st}\) generation catalyst) dissolved in 10 mL dry dichloromethane. When the solution had become sufficiently viscous (approximately 30 s), the polymerization was terminated by the rapid addition of excess (1 mL) of ethyl vinyl ether.
Figure 6-1: Methanol permeability apparatus
Figure 6-2: Synthesis of pendant cyclic phosphazene polymers.
6.2.4 Synthesis of poly[5-norbornene-2-methoxy-pentakis(3-methylphenoxy) cyclotriphosphazene] [N₃P₃(OCH₂C₇H₁₀)(OPhCH₃)₅]ₙ (6.3)

Sodium metal (13.47 g, 586 mmol) was suspended in 500 mL of dry THF. The reaction mixture was cooled to 0 °C, and excess (64 g, 593 mmol) m-cresol was added. Upon complete reaction, as evidenced by the total disappearance of the sodium metal, a clear and colorless solution was formed. This was rapidly added to a solution of 50 g of 6.2 in dichloromethane via a cannula, which resulted in precipitation of copious amounts of sodium chloride. To increase the boiling temperature of the reaction mixture, 500 mL dry dioxane was added via a cannula, and the reaction mixture was then heated under reflux. The progress of the reaction was monitored by ³¹P NMR, and was found to be complete after 7 days. The product was purified by precipitation into pH 3 water, followed by precipitations into neutral water, ethanol, and hexanes (twice). The polymer was dried under vacuum to yield a dark brown, adhesive, rubbery material. Yield 48.4g (53%).

6.2.5 Synthesis of poly[5-norbornane-2-methoxy-pentakis(3-methylphenoxy) cyclotriphosphazene] [N₃P₃(OCH₂C₇H₁₂)(OPhCH₃)₅]ₙ (6.4)

The hydrogenation of polymer 6.3 was accomplished by use of a modified literature procedure. 30 g of 6.3 (37.8 mmol) were dissolved in 500 mL anhydrous p-xylene. To this viscous solution was added a large excess of p-toluenesulfonylhydrazide (70.45g, 378 mmol). The resultant slurry was heated and the p-toluenesulfonylhydrazide
became soluble at around 90 °C. The solution was then heated to between 110 and 115 °C for 2 hours, during which time there was vigorous gas evolution. After 2 hours, the solution was cooled and filtered to remove the bulk of the excess p-toluenesulfonylhydrazide, the remainder of which was removed by precipitation of the polymer into methanol three times. The polymer was dried under vacuum to yield an amber solid. Yield 20.76 g (69%).

6.2.6 Sulfonation of poly[5-norbornane-2-methoxy-pentakis(3-methylphenoxy) cyclotriphosphazene] \([\text{N}_3\text{P}_3(\text{OCH}_2\text{C}_7\text{H}_{12})(\text{OPhCH}_3)_5]_n\) (6.4)

A standard solution of sulfur trioxide was prepared by dissolution of 40 g sulfur trioxide in 475.43 g of 1,2-dichloroethane to yield a 1.32 M solution. Samples of polymer 6.4 (0.75 g) were dissolved in 30 mL of 1,2-dichloroethane, and were sulfonated to different degrees by dropwise addition of aliquots of the sulfur trioxide solution at room temperature. The amounts of reagents used are outlined in Table 6-1. These amounts take into account the fact that the first 0.32 equivalents of sulfur trioxide are consumed by reaction with the nitrogen atoms in the phosphazene rings. Upon addition of the sulfur trioxide, the polymer precipitated from solution, and turned black. The reactions were allowed to proceed for 2.5 hours, after which time the reactions were quenched by addition of 10 mL of a saturated solution of sodium hydroxide in a 1:1 mixture of water and ethanol. The solvent was stripped under reduced pressure, and the dry polymers were soaked in 0.1 M hydrochloric acid for 24 hours. The polymers were then recovered by vacuum filtration and washed with de-ionized water until the filtrate had a neutral pH. The polymers were dried under vacuum, and films were cast from \(N, N-\)
dimethylacetamide. These films were then crosslinked by exposure to 20 MRad gamma irradiation from a $^{60}$Co source.

6.3 Results and discussion

The synthesis of polymer 6.3 was successful, and a reasonable yield was obtained. The identity of the product was confirmed by $^1$H and $^{31}$P NMR spectroscopy. A molecular weight of 193 kDa and a PDI of 2.7 were found by GPC. The $T_g$ of the polymer was found to be 2 °C by DSC.

The backbone of polymer 6.3 possesses carbon-carbon double bonds. These bonds are sensitive towards reaction with sulfur trioxide, and would also be unstable to conditions within a fuel cell due to the formation of hydroperoxy radicals. To alleviate these concerns, polymer 6.3 was hydrogenated to yield polymer 6.4.

The hydrogenation reaction proceeds by the generation of diimide in situ via the thermal decomposition of $p$-toluenesulfonylhydrazide. The hydrogenation reaction was facile and effective, as evidenced by the disappearance of the characteristic resonance at $\delta = 5.25$ ppm in the $^1$H NMR spectrum (Figure 6-3), and the disappearance of the alkene stretching frequency of 1655 cm$^{-1}$ in the infrared spectrum (Figure 6-4).
Table 6-1: Sulfonation of pendant cyclic phosphazene polymers.

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<th>Sample</th>
<th>Target sulfonation %</th>
<th>Volume SO₃ solution (mL)</th>
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<td>6.9</td>
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</table>
Figure 6-3: $^1$H NMR spectra of A: polymer 6.3 and B: polymer 6.4 (hydrogenated).
Figure 6-4: FT-IR spectra of polymers 6.3 (norbornene polymer) and 6.4 (hydrogenated polymer).
A molecular weight of 190 kDa and a PDI of 2.6 were found for polymer 6.4 which, given the margin of error of the instrument, are essentially unchanged from the non-hydrogenated polymer. The $T_g$ of the polymer was found to be 0 °C. Given that free rotation of the backbone of the polymer after hydrogenation is possible, a lower $T_g$ might have been expected. However, the $T_g$ of the polymer is probably largely determined by the steric bulk of the pendant cyclic phosphazene units.

