SYNTHESIS AND CHARACTERIZATIONS OF
NOVEL POLYMER ELECTROLYTES

A Dissertation in
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by
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ABSTRACT

Polymer electrolytes are an important component of many electrochemical devices. The ability to control the structures, properties, and functions of polymer electrolytes remains a key subject for the development of next generation functional polymers. Taking advantage of synthetic strategies is a promising approach to achieve the desired chemical structures, morphologies, thermal, mechanical, and electrochemical properties. Therefore, the major goal of this thesis is to develop synthetic methods for of novel proton exchange membranes and ion conductive membranes.

In Chapter 2, new classes of fluorinated polymer-polysilsesquioxane nanocomposites have been designed and synthesized. The synthetic method employed includes radical polymerization using the functional benzoyl peroxide initiator for the telechelic fluorinated polymers with perfluorosulfonic acids in the side chains and a subsequent in-situ sol-gel condensation of the prepared triethoxysilane-terminated fluorinated polymers with alkoxide precursors. The properties of the composite membranes have been studied as a function of the content and structure of the fillers. The proton conductivity of the prepared membranes increases steadily with the addition of small amounts of the polysilsesquioxane fillers. In particular, the sulfopropylated polysilsesquioxane based nanocomposites display proton conductivities greater than Nafion. This is attributed to the presence of pendant sulfonic acids in the fillers, which increases ion-exchange capacity and offers continuous proton transport channels between the fillers and the polymer matrix. The methanol permeability of the prepared membranes has also been examined. Lower methanol permeability and higher electrochemical selectivity than those of Nafion have been demonstrated in the polysilsesquioxane based nanocomposites.

In Chapter 3, the synthesis of a new class of ionic liquid-containing triblock copolymers with fluoropolymer mid-block and imidazolium methacrylate end-blocks is described for the first
time. The synthetic strategy involves the preparation of the telechelic fluoropolymers using a functional benzoyl peroxide initiator as the macro-chain transfer agent for subsequent RAFT polymerization of the imidazolium methacrylate monomer. As revealed in DSC, SAXS and dielectric relaxation spectroscopy (DRS) measurements, there was no microphase separation in the triblock copolymers, likely due to solubility of ionic liquid moieties in the fluoropolymer matrix. The anionic counterion has direct impact on the thermal properties, ionic conductivity and segmental dynamics of the polymers. The temperature dependence of the ionic conductivity is well described by the Vogel-Tamman-Fulcher model, suggesting that ion motion is closely coupled to segmental motion.

In Chapter 4 and 5, new solid electrolytes for lithium cations have been synthesized by catalyzed hydrosilylation reaction involving hydrogen atoms of polysiloxane and polyhedral oligomeric silsesquioxane (POSS) and double bonds of vinyl tris17-bromo-3,6,9,12,15-pentaoxaheptadecan-1-ol silane. The obtained structures are based on branched or dendritic with ionic liquid-ethylene oxide oligomer. High room temperature ionic conductivities have been obtained in the range of $10^{-4}-10^{-5}$ can be regarded as solid electrolytes. This is attributed to the high concentration of ions from ionic liquid moieties in the tripodand molecule, high segmental mobility, and high ion dissociation from ethylene oxide spacers. The influence of anion structures and lithium salts and concentration has been investigated.
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Chapter 1

Introduction and Background

1.1 Polymer electrolytes and applications

The energy crisis is a serious situation currently challenging the world. We are now facing a future where we must replace existing fossil fuels to new fuel sources which can alleviate the economical and ecological problems associated with fossil fuels. Consideration of alternative and renewal energy sources has been interesting in sight of our energy and environment needs. Electrochemical devices are under serious consideration as alternate energy sources as they are sustainable and environmentally friendly. Electrochemical devices are composed of a positive electrode and negative electrode connected by an electrolyte material. The two electrodes have different chemical potentials from chemical reactions that occur at each. When these electrodes are connected by an external device, electrons spontaneously flow from the negative to the positive potential side. Ions are transported through the electrolyte, maintaining the charge balance, and electrical energy can be tapped by the external circuit.

![Figure 1-1. Electrochemical cell assembly.](image-url)
Polymer electrolytes have been useful for applications in electrochemical devices due to the provide advantages such as improved mechanical strength, formability, lack of solvent leakage, decreased dendritic growth, and reduced interfacial reactions.\cite{1, 2} Generally, the basic requirements that polymer electrolytes should meet are following:

1. It has to be a good ionic conductor and electronic insulator.
2. It should have chemical, thermal, and electrochemical stability.
3. It should have proper mechanical properties.
4. It should be environmental friendly and safe to use.

Among energy sources, much attention has been focused on fuel cells and lithium ion secondary batteries. Fuel cells have caught people’s attention due to their clean and efficient power for applications like electric vehicles, residential power sources, and portable electronic devices.\cite{3} Lithium batteries have significantly high energy density, lighter weight, and are rechargeable. From these interesting characteristics, over decades numerous studies have been focused on the development of novel polymer electrolytes for fuel cell and lithium battery applications.

1.2 Polymer electrolytes for proton exchange membranes (PEMs)

The critical requirements for polymer electrolytes in fuel cells are as follows:\cite{4}

1. It should have high protonic conductivity but low electronic conductivity.
2. It should have low permeability of reactant.
3. It should allow water transport through diffusion and electro-osmosis.
4. It should have chemical and thermal stability.
5. It should have good mechanical properties.
Figure 1-2. The basic assembly of direct-methanol fuel cell.

Many investigations have focused on proton exchange membranes (PEMs) for fuel cells since the introduction of sulfonic acid groups, which lead to proton conductivity in fluoropolymers. Generally, PEMs are made from tetrafluoroethylene (TFE) and perfluorosulfonate monomers like Nafion®, Flemion®, and Hyflon Ion® because these membranes give high conductivities (up to 120 mS). These perfluorosulfonic polymers combine the extremely high hydrophobicity of the perfluorinated backbone with the extremely high hydrophilicity of the sulfonic acid functional groups to give hydrophobic/hydrophilic phase separation. The sulfonic acid functional groups aggregate to form a hydrophilic domain for proton conduction. While the well-connected hydrophilic domain is responsible for the transport of protons and water, the hydrophobic domain provides the stability for the polymer as shown in Fig.1-3. [5, 6]
However, they still have a major drawback which is that they have an unacceptably high rate of methanol crossover for direct methanol fuel cell (DMFC) application. This leads to a reduction of cell performance due to a mixed potential at the cathode and lowers fuel efficiency due to the loss of methanol reacting at the anode.

Organic-inorganic hybrid membranes have been studied in order to suppress the methanol permeability through PEMs by impregnating inorganic particles in the ionic channels to introduce a winding pathway for methanol molecules. Many approaches have been used to create the hybrid membranes such as dispersion of filler particles in an ionomer solution followed...
by casting[8,9] and growth of the filler particles within a preformed membrane or in an ionomer solution by sol-gel reactions.\textsuperscript{10,11}

![Figure 1-4. The sol-gel reaction of polysilisesquioxane.\textsuperscript{11}](image1)

![Figure 1-5. The synthesis of Nafion-stabilized SiO\textsubscript{2} nanoparticles.\textsuperscript{11}](image2)
However, the composite effect on the proton conductivity was not outstanding or even worse in some cases and the excessive addition of nonconductive inorganic particles results in proton conductivities lower than pristine Nafion.\textsuperscript{[12]} \textsuperscript{[13, 14]} Moreover, these techniques lack covalent bonds between the inorganic/organic interfaces. Therefore, the inorganic particles are easily separated from the membranes or exist outside the ionic channels (Fig.1-6).\textsuperscript{[15]} The hybrid membranes of nafion or other fluoropolymers, which have good bonding and distribution of inorganic particles in the ionic domains and also contain chemical tethered proton conducting groups at the particles to allow a continuity of proton conduction are highly interesting, due to the possibility of increasing the tortuosity of pathway for methanol molecules without affecting appreciably proton conductivity mechanism.