The sulfonation of polymer 6.4 was carried out by use of a modified synthetic procedure that was developed for sulfonation of poly[bis(aryloxy)phosphazenes]. The fact that the polymers turned very dark during the sulfonation process indicates that there was a reaction between sulfur trioxide and the polymer backbone in addition to a reaction with the aryloxide side units on the cyclic phosphazene. This hypothesis is borne out by the fact that the measured IECs of the sulfonated polymers were much lower than expected (Table 6-2). The sulfonated polymers still had good mechanical properties however, thus films of these materials were cast onto polypropylene plates from solutions of 0.25 g of each sulfonated polymer in 2 mL of N,N-dimethylacetamide. The films were dried in a vacuum oven at room temperature for 24 hours, and at 50 °C for 24 hours. The films were recovered, and the water uptake of each film was determined by comparison of the dry mass of each film and the fully hydrated mass of each film. The water uptake was calculated by use of Eq. 6.1.

$$ q_w = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \times 100 $$  \hspace{1cm} 6.1

Water uptake percentages are reported in Table 6-3.
Table 6-2: IECs of sulfonated polymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>IEC (m equivs g⁻¹)</th>
<th>Theoretical IEC (m equivs g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>0.237</td>
<td>0.888</td>
</tr>
<tr>
<td>6.6</td>
<td>0.267</td>
<td>1.16</td>
</tr>
<tr>
<td>6.7</td>
<td>0.397</td>
<td>1.42</td>
</tr>
<tr>
<td>6.8</td>
<td>0.129</td>
<td>1.68</td>
</tr>
<tr>
<td>6.9</td>
<td>–</td>
<td>1.56</td>
</tr>
</tbody>
</table>
Table 6-3: Water uptake of sulfonated polymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>IEC (m equivs g⁻¹)</th>
<th>Water uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>0.237</td>
<td>13.6</td>
</tr>
<tr>
<td>6.6</td>
<td>0.267</td>
<td>47.1</td>
</tr>
<tr>
<td>6.7</td>
<td>0.397</td>
<td>54.8</td>
</tr>
<tr>
<td>6.8</td>
<td>0.129</td>
<td>49.3</td>
</tr>
<tr>
<td>6.9</td>
<td>–</td>
<td>149.1</td>
</tr>
</tbody>
</table>
With the exception of polymer 6.8, the water uptake values increase as the IEC of the polymers increase. This is to be expected because, with a greater incorporation of sulfonate groups, a higher IECs and greater hydrophilicity are realized. The IEC and water uptake values for polymer 6.8 seem to be inconsistent compared to the other sulfonated polymers. A potential explanation for this is that the high level of sulfonation resulted in degradation of the polymer. Consequently, polymer 6.9 was synthesized with a target percent sulfonation of 27.5%. This level of sulfonation was chosen to be higher than polymer 6.7 to achieve a higher IEC and better conductivity, but not as high as polymer 6.8 to avoid any possible degradation of the polymer. However, an IEC of this material could not be detected, and the water uptake was excessive. This could also indicate degradation.

The through-plane ionic conductivities of films of the sulfonated polymers were measured by electrochemical impedance spectroscopy. Through-plane conductivity is a more realistic measurement of ionic conductivity in fuel cell membranes because, in an actual fuel cell, ionic conductivity is in a through-plane fashion. The room temperature ionic conductivities are reported in Table 6-4.

The ionic conductivities of the sulfonated polymers are quite low. This can be explained by the low IECs of the polymers. The highest measured ionic conductivity was for polymer 6.9 (4.81 x 10⁻⁴ S cm⁻¹), which is around two orders of magnitude lower than the commercial PEM material Nafion. This conductivity value, although low, is higher than some other PEM materials¹⁹-²¹ and thus this polymer is still a potentially viable PEM material.
Table 6-4: Ionic conductivities of sulfonated polymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity at 20 °C (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>2.79 x 10⁻⁷</td>
</tr>
<tr>
<td>6.6</td>
<td>4.77 x 10⁻⁵</td>
</tr>
<tr>
<td>6.7</td>
<td>3.46 x 10⁻⁵</td>
</tr>
<tr>
<td>6.8</td>
<td>2.65 x 10⁻⁶</td>
</tr>
<tr>
<td>6.9</td>
<td>4.81 x 10⁻⁴</td>
</tr>
</tbody>
</table>
The methanol permeabilities were measured as described above, and were calculated assuming that Fick’s first law (steady state diffusion) is applicable. Fick’s law can be simplified to the form shown in Eq. 6.2, where \( C_m \) is the concentration of methanol in the standard solution, \( C_w \) is the concentration of methanol in water after diffusion, and \( x \) is the thickness of the membrane.

\[
J_m = -D \frac{dC}{dx} = D \cdot \frac{C_m - C_w}{x} \tag{6.2}
\]

A mathematical solution to this equation is shown in Eq. 6.3, rearrangement of which yields the usable form of the equation, shown in Eq. 6.4, where \( D \) is the diffusion coefficient, \( V \) is the volume of solution, \( x \) is the thickness of the membrane, \( A \) is the cross-sectional area of the membrane, \( t \) is the time in minutes, \( C_w(t) \) is the concentration of methanol in the water after time \( t \), and \( C_m(0) \) is the concentration of methanol in the standard solution at \( t=0 \).

\[
C_w(t) = \frac{1}{2} C_m(0) \left( 1 - e^{-\frac{2ADt}{Vx}} \right) \tag{6.3}
\]

\[
D = -\frac{Vx}{2At} \ln \left( 1 - \frac{2C_w(t)}{C_m(0)} \right) \tag{6.4}
\]

The methanol permeabilities of polymers 6.5 – 6.9 are reported in Table 6-5. The diffusion coefficients follow the trend of the IEC values, and these data indicate that the methanol permeabilities of these materials are very low – typically an order of magnitude lower than for Nafion. This can be explained by the low IECs (and therefore the low ionic strength) of these materials. The methanol permeability for polymer 6.9 was abnormally high and this fact again suggests some degree of degradation.
Table 6-5: Methanol permeabilities of sulfonated polymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diffusion coefficient (x $10^{-7}$ g cm$^{-2}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>1.47</td>
</tr>
<tr>
<td>6.6</td>
<td>1.66</td>
</tr>
<tr>
<td>6.7</td>
<td>3.55</td>
</tr>
<tr>
<td>6.8</td>
<td>2.21</td>
</tr>
<tr>
<td>6.9</td>
<td>394</td>
</tr>
</tbody>
</table>
6.4 Conclusions

Organic polymers with pendant cyclic phosphazene species were synthesized and examined for use as proton conductive fuel cell membrane materials. The synthesis of these polymers was accomplished by polymerization of a mono-substituted cyclotriphosphazene, followed by post-functionalization with 3-methylphenoxy groups. This route proved effective, and the reaction time of the polymerization was very short.

Hydrogenation of the polymer backbone was accomplished via chemical means, and was facile and effective, and the use of catalysts and high-pressure hydrogen gas was avoided.