Figure 1-6. The SEM image of Nafion/ORMOSIL hybrid membranes.\textsuperscript{[16]}

1.3 Telechelic fluoropolymers

Fluoropolymers are very attractive materials due to their high thermal stability, chemical resistance, and high mechanical properties. However, their low surface energy and coefficient of
friction have limited their applications, particularly those in which surface adhesion and miscibility with other functional components are paramount. Introducing functional groups at both chain ends to create telechelic fluoropolymer structures are of great interest. This chain-end functionalization approach would keep the main-chain structures of fluoropolymers that have distinctive physical properties. Also, the functional chain ends of the telechelic structures have been used as building blocks to construct complex macromolecular architectures and composites. Our research group [17] has prepared functional benzoyl peroxides (BPOs) by the acylation of Li₂O₂ with benzoyl chloride substituted by the corresponding functional group. The BPO derivatives were also obtained through the reaction of functional group substituted benzoic acid with H₂O₂ in the presence of \( N,N' \) -dicyclohexylcarbodiimide (DCC) as shown in Fig1-7.

Figure 1-7. Synthesis and Chemical Structures of the BPO-Based Functional Initiators. [17]
The BPOs are capable of initiating the homopolymerization of vinylidene fluoride (VDF) as well as co- and terpolymerization of VDF with hexafluoropropene (HFP), chlorotrifluoroethylene (CTFE), and trifluoroethylene (TrFE). The telechelic fluoropolymers have been successfully polymerized predominately through the radical coupling reaction. It was confirmed by $^1$H NMR that there is no resonance of unsaturated bonds resulting from disproportionation reactions at 5.5 to 6.5 ppm.

![Diagram of fluoropolymer structure]

**Figure 1-8.** $^1$H NMR spectrum of P(VDF-co-CTFE) with tert-butyl ester as terminal groups.$^{[17]}$

Therefore, this general functional approach can open new possibilities for creating new polymer structure such as co- or terpolymer of fluoropolymers with other polymers and self- and directed assembly of inorganic nanoparticles in fluoropolymer matrix to form novel composite materials with uniform dispersibility and high thermal, chemical and mechanical stability.
1.4 Polymer electrolytes for lithium and lithium-ion battery

The basic configuration of lithium and lithium-ion batteries is shown in Fig. 1-9. The cell is composed of a positive and negative electrode connected by an electrolyte. By the electrochemical process, lithium ions can be cycling from one electrode to the other.\textsuperscript{[18]}

Figure 1-9. The basic structure of lithium batteries.\textsuperscript{[19]}

The basic requirements for polymer electrolytes in lithium battery applications should meet the following criteria:\textsuperscript{[20, 21]}

1. It should have a high dielectric constant ($\varepsilon$) in order to be able to dissolve salts to sufficient concentration.
2. It should have low glass transition temperature in order to facile ion transport.
3. It should have chemical, thermal, and electrochemical stability.
4. It should have dimensional stability and good mechanical properties.
5. It should also be safe and nontoxic.
The ionic conductivity can be determined by $\sigma = ne\mu$, where $n$, $e$, and $\mu$ are the effective number of mobile ions, the elementary electric charge, and the ion mobility, respectively.\textsuperscript{[22]} Since the number of free ions that can be effectively transported is an important parameter, a high degree of dissociation of the salt in the polymer is a prerequisite for high conductivity. In order to dissolve a sufficient amount of salts and also achieve a high fraction of free ions, the polymers which contain polar groups such as ether linkages (-O-), carbonyls (C=O), nitriles (C≡N), and sulfonyle (S=O) have been considered.

Ion mobility in the polymer electrolyte is greatly affected by the segmental motion of the polymer chains and thus with the glass transition phenomenon. Research has been done to search for low $T_g$ polymers with hopes of achieving high ionic conductivity because the high segmental motion facilitates the ion transport. Also amorphous polymers are preferred because the quicker molecular motion of the polymer chains leads to higher ion diffusion when compared with crystalline polymers.

In the lithium ion in PEO system, the Li ions are transported coupled with PEO chain through approximately five ether oxygen atoms of a PEO chain as shown in Fig. 1-10. Even though EO unit is excellent in ionic dissociation, oxyethylene structure easily becomes crystalline. Therefore, only PEO is not effective enough to use in polymer electrolytes for room temperature application.

![Figure 1-10. The segmental motion assisted diffusion of Li+ in the PEO chains.\textsuperscript{[22]}](image-url)
Many attempts have tried to introduce PEO into the low Tg polymer such as polysiloxane, and polyphosphazene.\textsuperscript{[23-27]} Besides the linear chain polymers of PEO with other polymers, comb polymers which attach PEO branch to other low Tg polymer backbone are also very interested because it can give high segmental motion and prevent the crystallinity of PEO. Examples of the polymer structures are shown in Fig. 1-11. Even though these polymer structures have improved the conductivity, they still lack electrochemical stability and mechanical properties.

Figure 1-11. Examples of polymer electrolyte structures.\textsuperscript{[22]}

1.5 Ionic liquids

Ionic liquids (ILs) are low-temperature molten salts composed of ions only. The salts are characterized by weak interactions, due to the combination of a large and dissymmetry cation and
a charge-delocalized anion.[19] The examples of cations and anions for ILS are show in Fig. 1-12.

**Cation**

\[
\begin{align*}
&\text{R}_1 = \text{Me, Bu} \\
&\text{R}_2 = \text{Me, H} \\
&\text{R}_3 = \text{Me, Et, Pr, iPr, Bu}
\end{align*}
\]

\[
\begin{align*}
&\text{R}_1 = \text{Me, Et, Pr, iPr, Bu} \\
&\text{R}_2 = \text{Me, Et, Pr, iPr, Bu}
\end{align*}
\]

\[
\begin{align*}
&\text{Me}^- \text{Pr} \\
&\text{R}_2 \text{N}^\text{+} \text{R}_1
\end{align*}
\]

\[
\begin{align*}
&\text{R}_1 \\
&\text{R}_2 \text{N}^\text{+} \text{R}_2
\end{align*}
\]

**Anion**

\[
\begin{align*}
&[\text{CF}_3\text{SO}_3]^+ \\
&[\text{BF}_4]^+ \\
&[\text{PF}_4]^+ \\
&[\text{C}(\text{CF}_3\text{SO}_2)_3]^+ \\
&[\text{N}(\text{CF}_3\text{SO}_2)_3]^+ \\
&[\text{CF}_3\text{CONCF}_3\text{SO}_2]^-
\end{align*}
\]

Figure 1-12. Examples of cations and anions in ionic liquids.\textsuperscript{[28]}

ILs have been of interest in electrolytes in energy devices due to their unique properties such as negligible vapor pressures, excellent ionic conductivity, wide electrochemical window, and high chemical and thermal stability. However, using ILs as electrolyte still has some problems. Since both ions in ILs can move lithium ion transference number in lithium battery application are often low. Moreover, ILs cannot prohibit dendrite growth of lithium which can lead to short circuits in devices (Fig. 1-13).
ILs offer great flexibility in designing cationic and anionic structures. Also from the benefits of chemistry, ILs can be tailored in vinyl structures which can be used in many reactions such as polymerization and hydrosilation. Many strategies have been used developed to prepare solid polymer electrolytes having IL moieties in polymer structures as shown in Fig. 1-14.\textsuperscript{[31]}

**Figure 1-13.** The picture of the dendrite growth at the Li surface.\textsuperscript{[29, 30]}

**Figure 1-14.** Variation of IL polymers.\textsuperscript{[31]}
One of the most versatile scaffolds of cation for ILs is imidazole as shown in Fig. 1-15.\cite{32}

The tertiary nitrogen atom ring is easily ionized upon quaternization, resulting in a permanent positive charge. In addition, various combinations of alkyl substituents and counteranions enable tuning of the properties of the ILs to meet the demands of the application. Imidazole has been interested for many reasons such as tunable structure, thermal stability, high ionic conductivity, and wide electrochemical window.