Sulfonation reactions were carried out with the use of sulfur trioxide. The resultant polymers had lower IECs and, as a consequence, lower conductivities than expected. This was attributed to side reactions of the sulfur trioxide with the polymer backbone. A sulfonation percentage of 27.5% gave the highest conductivity of $4.81 \times 10^{-4}$ S cm$^{-1}$, although this polymer likely suffered some degradation. The methanol permeabilities of these polymers were also low, and were generally of the order of $10^{-7}$ g cm$^{-2}$ min$^{-1}$. This is roughly an order of magnitude lower than the commercial polymer Nafion. This observation can be rationalized by the fact that the IECs (and hence ionic strengths) of these materials were low.

Although the ionic conductivities of these materials were low, their low methanol permeabilities indicate that they may be viable materials for use as proton exchange membranes in direct methanol fuel cells. However, further evaluation of these materials,
including assessment of their performance characteristics in fuel cell devices, is required to support this assertion.
6.5 References


Chapter 7

Novel anion-conductive polymer membranes for direct methanol fuel cells

7.1 Introduction

A strong impetus exists to develop new, more efficient power sources for both automotive applications and portable electronic devices. One of the most promising technologies, and the one that has attracted the most research interest, is the fuel cell.

The majority of recent fuel cell research has been devoted to proton exchange membrane (PEM) materials. A typical PEM material consists of a hydrophobic polymer with anionic groups bound to the polymer backbone. There are many examples of PEM materials, such as poly(styrene sulfonate), and the commercially available Nafion®.

However, PEM fuel cells suffer from a number of problems if methanol is used as the fuel. Methanol oxidation at the anode is relatively slow under acidic conditions\(^1\)-\(^4\). Consequently expensive, highly active oxidation catalysts, such as platinum and ruthenium, are required. These catalysts are susceptible to poisoning by carbon monoxide at low temperatures of operation\(^5\). A solution to this limitation is to operate the fuel cell at an elevated temperature – a temperature of 150 °C is considered optimal. However, this strategy causes further problems because water management at 150 °C is problematic and, although operation of a fuel cell at high pressure is possible, it is undesirable, because it would necessitate extra weight, bulk, and complexity. Furthermore, a low temperature of operation is required for portable electronic devices.
A further limitation of many PEM materials is that they suffer from high methanol permeabilities. In a direct methanol fuel cell, the minimization of methanol crossover is essential to prevent direct reaction of methanol at the cathode, which reduces the efficiency of the fuel cell. Although dilute solutions of methanol in water have been used to minimize this problem, this is an unwieldy and inefficient alternative.

A solution to these problems is to utilize anion exchange membranes (AEMs) as the polymer electrolyte. In an AEM material, a cationic species is bound to a polymer backbone, and movement of an anion, usually \( \text{HO}^- \), is responsible for conduction.

The advantages of AEMs are that the kinetics of catalytic oxidation at the anode are significantly faster than under acidic conditions\(^1\text{--}^4\). Furthermore, oxidation catalysts are typically less sensitive to poisoning under basic conditions\(^6\text{--}^9\). This means that cheaper, less active catalysts can be utilized, which would reduce the overall cost of the fuel cell. Indeed, it is often considered that the cost of fuel cells, including the cost of membrane materials and catalysts, is the main barrier to their commercialization.

A number of commercial AEM materials are available. However, relatively low IECs and high electrical resistance limits these materials\(^6\). Therefore, the synthesis of new AEM materials is investigated.

Polyphosphazenes are ideal candidates for AEM materials due to their inherent thermo-oxidative stability, and the unique ease with which their properties can be tailored. Displacement of the labile phosphorus-chlorine bonds in the macromolecular precursor poly(dichlorophosphazene) by metal alkoxide, metal aryloxide or amine nucleophiles is a well established technique – over 700 different polyphosphazenes produced by this technique are known\(^10\). Polyphosphazenes have already been shown to
be excellent PEM candidates\textsuperscript{11-13} and with appropriate side groups should be excellent AEM materials.

Thus, aryloxy polyphosphazenes with covalently attached aryl phosphonium ions were investigated. Aryloxide substituted polyphosphazenes are known to have good mechanical properties, film forming characteristics, and low methanol solubilities, and phosphonium ions are known to be thermally and chemically stable. The incorporation of phenyl phosphonium ions into polyphosphazenes is known\textsuperscript{14}, although their use as fuel cell membranes has never been investigated.

7.2 Experimental

This work was a collaborative effort between Arlin Weikel from the Department of Chemistry at the Pennsylvania State University, who was responsible for the synthesis of 10\% and 15\% phosphonium ion substituted polymers; and myself, who synthesized 15\% and 20\% phosphonium ion substituted polymers, measured water uptake values and ionic conductivities, and collected molecular weight and differential scanning calorimetry data.

7.2.1 Materials

Hexachlorocyclotriphosphazene was obtained from Ethyl Corp./Nippon Fine Chemical and was recrystallized from heptane and sublimed at 30 °C at 0.01 mm Hg before use. Poly(dichlorophosphazene) was prepared according to a literature
procedure\textsuperscript{15}. Sodium (ACS reagent grade, Aldrich), 4-bromophenol (99\%, Aldrich), tert-
butyllithium (1.7 M in pentane, Aldrich), \(p\)-chlorodiphenylphosphine (98\%, Aldrich), 1-
bromobutane (99\%, Aldrich), sodium hydroxide (ACS reagent grade, EMD), hexane
(98.5\%, EMD), ethanol (99.5\%, Pharmco), and \(N,N\)-dimethylacetamide (99\%, Aldrich)
were used as received. 3-Methylphenol (97\%, Aldrich) was distilled from calcium
chloride under reduced pressure before use. Tetrahydrofuran (99.99\%, EMD) was dried
by passage through Glass Contour alumina columns before use\textsuperscript{16}. De-ionized water was
obtained from a Barnstead Nanopure Diamond water purification system. All reactions
were carried out under an inert atmosphere of nitrogen.

7.2.2 Equipment

High field \(^1\text{H}\) (360.14 MHz) and \(^{31}\text{P}\) (145.79 MHz) NMR spectra were recorded
by use of a Bruker Avance-360 NMR spectrometer. \(^1\text{H}\) NMR spectra were referenced to
external tetramethylsilane; \(^{31}\text{P}\) NMR spectra were referenced to external 85\% aqueous
phosphoric acid. Thermal data were obtained by use of a TA Instruments Q10
differential scanning calorimeter (DSC), calibrated with indium, water, and cyclohexane
standards. Molecular weights and polydispersity indices were estimated by use of a
Hewlett-Packard 1090 gel permeation chromatograph equipped with a HP-1047A
refractive index detector, and Phenomenex Phenogel 10 \(\mu\)m linear columns calibrated
with polystyrene standards. All samples were eluted at a flow rate of 1.0 mL min\(^{-1}\) at 40
\(\circ\text{C}\) in a 0.3 wt \% solution of tetra-\(n\)-butylammonium nitrate in stabilized THF (EMD).
7.2.3 Synthesis of m-cresoxy/p-bromophenoxy substituted polyphosphazenes

The synthesis of m-cresoxy/p-bromophenoxy substituted polymers was accomplished by means of a modified literature procedure\textsuperscript{17}. The general synthetic scheme is shown in Figure 7-1, and is outlined below.