![Imidazole Ring and Imidazolium Ionic Liquid](image)

**Figure 1-15.** The imidazole ring and imidazolium ionic liquid.\cite{32}

The structure is uniquely tunable because the imidazole ring can accept and donate protons; it can function as both an acid and as a base. The acidic proton is located on N-1 and the basic site is N-3, protonation gives the imidazolium cation. This structure allows for substitution using facile SN₂ reactions at the 3-ring position. The 1-position on the ring is a secondary amine, which can undergo a variety of reactions. Moreover, the imidazolium cation is associated with a counteranion, which can be exchanged to further tune conductivity and other properties as shown in Table 1-1.\cite{28}
Table 1-1 Examples of properties of imidazolium ionic liquids.

<table>
<thead>
<tr>
<th>Ionic liquids</th>
<th>Melting point (°C)</th>
<th>$\sigma_{RT}$ (mS/cm)</th>
<th>Electrochemical window (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{EtMeIm}]^+ [\text{BF}_4]^{-}$</td>
<td>15</td>
<td>14</td>
<td>4.5</td>
</tr>
<tr>
<td>$[\text{EtMeIm}]^+ [\text{CF}_3\text{SO}_3]^{-}$</td>
<td>-9</td>
<td>8.6</td>
<td>4.1</td>
</tr>
<tr>
<td>$[\text{EtMeIm}]^+ [\text{N}($CF_3$)$\text{SO}_2)$]_2^{-}$</td>
<td>-16</td>
<td>8.8</td>
<td>4.5</td>
</tr>
<tr>
<td>$[\text{BuMeIm}]^+ [\text{PF}_6]^{-}$</td>
<td>-8</td>
<td>1.8</td>
<td>5.7</td>
</tr>
<tr>
<td>$[\text{BuMeIm}]^+ [\text{N}($CF_3$)$\text{SO}_2)$]_2^{-}$</td>
<td>-4</td>
<td>3.9</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Since imidazolium-based ionic liquids have ionic conductivities approaching in the range of $10^{-3}$-$10^{-2}$ S/cm. Therefore, they have been extensively studied in solid polymer electrolyte. By synthesizing imidazole with vinyl groups then using radical polymerization, ionic liquid based polymers can be prepared.\textsuperscript{[33-37]}

![Synthesis routes of polymerized ILs.\textsuperscript{[31]}](image)
Unfortunately, ionic liquid polymers showed very poor ionic conductivity, which is about \(10^4\) times lower than ionic liquid monomers. Fig. 1-17 shows the ionic conductivity of 1-ethyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide before and after polymerization.\(^{[33]}\) The decrease in ionic conductivity is attributed to the elevation of Tg and the reduced number of mobile ions after covalent bonding of the imidazolium cation on the polymer backbone.

![Figure 1-17. The ionic conductivity of 1-ethyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide before and after polymerization.\(^{[34]}\)](image)

Base on the fact that ionic conductivity depends on Tg and segmental mobility, reducing Tg would help increase ionic conductivity. Ohno has tried to introduce a flexible spacer group between imidazolim and the polymer backbone.\(^{[38]}\) Fig. 1-18 shows the effect of alkyl spacer chain length on the ionic conductivity and Tg of poly 1-ethyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide. When the spacer chain was introduced, the conductivity was higher by a factor of about \(10^3\) which is attributable to the increase of the free volume leading to a
drop in Tg. This result indicates that the introduction of spacer can improve the ionic conductivity.

![Graph showing the effect of alkyl spacer chain length on the ionic conductivity and Tg of ionic liquid polymer.]

Figure 1-18. Effect of alkyl spacer chain length on the ionic conductivity and Tg of ionic liquid polymer.\textsuperscript{[34]}

1.6 Motivation and thesis organization

Polymer structures are very important because they can directly determine the properties of the polymer electrolytes. In this thesis, novel synthetic methodologies to create new polymer electrolytes for electrochemical devices are discussed and investigated.

In Chapter 2, a telechelic poly(vinylidene fluoride-\textit{co}-perfluoro(4-methyl-3,6-dioxane-7-ene) sulfonic acid) (P(VDF-PFSVE)) has been prepared from free radical polymerization of
vinylidene fluoride and perfluoro(4-methyl-3,6-dioxaoct-7ene) sulfonyl fluoride monomers by using functional benzoyle peroxide as an initiator. The functional chain ends further reacted with TEOS and THOPS in sol-gel reactions to prepare the conductive polymer nanocomposite membranes. This synthesis route allows the inorganic components to have covalent bonds and uniform dispersibility into the fluorinated proton conductive polymers. Two different types of nanoparticale polysilsesquioxanes from TEOS and THOPS have been studied the continuity of proton transport. The membranes have been characterized by ATR-FTIR, TGA, DSC, and TEM. The transport properties of the nanocomposites have also been evaluated as a function of the content and the structure of polysilsesquioxanes.

In Chapter 3, a telechelic poly(vinylidene fluoride-co-hexafluoropropylene) [P(VDF-HFP)] have been prepared and then further altered to create chain ends with RAFT initiator. The new structure of ionic liquid monomer has been created to have triethylene oxide spacer in order to increase ion mobility and reduce Tg. RAFT polymerization has been used to produce a series of the triblock copolymers constituted of poly(vinylidene fluoride-co-hexafluoropropylene) [P(VDF-HFP)] mid-block and imidazolium IL methacrylate end-blocks. The structure and properties of the triblock copolymers with different composition and anions have been investigated.

In Chapter 4, a novel vinyl tripodant ionic liquid has been synthesized. Hexethylene oxide has been introduced in the IL structure in order to increase ion mobility and promote anion-cation dissociation. A new comblike polysiloxane structure with ionic liquid branches has been synthesized by hydrosilation of poly (hydromethylsiloxane) and the tripodant ionic liquid. In addition, chemical structures of anion and lithium salts on the polymer properties have been investigated.

In Chapter 5, polyhedral oligomeric silsesquioxane (POSS) has been used in hydrosilation reaction with the vinyl tripodant ionic liquid to create a novel solid hybrid
electrolyte. The obtained dendritic POSS structure has been studied by $^1$H NMR, and WADX. The properties of the hybrid electrolytes with two different salts which are LiTFSI and LiPF$_6$ have also been studied.

In Chapter 6, the conclusions of the thesis and suggestions for future work are presented.
Chapter 2

Proton Conductive Polymer Nanocomposite Membranes Prepared From Telechelic Fluorinated Polymers Containing Perfluorosulfonic Acid Side Chains

2.1 Introduction

Over the past few decades, considerable effort has been directed toward the development of new PEMs.\textsuperscript{[39]} One interesting strategy is the introduction of hydrosopic inorganic components into polymers to form composite membranes that integrate the complementary properties of their constituents.\textsuperscript{[40, 41]} For example, modification of Nafion with inorganic nanoparticles such as silicon oxide, diphenyl silicate, titanium oxide, zirconia, zirconium phosphate, and phosphotungstic acid gives rise to reduced methanol permeability of the membranes, which are attributed to the reduction in ionic channels and the increasing in tortuosity of hydrophilic paths for methanol transport by the incorporated nanoparticles. In general, the composite membranes have been prepared via dispersion of filler particles in an ionomer solution followed by solution casting\textsuperscript{[42, 43]} or impregnation of Nafion with precursors of inorganic fillers followed by sol-gel reactions.\textsuperscript{[44, 45]} The properties of these composite membranes not only depend on the nature of the ionomer and the filler but also on the content, distribution, orientation and size of the particles dispersed in the polymer matrix. It is well-known that fluorinated polymers generally de-mix with most organic and inorganic materials because of their low surface energy and interchain forces, and the dispersion of dopants in the fluorinated polymer matrix always become problematic. Usually, the inorganic nanoparticles produced via the sol-gel route are distributed much more homogeneously within the polymer matrix than the composites yielded from the direct mixing. The inorganic fillers, however, are easily separated from the membranes or exist outside the ionic channels due to the poor compatibility and the lack of
chemical bonds between the fillers and the polymer matrix.\[^{46}\] Furthermore, elevated temperatures would exacerbate uncontrolled macro-phase separation in polymer composites that are intrinsically thermodynamic instable.