Solutions of sodium m-cresoxide were prepared by the suspension of sodium metal in 100 mL of dry THF, followed by the addition of m-cresol. Upon complete reaction, a clear and colorless solution was formed. Solutions of sodium 4-bromophenoxide were prepared by the suspension of sodium metal in 100 mL of dry THF, followed by the addition of 4-bromophenol. Upon complete reaction, a white precipitate was formed.

5 g samples of poly(dichlorophosphazene) were dissolved in 500 mL of dry THF in the presence of 0.5 g tetrabutylammonium bromide. A previously prepared sodium m-cresoxide salt solution was added to the polymer solution via a cannula, which resulted in the precipitation of sodium chloride from solution. The reaction was allowed to proceed at room temperature for 1 hour after which time the reaction mixture was transferred to a high-pressure reactor via a cannula. A respective 4-bromophenoxide salt solution was added to the reaction mixture via a cannula, and the reaction vessel was sealed. The reaction proceeded at 150 °C for 26 hours.
Figure 7-1: Synthesis of $m$-cresoxy/$p$-bromophenoxy substituted polyphosphazenes.
The polymers were purified by successive precipitations into pH 3 water, neutral water, ethanol, and hexane (twice). The polymers were dried under vacuum.

$^1$H NMR (THF, $\delta$, ppm): 1.95 (br, OPhCH$_3$), 6.8 (br, OPhCH$_3$ and OPhBr). $^{31}$P NMR (THF, $\delta$, ppm): -16.2 (br, $P$(OPhCH$_3$)(OPhBr)), -19.7 (br, $P$(OPhCH$_3$)$_2$).

The quantities of reagents used are detailed in Table 7-1.

### 7.2.4 Synthesis of $m$-cresoxy/$p$-phenylphosphonium ion substituted polyphosphazenes

The $m$-cresoxy/$p$-bromophenoxy polymers were phosphonated by use of a modified literature procedure. The general reaction scheme is shown in Figure 7-2, and is outlined below. The quantities of reagents used are detailed in Table 7-2.

2 g samples of polymers 7.1 – 7.4 were dissolved in 300 mL dry THF. Each solution was cooled to -78 °C, and 2.5 equivalents per 4-bromophenoxy side group of 1.7 M tert-butyllithium were added dropwise from a syringe. Addition of the tert-butyllithium resulted in the formation of a white precipitate. Upon complete addition of the tert-butyllitium, a pale yellow-green solution formed. The reactions were allowed to proceed at -78 °C for 1 hour, after which time 5 equivalents of chlorodiphenylphosphine were rapidly added from a syringe. The solutions instantaneously tuned clear.
Table 7-1: Synthesis of \( m \)-cresoxy/\( p \)-bromophenoxy substituted polymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sodium ( m )-cresoxy salt</th>
<th>Sodium ( 4 )-bromophenoxy salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass sodium (g)</td>
<td>Mass ( m )-cresol (g)</td>
<td>Mass sodium (g)</td>
</tr>
<tr>
<td>[NP(OPhCH( <em>3 )]</em>{1.8}(OPhBr)_{0.2}]_n ( (7.1) )</td>
<td>1.78</td>
<td>8.38</td>
</tr>
<tr>
<td>[NP(OPhCH( <em>3 )]</em>{1.7}(OPhBr)_{0.3}]_n ( (7.2) )</td>
<td>1.69</td>
<td>7.91</td>
</tr>
<tr>
<td>[NP(OPhCH( <em>3 )]</em>{1.6}(OPhBr)_{0.4}]_n ( (7.3) )</td>
<td>1.59</td>
<td>7.45</td>
</tr>
<tr>
<td>[NP(OPhCH( <em>3 )]</em>{1.5}(OPhBr)_{0.5}]_n ( (7.4) )</td>
<td>1.49</td>
<td>6.98</td>
</tr>
</tbody>
</table>
After the reactions had been allowed to warm slowly to room temperature, 10 equivalents of 1-bromobutane were added from a syringe. The solutions were heated under reflux for 24 hours, after which time the solutions were cooled, and poured into 12-14,000 molecular weight cut-off dialysis membranes, and the solutions dialyzed against THF. The dialysis medium was refreshed four times, at intervals of 24 hours. After dialysis was complete, the polymers were precipitated into 1 M NaOH (aq) solutions, and then rinsed with de-ionized water until a neutral pH was achieved.

$^{31}$P NMR (THF, δ, ppm): 24.0 (s, [OPhP(Ph$_2$Bu)$^+-$OH), -16.2 (br, $P$(OPhCH$_3$)(OPhBr), -19.7 (br, $P$(OPhCH$_3$)$_2$).
Figure 7-2: Synthesis of phenylphosphonium ion substituted polyphosphazenes
Table 7-2: Synthesis of phenylphosphonium ion substituted polyphosphazenes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Vol. tBuLi solution (mL)</th>
<th>Mass PPhCl (g)</th>
<th>Mass BuBr (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5</td>
<td>2.16</td>
<td>1.62</td>
<td>2.02</td>
</tr>
<tr>
<td>7.6</td>
<td>3.17</td>
<td>2.38</td>
<td>2.95</td>
</tr>
<tr>
<td>7.7</td>
<td>4.13</td>
<td>3.10</td>
<td>3.85</td>
</tr>
<tr>
<td>7.8</td>
<td>5.04</td>
<td>3.78</td>
<td>4.70</td>
</tr>
</tbody>
</table>
7.3 Results and discussion

The synthesis of the \textit{m}-cresoxy/\textit{p}-bromophenoxy substituted polymers was successful. The side group ratios were confirmed by $^1$H and $^{31}$P NMR spectroscopy. In the $^1$H NMR spectrum for each polymer, there was a broad resonance centered at 6.8 ppm, which corresponds to the aromatic protons of both the \textit{m}-cresoxy and \textit{p}-bromophenoxy side groups; and a broad resonance centered at 1.95 ppm, which corresponds to the methyl protons of the \textit{m}-cresoxy groups. In the $^{31}$P NMR spectrum for each polymer there were broad resonances at -19.7 ppm, which corresponds to a bis \textit{m}-cresoxy substituted phosphorus atom, and at -16.2 ppm, which corresponds to a \textit{m}-cresoxy/\textit{p}-bromophenoxy substituted phosphorus atom.