Herein, we reported the synthesis, preparation and characterization of novel covalent-bonded nanocomposites based on polysilsesquioxane and poly(vinylidene fluoride-co-perfluoro(4-methyl-3,6-dioxane-7-ene) sulfonic acid) (P(VDF-PFSVE)) via in-situ sol-gel reactions. The strategy involves a new synthetic approach to the telechelic P(VDF-PFSVE) with triethoxysilane end groups and subsequent sol-gel reactions with tetraethyl orthosilicate (TEOS) and 3-(trihydroxysilyl) propane-1-sulfonic acid (THPSA). This method allows the incorporation of inorganic components into the fluorinated proton conductive polymers with uniform dispersibility and high stability in a controlled manner. Furthermore, covalent assembly of multiple proton conductive components ensures continuity of proton transport, great reproducibility, and synthetic tailorability. The transport properties of the nanocomposites have been evaluated as a function of the content and the structure of polysilsesquioxanes.

2.2 Results and Discussion

2.2.1 Polymer Synthesis

![Scheme 2-1. Synthesis of the functional BPO initiator.](image)
Scheme 2-2. Synthesis of the telechelic P(VDF-PSFVE) with triethoxysilane end groups.

Scheme 2-3. Chemical structures of the oxide precursors.

The prepared P(VDF-PFSVE) (P1) was determined to contain 91.5 mol% VDF and 8.5 mol% PFSVE with the number-average molecular weight (Mn) of the P(VDF-PSFVE) copolymer was around 22 kDa. Conversion of the sulfonyl fluoride groups in the polymer P2 to the organic SO$_3^-$.
N\(^*\)(C\(_2\)H\(_3\))\(_3\)CH\(_3\) in the polymer P\(_3\) was evidenced by emergence of the signals at 1.21 ppm corresponding to methyl protons in the \(^1\)H NMR spectrum. The reaction of the hydroxyl end groups in P\(_3\) with (3-isocyanatopropyl) triethoxysilane readily gave the corresponding triethoxysilane end groups in P\(_4\), which was confirmed by the appearance of the methylene peaks at 1.53, 1.73, and 1.88 ppm and the peak at 8.75 ppm ascribed to the amides as shown in Fig. 2-1.

Figure 2-1 \(^1\)H NMR spectrum of the telechelic P(VDF-PSFVE) with triethoxysilane end-groups.

2.2.2 Membrane Synthesis. The cross-linked nanocomposites were formed via a sol-gel reaction between the triethoxysilane end groups of P(VDF-PFSVE) and THPSA or TEOS whose structures are illustrated in Scheme 2-3. The formation of polysilsesquioxanes and sulfonated polysilsesquioxanes in the membranes was verified by the appearance of the absorption band at 1074 cm\(^{-1}\) due to the asymmetric stretching vibration of Si-O-Si groups and the absorbance at 800 cm\(^{-1}\) assignable to the symmetric stretching vibration of Si-O-Si groups.\(^{[46, 47]}\) The disappearance
of the Si-OH vibration bands at 955 cm\(^{-1}\) provides evidence of a completed condensation reaction. The membranes were subject to acidification with HCl to afford the nanocomposites with sulfonic acid groups, in which the characteristic band of S-F stretching vibration at 816 cm\(^{-1}\) was not detected.

Figure 2-2. FTIR spectra of the TEOS, and THPSA containing nanocomposites.

**2.2.3 Thermal Properties and Membrane Morphology.** The thermal stability of the cross-linked hybrid membranes were evaluated by means of TGA under a nitrogen atmosphere. It appears that the nanocomposite membranes exhibit similar thermal properties that are characterized by four distinct regions of mass loss: (i) loss of the absorbed water molecules that are bound to the sulfonic acid group of the membrane from 40 to \(~230^\circ\)C, (ii) elimination of
sulfonic acid groups at 290-320 °C, (iii) decomposition of perfluorovinyl ether side chains at 320 - 440 °C, and (iii) degradation of the polymer backbones at above 440°C. The onset of thermal degradation attributed to desulfonation was found to be ~ 300 °C for the nanocomposites, which is comparable to the Nafion membrane with an onset decomposition temperature of ~ 290 °C. It turns out that the existence of the covalent bonds and the interaction between the hydrophilic polysilsesquioxanes and the sulfonic acid groups renders high thermal stability of the membranes. TEM has been applied to the investigation of the morphological structures of the membranes. Fig. 2-3 displays cross-sectional TEM images of the 1.0 wt% THSPSA composite, 1.0 wt% TEOS composite and recast Nafion membranes stained with lead acetate, in which the hydrophilic ionic domains appear as dark areas and the bright areas correspond to the hydrophobic phases. It is apparent that a phase-separated morphology between the hydrophilic ionic aggregates and the hydrophobic fluorinated polymer regions exists in the membranes. The average size of the hydrophilic ionic aggregates is around 5 - 8 nm in the nanocomposite membranes, which is similar to those in Nafion whose compositional heterogeneity is on the scale of 5-10 nm. In addition, as verified in the lower magnification TEM images, the hydrophilic ionic aggregates are distributed relatively uniformly in the composite membranes.

Figure 2-3. Cross-sectional TEM images of a) 1.0 wt% TEOS nanocomposites, b) 1.0 wt% THSPSA nanocomposites, and c) Nafion. The scale bar denotes 50 nm.
2.2.4 Ion-Exchange Capacity, Hydration Number and Water Uptake. Table 2-1 summarizes the water sorption and swelling characteristics of the membranes. In comparison with Nafion, although the P(VDF-PSFVE)-TEOS composite membranes have lower ion-exchange capacity (IEC), they exhibit higher water uptake. This could be attributed to the hydrophilic nature of the polysilsesquioxane fillers that form strong hydrogen bonds with water molecules and facilitate the binding of water to the membranes. This result is fully consistent with the fact that the water uptake increases monotonically from 35 to 52 wt% with the increase of the TEOS content from 0.5 to 3.0 wt% in the composites despite their progressively reduced IECs. Correspondingly, the hydration number ($\lambda$), the average number of water molecule per sulfonic acid group, increases gradually from 22.2 for the 0.5% TEOS composite to 33.8 for the 3.0% TEOS composite. The $\lambda$ values of the P(VDF-PSFVE)-TEOS composites are greater than that of Nafion, indicating that the nanocomposite membranes can be effectively hydrated for proton conduction. In the P(VDF-PSFVE)-THSPSA composites, increasing the THSPSA content results in concomitant increase of IECs accompanied by a related change of water uptake and $\lambda$ value, which is due to the increased concentration of sulfonic acids introduced by THSPSA. The water uptake of the P(VDF-PSFVE)-THSPSA composite membranes increase steadily from 42 to 69 wt% with increasing the THSPSA content from 0.5 to 3.0 wt%. Compared with the corresponding TEOS hybrid membranes with the same filler content, the THSPSA nanocomposites have much higher water uptake and $\lambda$ values, owing to their higher IECs as a result of a greater number of the sulfonic acids from the sulfopropylated polysilsesquioxane units.
Table 2-1. The water absorption characteristics of the nanocomposite membranes and Nafion.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>IEC (meq/g)</th>
<th>Water Uptake (wt%)</th>
<th>λ</th>
<th>ΔH_f</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5% TEOS</td>
<td>0.867</td>
<td>35</td>
<td>22.2</td>
<td>85</td>
</tr>
<tr>
<td>1.0% TEOS</td>
<td>0.871</td>
<td>38</td>
<td>24.2</td>
<td>93</td>
</tr>
<tr>
<td>2.0% TEOS</td>
<td>0.862</td>
<td>41</td>
<td>26.4</td>
<td>99</td>
</tr>
<tr>
<td>3.0% TEOS</td>
<td>0.854</td>
<td>52</td>
<td>33.8</td>
<td>109</td>
</tr>
<tr>
<td>0.5% THSPSA</td>
<td>0.900</td>
<td>42</td>
<td>25.9</td>
<td>106</td>
</tr>
<tr>
<td>1.0% THSPSA</td>
<td>0.920</td>
<td>48</td>
<td>29.0</td>
<td>113</td>
</tr>
<tr>
<td>2.0% THSPSA</td>
<td>1.002</td>
<td>53</td>
<td>30.6</td>
<td>118</td>
</tr>
<tr>
<td>3.0% THSPSA</td>
<td>0.961</td>
<td>69</td>
<td>38.3</td>
<td>124</td>
</tr>
<tr>
<td>Nafion</td>
<td>0.910</td>
<td>29</td>
<td>17.7</td>
<td>101</td>
</tr>
</tbody>
</table>