The molecular weights of polymers 7.1 – 7.4 were determined by GPC, and are reported in table (Table 7-3). The PDIs of these materials is broad, as is usual for polyphosphazenes made via the ring-opening polymerization of hexachlorocyclotriphosphazene.
Table 7-3: Molecular weight data for polymers 7.1 – 7.4

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn ( \times 10^3 )</th>
<th>Mw ( \times 10^3 )</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1</td>
<td>114</td>
<td>652</td>
<td>5.72</td>
</tr>
<tr>
<td>7.2</td>
<td>91</td>
<td>295</td>
<td>3.23</td>
</tr>
<tr>
<td>7.3</td>
<td>107</td>
<td>539</td>
<td>5.06</td>
</tr>
<tr>
<td>7.4</td>
<td>193</td>
<td>391</td>
<td>2.02</td>
</tr>
</tbody>
</table>
The phosphonation and subsequent alkylation reactions were successful, as evidenced by the appearance of a sharp singlet peak at 24 ppm in the $^{31}$P NMR spectrum for each polymer. This chemical shift is consistent with a tertiary phosphonium ion, and is in agreement with literature values$^{14}$. The complete phosphonation and complete formation of the phosphonium ions were confirmed by the fact that the peak integrals in the $^{31}$P NMR spectra for the phosphonium ion and the $p$-bromophenoxy substituted phosphorus atoms were identical.

The glass transition temperatures, water uptake values, and ionic conductivities of polymer 7.5 – 7.8 were ascertained, and are reported in Table 7-4. The $T_g$s of these polymers are consistent with $m$-cresoxy substituted polyphosphazenes, and increase as the incorporation of the phenylphosphonium ion increases. This is attributable to the steric bulk of the side group. All of these $T_g$s are acceptably low.

The water uptake values seem anomalous, and decrease as the amount of phenylphosphonium ion incorporation increases. Multiple measurements were made, but similar results were found each time. The water uptake for polymer 7.8 does not fit this trend, however, and is a more reasonable value of 60.5%.
Table 7-4: Characterization data of phenylphosphonium ion functionalized polymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ ($^\circ$C)</th>
<th>Water swelling (%)</th>
<th>Conductivity (S cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5</td>
<td>-18</td>
<td>45.2</td>
<td>$7.7 \times 10^{-8}$</td>
</tr>
<tr>
<td>7.6</td>
<td>-15</td>
<td>37.1</td>
<td>$8.6 \times 10^{-7}$</td>
</tr>
<tr>
<td>7.7</td>
<td>-3</td>
<td>25.8</td>
<td>$5.2 \times 10^{-7}$</td>
</tr>
<tr>
<td>7.8</td>
<td>12</td>
<td>60.5</td>
<td>$1.5 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
The ionic conductivities of these polymers are low. The highest measured conductivity was $1.5 \times 10^{-6} \text{ S cm}^{-1}$, which is about 4 orders of magnitude lower than anticipated. A possible explanation of this is that no IECs were detected for these materials, which indicates that the ion-exchange reaction to exchange bromide ions with hydroxide ions does not proceed adequately. This hypothesis is supported by the absence of any peaks in the $^1\text{H}$ NMR spectra that would indicate presence of a hydroxide species and the anomalous water uptake values. The measured ionic conductivities were therefore probably for conduction of bromide ion which may explain why the conductivities were so low. Further experiments to fully ion-exchange these materials are required.

7.4 Conclusions

A series of polyphosphazenes with phenylphosphonium ion side groups were synthesized and evaluated for use as anionic conductive materials. $T_g$s of these materials were acceptably low, however the ionic conductivities of these materials were poor. This is attributed to incomplete ion-exchange reactions, and further investigations of these materials are required.
7.5 References


Chapter 8

The state of water in proton exchange membranes

8.1 Introduction

There is an impetus to develop new power technologies for both stationary and mobile applications, especially for automobile fuel cells. This imperative is driven by the following reasons: a primary need is to curtail carbon dioxide emissions from automobile engines, and reduce the impact that the burning of fossil fuels has on the levels of atmospheric carbon dioxide – a suspected key factor in global warming. A reduced dependence on foreign oil imports is another critical factor, both in terms of economics and politics. Increased power conversion efficiency is also desired.

Currently, the most attractive technology, and the one that has stimulated the most research interest, is the hydrogen/oxygen fuel cell. A hydrogen/oxygen fuel cell has the advantage that atmospheric oxygen can be used as the oxidant, and the waste stream consists only of water vapor.

The most critically important part of any fuel cell is the electrolyte. The electrolyte must separate the two halves of the fuel cell and allow proton conduction. Thus, it must be an ionic conductor and function as an electronic insulator. Also it needs to have good mechanical and chemical stability and low permeability to hydrogen and oxygen.
Current fuel cell research interest has centered around polymer electrolyte membrane (PEM) fuel cells, because these are considered to offer a good combination of performance, cost, and energy density on a watt hours per kilogram basis\(^1\). The benchmark PEM material is Nafion®, the proton conductivity of which is in the range of 100 mS cm\(^{-1}\) at 80 °C – a value which is yet to be bettered.

However, Nafion® is not without its problems. Water management is a known issue, due to both electro-osmotic drag and dehydration, accompanied by a loss of mechanical stability, at temperatures above 80 °C.

Water is essential for proton conductivity in Nafion®, and a great deal is known about the role of water and proton conductivity in this material. Several groups have studied the nature of water in hydrated Nafion membranes\(^2-7\), and have shown that water exists in two major states – tightly bound water and “free” water. Other studies have investigated how different cations in Nafion affect the state of water and the degree of water uptake\(^4,8\). The conductivity of Nafion as a function of water content has also been investigated\(^9-11\), and it was shown that conductivity increased with increased water uptake. Diffusion rates in hydrated Nafion membranes were studied by solid state NMR techniques\(^3,12,13\). Based on these results, mechanisms of proton conduction and the role of water have been suggested\(^14-18\).

A great deal of effort has been spent both in academia and by private industry to improve upon Nafion®. Numerous materials have been evaluated for use as PEMs such as polystyrene based polyelectrolytes\(^19-26\), poly(arylene ether)s\(^27-32\), poly(imide)s\(^33-35\), poly(phenylene oxide)s and other high performance polymers\(^36-41\), poly(benzimidazole)s\(^42-46\), and polyphosphazenes\(^47,48\). The majority of these are
sulfonated materials, although there are examples of phosphonated and sulfonimide based membranes.