2.2.5 The State of Absorbed Water in the Membranes. The state of the absorbed water inside PEMs has been suggested to play a significant role in determining the transport properties through ionic domains.\textsuperscript{[48]} The absorbed water in hydrated PEMs is generally described in three distinguishable forms depending on the degree of hydration and interaction with PEMs.\textsuperscript{[49]} The water taken up initially is closely bound to the sulfonic acid groups and is known as “bound water”. The water taken up thereafter is present as “loosely bound water” and “free water”. It is believed that the proton transport through PEMs is strongly correlated to the loosely bound and free water, and not simply the total water present in a membrane. Low temperature DSC was
performed to elucidate the state of water within hydrated membranes, where the melting endotherm at 0°C is ascribed to the un-bound and weakly bound water. The bound water forms a true solution with the polymer and does not freeze at 0°C. As depicted in Fig. 1-4, two melting peaks are clearly observed near 0°C in the nanocomposite membranes. The first sharp peak belongs to the free water and the second broad peak is attributed to the loosely bound water whose motion is partially restricted.\[50] Table 1-1 lists the calculated the heat of fusing (\(\Delta H_f\)) of the absorbed water in the membranes, which is generally proportional to the fraction of the free and weakly bound water. Analogous to the water uptake and \(\lambda\), the state of the absorbed water is also strongly dependent on the structure and content of the polysilsesquioxane fillers. The 0.5 and 1.0 wt% TEOS- P(VDF-PSFVE) hybrid membranes contain primarily bound water as indicated by their low \(\Delta H_f\). It was observed that the content of the free and loosely bound water increases with increasing the amount of THSPSA and TEOS, following the same trend as the water uptake. This could also be correlated to higher concentration of polysilsesquioxanes that interact with water molecules through hydrogen bonding. It should be noted that the P(VDF-PFSVE)-THSPSA composite membranes contain higher portions of the weakly bound and free water than the corresponding P(VDF-PFSVE)-TEOS composites and Nafion, which is consistent with the results on IEC and water uptake.
2.2.6 Proton Conductivity. The proton conductivities of the prepared membranes measured at 30°C under fully hydrated conditions are presented in Table 2-2. It is noteworthy that the proton conductivity of the P(VDF-PSFVE)-TEOS nanocomposites improves from 0.059 to 0.072 and 0.076 S/cm as the TEOS content is increased from 0.5 to 1.0 and 2.0 wt%, respectively. This result is in marked contrast to the conventional Nafion/silica composites,[40, 41] where the
incorporated silica restricts the transport of proton and leads to a significantly reduced conductivity. A further increase of the TEOS content from 2.0 to 3.0 wt% lowers the conductivity to 0.069 S/cm, which is attributed to the reduced proton concentration as a result of the decreased IEC from 0.862 to 0.854 meq/g and the increased water uptake from 41 to 54 wt%.

**Table 2-2.** Transport properties of the P(VDF-PSFVE) based nanocomposites and Nafion.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Proton Conductivity (S/cm)</th>
<th>$E_a$ (kJ/mol)</th>
<th>Methanol Permeability ($10^{-7}$ cm$^2$/s)</th>
<th>Selectivity ($10^4$ Ss/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5% TEOS</td>
<td>0.059</td>
<td>8.8</td>
<td>9.6</td>
<td>6.1</td>
</tr>
<tr>
<td>1.0% TEOS</td>
<td>0.072</td>
<td>9.6</td>
<td>6.9</td>
<td>10.4</td>
</tr>
<tr>
<td>2.0% TEOS</td>
<td>0.076</td>
<td>11.7</td>
<td>6.6</td>
<td>11.5</td>
</tr>
<tr>
<td>3.0% TEOS</td>
<td>0.069</td>
<td>15.5</td>
<td>6.1</td>
<td>11.3</td>
</tr>
<tr>
<td>0.5% THSPSA</td>
<td>0.076</td>
<td>5.4</td>
<td>15.6</td>
<td>4.9</td>
</tr>
<tr>
<td>1.0% THSPSA</td>
<td>0.085</td>
<td>6.2</td>
<td>11.9</td>
<td>7.1</td>
</tr>
<tr>
<td>2.0% THSPSA</td>
<td>0.089</td>
<td>8.9</td>
<td>10.8</td>
<td>8.2</td>
</tr>
<tr>
<td>3.0% THSPSA</td>
<td>0.052</td>
<td>9.9</td>
<td>10.2</td>
<td>5.1</td>
</tr>
<tr>
<td>Nafion</td>
<td>0.075</td>
<td>8.7</td>
<td>11.9</td>
<td>6.3</td>
</tr>
</tbody>
</table>

More interestingly, conductivities higher than those of the corresponding TEOS nanocomposites and Nafion have been demonstrated in the P(VDF-PSFVE)-THSPSA nanocomposites. With the increase of the THSPSA concentration from 0.5 to 1.0 and 3.0 wt%, the proton conductivity is improved from 0.076 to 0.085 and 0.089 S/cm, which is in accordance with the IEC, water uptake and $\Delta H_f$ trends presented in Table 2-1. The high conductivity can be
credited to the presence of pendant sulfonic acid groups in the fillers, which provide continuous proton-conducting pathways between the filler and the matrix in the composite membranes and thus facilitate the proton transports. This argument is further substantiated by the dependence of proton conductivity on temperature. The activation energy ($E_a$), minimum energy required for the proton transport across the membrane, was estimated from the slope of $\ln k$ versus $1000/T$ plots ($k$ is the proton conductivity, $T$ is the absolute temperature). As compared in Table 2-2, the P(VDF-PSFVE)-THPSA nanocomposites exhibit considerably lower $E_a$ values than Nafion and the corresponding TEOS composites, implying that the proton conduction is more facile in the nanocomposites with the sulfonated polysilsesquioxanes. The observed $E_a$ at around 6-8 kJ/mol for the P(VDF-PSFVE)-THPSA composite membranes suggest the conduction at room temperature may occur primarily via the hopping mechanism, in which the proton forms as $H_3O^+$ ion and jumps to the neighboring lone pair electrons of $H_2O$ molecule. Similarly, the conductivity of the THPSA composite drops to 0.052 S/cm when the THPSA content is further increased to 3 wt%, which is presumably due to the largely increased water uptake for a low concentration of proton and/or disruption of the proton diffusion paths from the formation of large size of the polysilsesquioxane filler.

2.2.7 Methanol Permeability and Electrochemical Selectivity. The evaluation of the methanol transport properties of the prepared membranes reveals that the methanol permeability decreases with increasing the polysilsesquioxane content in the composites as shown in Table 1-2. It is considered that the incorporated inorganic fillers reduce methanol crossover by obstructing or winding diffusion pathways for methanol. The increase of TEOS content from 0.5 to 1 wt% in the P(VDF-PSFVE)-TEOS membranes leads to a large reduction in the methanol permeability from $9.6 \times 10^{-7}$ to $6.9 \times 10^{-7}$ cm$^2$/S that is 43% lower than that of Nafion. To directly compare the applicability for DMFCs between the membranes, the electrochemical selectivity, defined as the
ratio of proton conductivity to methanol permeability, was calculated.\[52,53\] It is evident that all of the P(VDF-PSFVE)-TEOS membranes have shown high selectivities. Especially, as the filler content is increased from 0.5 to 2 wt%, the improvement of the proton conductivity is accompanied by a decline in the methanol permeability. The typical trade-off between the reduced methanol permeability and decreased conductivity in the PEMs was not observed.\[54\] The most pronounced effect was achieved in the P(VDF-PSFVE)- 2.0 wt% TEOS composite membrane with an electrochemical selectivity of ~ 1.8 times that of Nafion. One the other hand, the P(VDF-PSFVE)-THSPSA composites display much higher methanol permeability than the corresponding TEOS composites, which is the result of higher values of the water uptake introduced by the sulfopropylated polysilsesquioxanes. As methanol molecules transport along with solvated protons (H$_3$O$^+$ or H$_5$O$_2^+$) in the water-filled hydrophilic domains, the increase of sulfonic acid concentration in the membranes results in a rise of water uptake and in turn simultaneous enhancement of both the proton conductivity and the methanol permeability, thus adversely affecting the electrochemical selectivity.