However, the development of alternative materials has been a slow process, and there have been few improvements over the properties of Nafion®. This can be attributed to the fact that comparatively little is known about the role of water in these polymer systems.

The state of water in hydrated PEMs can be assessed via the measurement of $^2$H T$_1$ relaxation times with the use of solid state NMR techniques. NMR relaxation measurements allow observation of molecular reorientational dynamics. Recent work utilized $^2$H T$_1$ relaxation measurements to show that room temperature ice-like water is present in a variety of $^2$H$_2$O-hydrated porous solids, including kanemite, zeolite A, highly porous glass, silica gel, and the hydration products of tricalcium silicate. A similar approach can be applied to PEMs.

Hence, a study to evaluate the state of water in polyphosphazene based proton exchange membranes was performed. Polyphosphazenes are ideal candidates for this study due to the unique ease with which their properties can be changed through variations to the basic synthesis processes. Furthermore, polyphosphazenes have already been shown to be excellent candidates for PEMs.
8.2 Experimental

This work was a collaborative effort between Dr. Elena Chalkova from the Energy Institute at the Pennsylvania State University, who graciously supplied samples of Nafion; Bernie O’Hare from the Department of Chemistry at the Pennsylvania State University, who measured $^2$H $T_1$ relaxation times via solid state NMR techniques; and myself, who performed all the synthetic work, and was responsible for the hydration of samples and the determination of their water uptake values.

8.2.1 Materials

Poly(dichlorophosphazene) was prepared according to literature procedures\textsuperscript{13}. Sodium hydride (95%, Aldrich), $p$-cresol (99%, Aldrich), 4-methoxybenzenesulfonyl chloride (99%, Aldrich), sodium ethanethiolate (80%, Aldrich), trifluoromethane sulfonamide (98 %, TCI), methanol (99.8%, EMD), chloroform (99.8%, EMD), hydrochloric acid (36.5-38.0%, EMD), $N,N$-dimethylformamide (99.8%, Alfa Aesar), and deuterium oxide (Cambridge Isotope Labs, 99.9%) were used as received. Tetrahydrofuran was purchased from EMD Chemicals and distilled from sodium benzophenone ketyl prior to use. Acetone was purchased from EMD and distilled from calcium sulfate prior to use. Triethylamine was purchased from EMD and distilled from calcium hydride prior to use. All reactions were performed under an atmosphere of dry argon.
8.2.2 Instruments

High field $^1$H (360.14 MHz) NMR spectra were recorded using a Bruker AMX-360 NMR spectrometer. $^2$H solid state NMR spectra were recorded on a Chemagnetics CMX-300 spectrometer by use of the T$_1$ inversion recovery experiment. Masses were recorded from an Ohaus Explorer E10640 balance.

8.2.3 Synthesis of sulfonimide substituted polyphosphazene

The synthesis of sulfonimide substituted polymers is described elsewhere$^{54}$. The reagent quantities used to synthesize a 17% sulfonimide/83% p-cresoxy polyphosphazene are listed in Table 8-1. The polymer was purified by dialysis against isopropanol in 12-14,000 molecular weight cut-off dialysis membrane, followed by precipitation into hexane. The ratio of side groups and the purity of the polymer were confirmed by $^1$H NMR. The polymer was cast into a film from a solution of N,N-dimethylacetamide.

8.2.4 Hydration of PEMs

Samples of the sulfonimide substituted polyphosphazene and Nafion were immersed in $^2$H$_2$O for 7 days to ensure that they were completely hydrated. Samples of each polymer (0.2 g) were then placed under high vacuum in a desiccator to evaporate water from the materials. Samples were removed at five minute intervals to achieve a range of hydration values. The hydrated films were then sealed in glass NMR tubes, and the $^2$H T$_1$ relaxation times were measured by solid state NMR techniques.
Table 8-1: Synthesis of 17% sulfonimide/83% p-cresoxy polymer: amounts of reagents used.

<table>
<thead>
<tr>
<th></th>
<th>(NPCl₂)₂</th>
<th>50% sodium p-cresoxide salt</th>
<th>17% sodium sulfonimide salt</th>
<th>50% sodium p-cresoxide salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (g)</td>
<td>4.00</td>
<td>0.83</td>
<td>0.28</td>
<td>0.83</td>
</tr>
<tr>
<td>mmol</td>
<td>34.5</td>
<td>34.5</td>
<td>11.7</td>
<td>34.5</td>
</tr>
<tr>
<td>(NPCl₂)₂</td>
<td></td>
<td>NaH</td>
<td>NaH</td>
<td>NaH</td>
</tr>
<tr>
<td>50% sodium</td>
<td></td>
<td>p-cresol</td>
<td>sulfonimide</td>
<td>p-cresol</td>
</tr>
<tr>
<td>p-cresoxide</td>
<td></td>
<td></td>
<td>3.83</td>
<td>3.72</td>
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<tr>
<td>salt</td>
<td></td>
<td></td>
<td>34.5</td>
<td>34.5</td>
</tr>
<tr>
<td>17% sodium</td>
<td></td>
<td></td>
<td>11.7</td>
<td>34.5</td>
</tr>
<tr>
<td>sulfonimide</td>
<td></td>
<td></td>
<td>34.5</td>
<td>34.5</td>
</tr>
<tr>
<td>salt</td>
<td></td>
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<tr>
<td>salt</td>
<td></td>
<td></td>
<td>34.5</td>
<td>34.5</td>
</tr>
</tbody>
</table>
8.3 Results and discussion

The $^2$H T$_1$ relaxation times for the sulfonimide substituted polyphosphazene and Nafion are reported in Table 8-2. The $^2$H T$_1$ relaxation time for the fully hydrated phosphazene sample is much longer than for fully hydrated Nafion. This is indicative that the phosphazene absorbs much more water – an observation that is supported by the gravimetric water uptake data for these polymers.$^{54}$

The percent content of solid-state water was calculated according to Eq. 8.1, where $\chi_{\text{solid}}$ is the mole fraction of solid water, $\chi_{\text{liquid}}$ is the mole fraction of liquid water, $T_{1,\text{solid}}$ is the T$_1$ relaxation time of solid water (4 to 10 ms depending on the magnetic field) and $T_{1,\text{liquid}}$ is the T$_1$ relaxation time of liquid water (400 ms independent of the magnetic field).

$$\frac{1}{T_{\text{observed}}} = \frac{1}{T_{1,\text{solid}}} + \frac{\chi_{\text{liquid}}}{T_{1,\text{liquid}}}$$  \hspace{1cm} \text{8.1}$$

Fully hydrated Nafion has a greater mole fraction of ice-like water in it than the polyphosphazene, although this is a consequence of the fact that Nafion absorbs less water. Samples of Nafion and the polyphosphazene that have similar T$_1$ relaxation times have similar mole fractions of ice-like water. This indicates that there are similar attractive forces between Nafion and water and the sulfonimide substituted polyphosphazene and water, and that the formation of surface ice-like water affects both polymers in a similar way. This is supported by the fact that these polymers have similar
conductivities. However, it does not necessarily follow that all proton exchange membrane materials behave in the same way, and further studies to assess the state of water in other materials is required. Moreover, a systematic study of the factors that influence the state of water and whether the state of water influences proton conductivity is required.