2.3 Summary

Telechelic P(VDF-PSFVE) containing perfluorosulfonic acid side chains have been successfully prepared by radical polymerization using the functional initiator. The resulting triethoxysilane terminated P(VDF-PSFVE) underwent in-situ sol-gel reaction with an oxide precursor such as TEOS and THSPSA to form novel classes of proton conductive fluorinated polymer nanocomposites with uniform filler dispersion and great stability. Membranes properties such as IEC, water uptake, the state of the absorbed water, proton conductivity and methanol permeability were found to be highly dependent on the concentration and structure of the polysilsesquioxane fillers. The improvement in the proton conductivity with the presence of a small amount of the fillers has been demonstrated in the prepared nanocomposites. Notably, the
incorporation of the inorganic fillers with pendent sulfonic acids to the fluorinate polymer matrix results in the composite membranes outperforming Nafion in the proton conductivity. In addition, the polysilsesquioxane-P(VDF-PSFVE) composite membranes display suppressed methanol permeability without sacrificing the proton conductivity and thus achieve better electrochemical selectivity in comparison to Nafion.

2.4 Experimental Section

2.4.1 Materials

3-(Trihydroxylsilyl)propane-1-sulfonic acid (THSPSA) (35 wt.% in water) was purchased from Gelest. Inc. Tetraethyl orthosilicate (TEOS), (3-isocyanatopropyl) triethoxysilane, and others chemicals were purchased from Aldrich. Vinylidene fluoride, perfluoro(4-methyl-3,6-dioxaoct-7ene) sulfonyl fluoride (PFSVE), and 1,1,1,3,3-pentafluorobutane were purchased from SynQuest Laboratory Inc. All manipulations of gas-condense transfer were carried out with rigorous exclusion of oxygen and moisture on a dual-manifold Schlenk line with 10⁻⁶ Torr high vacuum.

2.4.2 Synthesis

4-[(Tetrahydroxyran-2-yloxy) methyl] benzoyl Peroxide (3). To a stirred solution of methyl 4-(hydroxymethyl) benzoate (2.66 g, 16 mmol) in anhydrous dichloromethane (120 mL) was added 3,4-dihydro-2H-pyran (2.0 g, 24.0 mmol) and pyridinium p-toluensulfonate (0.40 g, 1.6 mmol). After 18 h, the reaction mixture was extracted with diethyl ether (80 mL) and washed with brine (2x30 mL). The aqueous phase was extracted with diethyl ether (2x30 mL). The combined organic phases were dried over MgSO₄ and concentrated in vacuo. Purification by column chromatography (SiO₂, 1:5 ethyl acetate: hexane) gave methyl 4-[(tetrahydroxyran-2-yloxy) methyl] benzoate (1, 3.8 g, 96%) as a colorless oil. ¹H NMR (CDCl₃, ppm): δ 8.02 (d, 2H,
ArH), 7.38 (d, 2H, ArH), 4.8 (d, 1H), 4.7-4.6 (m, 1H), 4.53 (d, 1H), 4.0-3.7 (m, 1H), 3.89 (s, 3H), 3.65-3.35 (M, 1H), 2.0-1.4 (m, 6H).

Saponification of the benzoate 1 (2.5 g, 10.0 mmol) was carried out with potassium hydroxide (1.1 g, 20 mmol) in aqueous methanol (80 mL, 1:3 water:methanol) and gave 4-[(tetrahydropyran-2-yloxy) methyl] benzoic acid (2) as a white solid (1.8 g, 80%). $^1$H NMR (d$_6$-acetone, ppm): d 7.98 (d, 2H, ArH), 7.43 (d, 2H, ArH), 4.76 (d, 1H), 4.77-4.65 (m, 1H), 4.55 (d, 1H), 4.0-3.7 (m, 1H), 3.66-3.35 (m, 1H), 2.0-1.4 (m, 6H).

To a mixture of DCC dichloromethane solution (2.1 mL, 1M) and H$_2$O$_2$ aqueous solution (1.3 mL, 30%), 4-[(tetrahydropyran-2-yloxy) methyl] benzoic acid (2, 470 mg, 2 mmol) in dichloromethane (8 mL) was slowly added at -10 ºC. The reaction mixture was stirred at 0 ºC for 5 h. The reaction mixture was filtered and the filter cake was washed with cold dichloromethane several times. The filtrates were combined and the solvent was evaporated in vacuo. The residue was re-dissolved in cold dichloromethane and the above step was repeated twice to give a white solid (3). $^1$H NMR (CDCl$_3$, ppm): δ 8.06 (d, 2H, ArH), 7.37 (d, 2H, ArH), 4.91 (d, 1H), 4.75-4.64 (m, 1H), 4.59 (d, 1H), 3.92 (m, 1H), 3.60 (m, 1H), 2.0-1.4 (m, 6H).

**P(VDF-PFSVE) with Hydroxyl End Groups (P2).** A stainless steel vessel equipped with magnetic stir bar was charged with 150 mg of 4-[(tetrahydropyran-2-yloxy) methyl] benzoyl peroxide (3, 0.50 mmol), 15 mL of acetonitrile, 15 mL of 1,1,1,3,3-pentafluorobutane, and 12 g (0.027 mol) of PFSVE. Vinylidene fluoride (21 mL, 0.202 mol) was transferred and condensed through a dual-manifold Schlenk line. The reactor was immersed in oil bath at 90 ºC. After 8 h the reactor was cooled down, the residue gas was discharged and the solution was collected. The tetrahydropyran ether terminated P(VDF-PFSVE) (P1) was precipitated in cold pentane, and dried in vacuo at 60 ºC.
To a mixture of tetrahydropyran ether terminated P(VDF-PFSVE) (P1, 150 mg) in THF (100 mL) was added 3M HCl (5 mL) and acetic acid (20 mL). The mixture was stirred at 60 °C for 3 h, and then condensed in vacuo and poured into de-ionized water (50 mL) to precipitate polymer. The hydroxyl terminated P(VDF-PFSVE) polymer (P2) was collected by filtration, washed by de-ionized water and dried in vacuo at 60 °C. 1H NMR (d6-DMSO, ppm): δ 7.98 (d, ArH), 7.59 (d, ArH), 4.61(-CH2-), 2.9 (-CF2CH2-CF2CH2-, head-to-tail structure), 2.3 (-CF2CH2-CH2CF2-, tail-to-tail structure). 19F NMR (d6-DMSO, ppm): δ -77.0 to -80.0 (-OCF2CF(CF3)OCF2CF2SO2F), -92.4 to -95.8 (-CH2CF2CH2-), -110.2 to -110.8 (-CH2CF2- CF2CF(ORF2SO2F)), -112.3 (-OCF2CF2SO2F), -114.8 and -116.5 (-CH2CF2CF2CH2-), -123.2 (-CF2CF(ORF2SO2F)), -127.8 (-CF(ORF2SO2F)-CF2CH2-), -145.9 (-OCF2CF(CF3)OCF2CF2SO2F). Mn (MNR) = 21,700 g/mol.

**P(VDF-PFSVE) with Triethoxysilane End Groups (P4).** To a mixture of hydroxyl terminated P(VDF-PFSVE) (P2, 150 mg) in methanol (30 mL) was added de-ionized water (30 mL) and triethylamine (3 mL). The mixture was stirred at room temperature for 24 h, and then condensed in vacuo and filtered. The ammonium substituted copolymer (P3) was obtained by washing with de-ionized water and drying in vacuo at 60 °C overnight. 1H NMR (d6-DMSO, ppm): δ 7.98 (d, ArH), 7.59 (d, ArH), 4.61(-CH2-), 2.9 (-CF2CH2-CF2CH2-, head-to-tail structure), 2.3 (-CF2CH2-CH2CF2-, tail-to-tail structure), 1.19 (d, -CH3).