8.4 Conclusions

In an effort to help elucidate the role of water in proton exchange membrane materials, $^2$H $T_1$ relaxation times of in D$_2$O swollen membranes were measured. A 17% sulfonimide/83% $p$-cresoxy substituted polyphosphazene and Nafion were compared. It was found that the amount of solid ice-like water present in the system was independent of the amount of free water in the system, and that both polymers had similar amounts of ice-like water present in them. This can be accounted for by the fact that both polymers have similar conductivities. Further studies are required to assess the usefulness of this technique in the determination of the role of water in proton conduction.
Table 8-2: $^2$H $T_1$ relaxation times as a function of percent dehydration

<table>
<thead>
<tr>
<th>Sample</th>
<th>% dehydration</th>
<th>$T_1$ (ms)</th>
<th>% solid water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfonimide substituted polyphosphazene</td>
<td>0.0</td>
<td>232.1</td>
<td>1.1%</td>
</tr>
<tr>
<td></td>
<td>26.5</td>
<td>228.7</td>
<td>1.1</td>
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<tr>
<td></td>
<td>44.8</td>
<td>157.3</td>
<td>2.3</td>
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<td></td>
<td>62.1</td>
<td>54.34</td>
<td>9.7</td>
</tr>
<tr>
<td></td>
<td>61.0</td>
<td>13.4</td>
<td>43.9</td>
</tr>
<tr>
<td></td>
<td>64.0</td>
<td>27.8</td>
<td>20.4</td>
</tr>
<tr>
<td></td>
<td>64.2</td>
<td>10.8</td>
<td>54.9</td>
</tr>
<tr>
<td></td>
<td>66.2</td>
<td>8.5</td>
<td>70.1</td>
</tr>
<tr>
<td>Nafion</td>
<td>0</td>
<td>163.9</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>8.9</td>
<td>43.1</td>
<td>12.6</td>
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<tr>
<td></td>
<td>9.8</td>
<td>38.1</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>10.5</td>
<td>27.7</td>
<td>20.5</td>
</tr>
</tbody>
</table>
8.5 References


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44. Glipa, X.; El Haddad, M.; Jones, D. J.; Roziere, J. *Solid State Ionics 
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Appendix A

An NMR study of the thermal stability of trichloro-N-silylphosphoranimine

A.1 Introduction

Polyphosphazenes are a versatile class of polymers, and the unique ease with which their properties can be customized by judicious choice of side groups makes them attractive candidates for numerous applications, including biomaterials, flame retardants, high performance elastomers, and electrolytes.

The synthesis of phosphazenes is usually accomplished through the thermal ring-opening polymerization of hexachlorocyclotriphosphazene either in the melt or in solution to yield the reactive macromolecular intermediate poly(dichlorophosphazene). This method yields high molecular weight polymers, with degrees of polymerization typically around 15,000. Although the molecular weight of poly(dichlorophosphazene) can be controlled through the addition of a Lewis acid catalyst to the polymerization\(^1-4\), there is little control over the molecular weight distribution, and polydispersities are typically broad.

For these reasons, a controlled living polymerization method was developed which allows for precise control of molecular weights and the possibility of several different polymer architectures, such as block, comb, and graft copolymers\(^5-9\). This method involves the cationic polymerization of trichloro-N-trimethylsilylphosphoranimine.
Discovery of this room temperature cationic polymerization greatly expanded the field of polyphosphazene study. The improved molecular weight control, low thermal energy input, and architectural control makes this is one of the most promising routes for commercialization of the versatile polyphosphazenes. However, storage of trichloro-\(N\)-trimethylsilylphosphoranimine is problematic – storage for moderate lengths of time, even at -25 °C under an inert atmosphere results in decomposition of the phosphoranimine to poly(dichlorophosphazene) and hexachlorocyclotriphosphazene.

Therefore, to develop the utility of phosphoranimine monomers as precursors to poly(dichlorophosphazene) further, we endeavored to study the reactions of trichloro-\(N\)-trimethylsilylphosphoranimine in 5 solvents – tetrahydrofuran, diethyl ether, dichloromethane, benzene, and toluene – at two different temperatures (21 °C and -3 °C) in an effort to identify optimal conditions for long-term storage. Formation of poly(dichlorophosphazene) and hexachlorocyclotriphosphazene were monitored as a function of time by \(^{31}\text{P}\) NMR, and the results were compared to neat samples of trichloro-\(N\)-trimethylsilylphosphoranimine at -3 °C and 21 °C respectively.

**A.2 Experimental**

This work was a collaborative effort between Lee Steely from the Department of Chemistry at the Pennsylvania State University, who synthesized and purified trichloro-\(N\)-trimethylsilylphosphoranimine, prepared NMR samples, obtained differential scanning calorimetry data, performed Karl Fischer titrimetry, and obtained \(^{31}\text{P}\) NMR spectra; and
myself, who prepared NMR samples, performed Karl Fischer titrimetry and obtained $^{31}\text{P}$ NMR spectra.

A.2.1 Materials

Lithium bis(trimethylsilyl)amide (Aldrich, 97%), phosphorus trichloride (Aldrich, 98%), sulfuryl chloride (Aldrich, 97%), and $d_6$-acetone (Cambridge Isotope Laboratories, 99.9%) were used as received. Tetrahydrofuran (EMD, 99.99%), diethyl ether (EMD, 99%), dichloromethane (99.8%, EMD), benzene (EMD, ACS reagent grade), and toluene (EMD, ACS reagent grade) were dried via passage through Glass Contour alumina drying columns before use. The water content of each solvent was evaluated via Karl Fischer titrimetry before use. All chemicals were manipulated in an argon atmosphere drybox.