To a mixture of the polymer P3 (150 mg) in acetone (50 mL) was added (3-isocyanatopropyl) triethoxysilane (0.5 mL). The mixture was stirred at 70 °C for 24 h, and then condensed in vacuo. The solid was precipitated in hexane and dried under vacuum at room temperature to yield a yellowish triethoxysilane-terminated P(VDF-PFSVE) copolymer (P4). 1H NMR (d6-DMSO, ppm): δ 7.98 (d, ArH), 7.59 (d, ArH), 4.61(-CH2-), 2.9 (-CF2CH2-CF2CH2-, tail-to-tail structure), 1.19 (d, -CH3).
head-to-tail structure), 2.3 (-CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>-, tail-to-tail structure), 2.0-1.53 (m, -CH<sub>2</sub>CH<sub>2</sub>-), 1.19 (d, -CH<sub>3</sub>).

**In-situ Sol-gel Reaction and Membrane Preparation.** 500 mg of the triethoxysilane-terminated P(VDF-PFSVE) copolymer (P4) was dissolved in DMF (5 mL). THSPSA or TEOS (0.5, 1, 2 and 3 wt %) were introduced to obtain the varied polysilsesquioxane loading in the membranes. A few drops of de-ionized water and hydrochloric acid were added to promote the hydrolysis. After stirring overnight at room temperature, the solution was cast on a Teflon sheet. The film was dried under atmospheric pressure at 50 °C for 12 h, and then the temperature was increased to 75 °C for 6 h. Afterwards, increasing temperature to 100 °C for 6 h, 125 °C for 6 h and 150 °C for 24 h in vacuum to remove residual solvent and anneal the films. The resulting membranes were peeled from the substrates and treated with 2 M HCl for 12 h, washed several times with de-ionized water, and then stored in de-ionized water.

**2.4.3 Characterizations**

The chemical composition of P(VDF-PFSVE) was determined from <sup>1</sup>H and <sup>19</sup>F NMR on a Bruker AM-300 spectrometer. The thermogravimetric analysis (TGA) measurement was performed on a TA Instrument model Q50 at a heating rate of 10 °C/min under N<sub>2</sub> from room temperature up to a maximum of 750 °C. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet 6700. Transmission electron microscopy (TEM) images were taken on a JEOL JEM-1200 EX II TEM equipment. For TEM measurement, the membranes were stained with a saturated lead acetate solution by ion exchange of sulfonic acid groups, then washed with de-ionized water several times and dried under vacuum at 60 °C for 24 h. The stained membranes were embedded in epoxy resin and sectioned to yield 100 nm thick samples using a microtome, and then placed on copper grids.
**Water Uptake.** Water uptake on mass basis was determined gravimetrically. Membranes in acid form were dried under vacuum at 60 °C for 24 h, and cooled to room temperature in desiccators before measuring the weight in dry state ($W_{dry}$). The membranes were then allowed to equilibrate in de-ionized water at 30 °C for overnight. After removal of water on the surface of membrane, the weight was measured in wet state ($W_{wet}$). The water uptake (%) was calculated by using the following equations.

\[
Water\ uptake = \frac{(W_{wet} - W_{dry})}{W_{dry}} \times 100\%
\]  

(2-1)

**Water State.** Low temperature dynamic scanning calorimetry (DSC) measurements were performed to characterize the water state in hydrated membranes. Fully hydrated membrane samples (~15 mg) were blotted with a lab wipe to remove surface water, and then instantly placed into a DSC pan (O-ring model-TA Instruments) and sealed. The sample was immediately put in the calorimeter and cooled to -65 °C. In a typical run, after being held at -65 °C for 15 min., the samples were heated to 100 °C at a heating rate of 5 °C/min. The heat of fusion for the water in the membranes was estimated from $\Delta H_f = H/m_{H_2O}$, where $\Delta H_f$ is the heat of fusion for the water contained in the sample, $m_{H_2O}$ is the mass of water within the sample, and $H$ is the integrated energy from the melting endotherm. The $\Delta H_f$ value for bulk water is 334 J/g.

**Proton Conductivity.** In-plane proton conductivity ($\sigma$) of membranes was measured by the electrochemical impedance spectroscopy (EIS) technique. Impedance data was acquired using a Solartron 1260 gain phase analyzer over the frequency range from 1 Hz – 100 kHz. Conductivity measurements were measured under fully hydrated conditions after the samples
were equilibrated in water at various temperatures for at least 4 h. Temperature was varied from room temperature to 80 °C. The conductivity was calculated using the equation:

$$\sigma = \frac{L}{RA}$$ (2-2)

Where $\sigma$, $L$, $R$, and $A$ denote the membrane conductivity, thickness of the membrane, the measured resistance on the membrane, and cross-sectional area of the membrane perpendicular to current flow, respectively.

**Methanol Permeability.** Methanol permeability was determined in a standard membrane separated diffusion cell. The methanol permeability was carried out with a permeation-measuring cell that has two compartments. Compartment A was filled with 20 mL of 1 M methanol solution in de-ionized water, and compartment B was filled with 20 mL of de-ionized water. The membrane was mounted between the two compartments, and the diameter of the diffusion area was 3.0 cm. The solution in compartment A was magnetically stirred. The methanol concentration in compartment B was monitored using a differential refractometer. Methanol permeability was calculated from the slope of the straight-line plot of methanol concentration versus permeation time.
Chapter 3

Synthesis of Triblock Copolymers Composed of Poly(vinylidene fluoride-co-hexafluoropropylene) and Ionic Liquid Segments

3.1 Introduction

Ionic liquids (ILs) are room temperature melten salts. ILs have been of great interest because of their unique physiochemical properties including negligible vapor pressures, excellent ionic conductivity, wide electrochemical window, and high chemical and thermal stability.\textsuperscript{[19, 55]}

Of particular interest are polymerized ionic liquids (PILs) where the IL moieties are covalently incorporated into the polymer structures. PILs have attracted recent attention as solid-state electrolytes for electrochemical devices such as fuel cells, batteries and dye-sensitized solar cells.\textsuperscript{[56-59]} Unlike ILs where both the organic cation and anion are mobile, the IL moiety is covalently attached to the macromolecule in a PIL. Therefore, PILs differ in that the cation or anion is restricted in mobility, so-called single-ion conductors. PILs alleviate shortcomings of liquid electrolytes in electrochemical devices (e.g., leakage, stability), but usually results in lower ionic conductivity when compared to ILs.

In general, PILs are of interest due to the unique properties of ILs and the broad range of new polymer electrolytes that can be realized with a highly tunable and facile synthesis. It is evident that ionic conductivity of the PILs is strongly associated with the chemical composition and structure of polymer and the nature of anion and cation of ILs.\textsuperscript{[60-62]} Recent results also indicate that the macromolecular architecture may play an important role in ion conduction.\textsuperscript{[63-65]}

To understand the dependence of the ion conduction on polymer structure and film morphology, various IL-containing polymers with different architectures including random copolymers,\textsuperscript{[60]} block copolymers,\textsuperscript{[62]} and main-chain IL polymers\textsuperscript{[66, 67]} have been reported. However, only a few
IL-containing block copolymers have been recently synthesized. A popular approach involves the post-modification of the performed well-defined block copolymers with imidazoles. More recently, ring-opening polymerization and reversible addition fragmentation chain transfer (RAFT) process have been employed for the direct synthesis of IL block copolymers from the norbornene and (meth)acryloyl based monomers.

Prior work with the IL-based block copolymers have exclusively focused on hydrocarbon polymers. In this chapter, we report the synthesis and characterization of a series of the triblock copolymers constituted of poly(vinylidene fluoride-co-hexafluoropropylene) [P(VDF-HFP)] mid-block and imidazolium IL methacrylate end-blocks. Fluoropolymers, i.e. polymers having a fluorinated backbone, have been widely used as membranes in a variety of electrochemical devices. For example, P(VDF-HFP) copolymers function as separators in polymer batteries because of its good mechanical stability and easy film formation. This copolymer has also been shown to be a promising matrix for liquid electrolytes, where its high dielectric constant of $\varepsilon = 8.4$ promotes the adsorption of electrolyte and lithium salt dissociation. It is thus envisioned that the integration of fluoropolymers with IL moieties would represent an enticing opportunity to develop a new class of polyelectrolytes with synergic properties. It was found herein that the P(VDF-HFP) based triblock copolymers form single-phase materials and the anionic counterion has remarkable impact on the thermal properties, ionic conductivity and segmental dynamics of the polymers.
3.2 Results and Discussion

Scheme 3-1. Synthesis of the P(VDF-HFP) based triblock copolymers.