A.2.2 Equipment

High field $^1\text{H}$ (360.14 MHz) and $^{31}\text{P}$ (145.79 MHz) NMR spectra were recorded by use of a Bruker Avance-360 NMR spectrometer, and spectra were referenced to external 85% phosphoric acid. Karl Fischer titrations were performed by use of a Mettler Toledo DL32 Karl Fischer coulometer. Thermal analysis was performed on a TA Instruments Q10 differential scanning calorimeter calibrated with indium, water, and cyclohexane standards.
A.2.3 Sample preparation

Trichloro-N-trimethylsilylphosphoranimine was prepared according to a literature procedure\textsuperscript{11}. After several distillations of the product, the \textsuperscript{31}P NMR spectrum consisted of one singlet at -54.74 ppm and the \textsuperscript{1}H NMR consisted of one singlet at 0 ppm. Sealed glass capillaries of deuterated acetone were prepared and oven dried then placed under vacuum to remove water from the surface of the glass and to confirm a complete seal of the capillary. NMR tubes were heated and placed under vacuum to remove trace amounts of water on the surface of the glass.

Each sample of trichloro-N-trimethylsilylphosphoranimine was assembled in an argon atmosphere dry box by the addition of 0.16 mL of the phosphoranimine, 0.50 mL of solvent, and a deuterated acetone capillary. Neat samples of trichloro-N-trimethylsilylphosphoranimine contained 0.66 mL of the phosphoranimine and a deuterated acetone capillary. The NMR tubes were then sealed under vacuum with an oxygen/methane torch. Samples were stored at -3 °C ± 0.5 °C or at 21 °C ± 1 °C, and the decomposition reactions were monitored by consumption of the phosphoranimine and the production of poly(dichlorophosphazene) and hexachlorocyclotriphosphazene by \textsuperscript{31}P NMR.

A.3 Results and discussion

The degradation of trichloro-N-trimethylsilylphosphoranimine at 21 °C is shown in Figure A-1, and the degradation of trichloro-N-trimethylsilylphosphoranimine at -3 °C is shown in Figure A-2.
For the samples at -3 °C, reaction of the monomer was fastest in THF, and slowest in dichloromethane and diethyl ether. This would appear to indicate that more polar solvents promote the reactions, suggesting an S\textsubscript{N}2 type reaction. It is interesting to note that at low temperature, the neat monomer reacted only as fast as when dissolved in diethyl ether or dichloromethane. The concentration of monomer is clearly higher in the neat sample, so this would indicate that the monomer itself is poor solvent for S\textsubscript{N}2 type reactions. The rate of reaction in benzene and toluene were similar, but were faster than for diethyl ether and dichloromethane. This result is unexpected, because benzene and toluene are less polar than diethyl ether and dichloromethane. Possible explanations for this are that the concentrations of monomer in these two samples were not consistent with the other samples, or that there may have been traces of water in the benzene and toluene, which could have promoted the reaction of the monomer. However, the water contents of the solvents as measured by Karl Fischer titration (Table A-1) do not support this. It is possible, therefore, that benzene and toluene are better solvents for this particular reaction.

For the samples at 21 °C, there was a much faster rate of reaction than the samples at -3 °C. The neat sample was the fastest to react overall, although the rate of reaction in toluene was initially higher. The rates of reaction in benzene and toluene were again somewhat unexpected, and this is consistent with the above postulate that they are better solvents. The solvents in which the rate of reaction was slowest were again dichloromethane and diethyl ether. The rate of reaction in THF at 21 °C seems anomalous – the datum at ca. 2500 hours is likely due to experimental error.
The samples in solution all followed the same basic profile, with the rate of reaction slowing as monomer is consumed. The rate of reaction of the neat monomer is of interest, though, as it showed almost linear behavior. This is indicative of a living polymerization reaction, where there is a linear relationship between molecular weight increase and time. This indicates that the rate of the living polymerization reaction is faster in the neat sample due to the high concentration of the monomer (vide infra).

In all samples, the formation of oligomers was observed before the formation of trimer. An explanation for this phenomenon is that monomer will react first to form oligomers with living chain ends. These living chain ends can react with either more monomer and form polymers, or undergo an intramolecular reaction and cyclize to form trimer. When the concentration of monomer falls because it is consumed, the probability of polymerization falls also. Consequently, the probability of the cyclization reaction increases, thus trimer begins to form. This can only happen if the rate of the polymerization reaction is slow – in reactions where the polymerization is catalyzed with PCl₅, the formation of trimer is not observed. The uncatalyzed, thermal polymerization reaction, however, appears to be slow enough to allow this to happen.
Figure A-1: Degradation of trichloro-N-trimethylsilylphosphoranimine at 21 °C
Figure A-2: Degradation of trichloro-N-trimethylsilylphosphoranimine at -3 °C
Table A-1: Water content of solvents measured by Karl Fisher titration

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Water content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.60</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>0.63</td>
</tr>
<tr>
<td>Ether</td>
<td>2.54</td>
</tr>
<tr>
<td>THF</td>
<td>1.48</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.27</td>
</tr>
</tbody>
</table>
Storage of the phosphoranimine in the solid state was investigated. The freezing point of trichloro-\textit{N}-trimethylsilylphosphoranimine was determined by DSC (Figure A-3) to be -55 °C. This temperature was considered too low to be a viable method for the medium to long term storage of the phosphoranimine. Data from the DSC also indicated a broad exothermic transition that peaks at ca. 189 °C, which is attributed to the thermal polymerization of the phosphoranimine into poly(dichlorophosphazene).

**A.4 Summary**

The ability to store trichloro-\textit{N}-trimethylsilylphosphoranimine for intermediate lengths of time is a crucial step towards the wider commercialization of polyphosphazenes. Thus, conditions under which trichloro-\textit{N}-trimethylsilylphosphoranimine can be stored were investigated. Several solvents, and two different temperatures were examined, and it was found that storage of the phosphoranimine in ether at -3 °C were reasonable storage conditions, under which only 1.2% of the phosphoranimine had been consumed after 2800 hours. Further experiments that will investigate storage conditions under which there is no medium-term degradation at room temperature are to be performed.
Figure A-3: DSC thermogram of trichloro-\(N\)-trimethylsilylphosphoranimine
A.5 References


Richard Martin Wood

Richard Martin Wood, son of Jean and David Wood of Bicester, Oxfordshire, UK, was born on May 9th 1979 in Bournemouth, Dorset, UK. He attended the University of Bath, Bath, UK and in 2001 earned his advanced Bachelor of Science degree in Chemistry (M. Chem). In August 2001, he began his graduate studies at the Pennsylvania State University in the laboratory of Dr. Harry R. Allcock.