Scheme 3-1 illustrates the synthetic route to the P(VDF-HFP)-based triblock copolymers. The telechelic P(VDF-HFP) with benzyl chloride end-groups was prepared via radical polymerization using 4-chloromethyl benzoyl peroxide (2) as the initiator. The assignments of the chemical shifts of the $^{19}$F NMR spectrum of P(VDF-HFP) are summarized in Table 3-1. The chemical composition of P(VDF-HFP) was calculated according to the following equation:
It was found that the telechelic P(VDF-HFP) contained 73 mol% VDF and 27 mol% HFP. End-group analysis by the integration of the phenyl and benzylic protons against the hydrogens in VDF revealed an approximate number-average molecular weight ($M_n$) of 16 kDa, while triple-detection gel permeation chromatography (GPC) measurements in DMF gave a $M_n$ of 14.3 kDa and a polydispersity of ~1.51.

Figure 3-1. $^1$H NMR spectrum of the telechelic P(VDF-HFP) terminated with benzyl chlorine groups.
Figure 3-2. $^{19}$F NMR spectrum of the telechelic P(VDF-HFP) terminated with benzyl chlorine groups.

Table 3-1. Assignments of the $^{19}$F NMR signals of the telechelic P(VDF-HFP).

<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>Structure</th>
<th>Integrals</th>
</tr>
</thead>
<tbody>
<tr>
<td>-70 to -80</td>
<td>-CF$_2$CF(CF$_3$)-</td>
<td>I$_1$</td>
</tr>
<tr>
<td>-88 to -95</td>
<td>-CH$_2$CF$_2$-CH$_2$CF$_2$-</td>
<td>I$_2$</td>
</tr>
<tr>
<td>-110</td>
<td>-CH$_2$CF$_2$-CF$_3$CF(CF$_3$)-</td>
<td>I$_3$</td>
</tr>
<tr>
<td>-113, -116</td>
<td>-CH$_2$CF$_2$-CF$_2$CH$_2$-</td>
<td>I$_4$</td>
</tr>
<tr>
<td>-119</td>
<td>-CH$_2$CF$_2$-CF$_3$CF(CF$_3$)-</td>
<td></td>
</tr>
<tr>
<td>-179, -185</td>
<td>-CF(CF$_3$)CF$_2$</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3-3. GPC data of the telechelic P(VDF-HFP) terminated with benzyl chlorine groups.
Next, the benzyl chloride-terminated P(VDF-HFP) was reacted with 3-mercaptopropionic acid and carbon disulfide to afford P(VDF-HFP) with trithiocarbonates end-groups as the macro-chain transfer agent (macro-CTA) for RAFT polymerization of the imidazolium methacryloyl monomer (MDBIm-BF₄). The synthesis of the methacrylate monomers with imidazolium pendant cation and tetrafluoroborate (BF₄⁻) counter-anion (MDBIm-BF₄) is outlined in Scheme 3-2. Triethylene glycol was specifically chosen as the spacer because the interactions between the oxygen atoms of ethyleneoxy moieties and the hydrogen atoms of the imidazolium rings may result in a reduction of cation-anion pair dissociation energy and in turn a lower energy barrier for anion hopping to benefit the ion conduction. Triethyleneoxy units were readily introduced by substitution of methacryloyl chloride with 8-iodo-3,6-dioxaoctan-1-ol. The subsequent quaternization reactions with the 1-butyl imidazoles and ion exchange furnished the monomer with BF₄⁻ counterions.
Scheme 3-2. Synthesis of the methacrylate IL monomer.

Figure 3-5. $^1$H NMR spectrum of the monomer MDBIm-BF$_4$. 
Figure 3-6. Mass spectrum of the monomer MDBIm-BF₄, [C₁₇H₂₉O₄N₂]⁺ calcd. 325, found 325.

Figure 3-7. ¹³C NMR spectrum of the monomer MDBIm-BF₄.

The RAFT polymerization of the monomer MDBIm-BF₄ was carried out in the presence of the macro-CTA and AIBN in DMF at 70 °C. The ¹H NMR spectrum confirmed the formation of the block polymers; the vinyl protons of the monomer (δ:5.07 and 6.01 ppm) completely
disappeared after polymerization. Additional peaks assigned to the methacrylate IL segments were clearly observed in Fig. 3-8.

Figure 3-8. $^1$H NMR spectrum of the P(VDF-HFP) based triblock copolymers with ILs.

The compositions of the triblock copolymer were determined by integrating distinct $^1$H NMR signals indicative of each block in eq.3-2. The peak at 9.1-9.5 ppm is attributed the N-CH-N proton of the imidazolium ring in IL units, whereas the signal at 2.3-3.5 ppm corresponds to the methylene protons of the VDF units. By varying the concentration of the IL monomer in the RAFT polymerization, a series of the triblock structures with different ratios of the IL component were successfully formed as summarized in Table 3-2. Ion exchange reaction led to the polymers with bis(trifluoromethane sulfonyle)imide (TFSI) counterions. The prepared polymers are soluble in polar aprotic solvents, such as acetone, acetonitrile, DMF and DMSO.

$$\frac{1(x)}{2(1-x)} = \frac{\text{Integral at } 9.1-9.5}{\text{Integral at } 2.3-3.5}$$  (3-2)
Table 3-2. Chemical compositions and thermal properties of the triblock copolymers.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Counter-Anion</th>
<th>Molecular Weight (kda)</th>
<th>IL Content (mol%)</th>
<th>$T_g$ ($^\circ$C)</th>
<th>$T_{d1}$ ($^\circ$C)</th>
<th>$T_{d2}$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BF$_4^-$</td>
<td>21</td>
<td>6.8</td>
<td>4</td>
<td>335</td>
<td>483</td>
</tr>
<tr>
<td>2</td>
<td>BF$_4^-$</td>
<td>23</td>
<td>9.4</td>
<td>6</td>
<td>303</td>
<td>488</td>
</tr>
<tr>
<td>3</td>
<td>BF$_4^-$</td>
<td>26</td>
<td>13.5</td>
<td>10</td>
<td>288</td>
<td>492</td>
</tr>
<tr>
<td>4</td>
<td>TFSI</td>
<td>22</td>
<td>6.8</td>
<td>2</td>
<td>374</td>
<td>483</td>
</tr>
<tr>
<td>5</td>
<td>TFSI</td>
<td>25</td>
<td>9.4</td>
<td>3</td>
<td>333</td>
<td>493</td>
</tr>
<tr>
<td>6</td>
<td>TFSI</td>
<td>29</td>
<td>13.5</td>
<td>5</td>
<td>302</td>
<td>495</td>
</tr>
</tbody>
</table>

Table 3-2 lists the thermal properties of the IL-containing triblock copolymers. The telechelic P(VDF-HFP) and the block copolymers displayed no detectable crystallization or melting in the temperature range of -80 to 150 °C and showed only one glass transition temperature ($T_g$) in the DSC traces. This indicates an amorphous structure and no phase separation in the triblock copolymers, which were further verified in small-angle X-ray scattering (SAXS) measurements. The formation of single phase in the triblock copolymers can be mostly explained by solubility of ILs in P(VDF-HFP).

Especially, ILs with TFSI$^-$ anion are generally hydrophobic due to fluorine-rich chemical structure and become miscible in fluoropolymer matrix. Meanwhile, it is clear that $T_g$ increases monotonically with increasing the concentration of IL moieties, attributable to the increase of the content of methacrylate backbone and/or the coulombic force between cations and anions. Replacing BF$_4^-$ with TFSI consistently lowers $T_g$ due to the presence of weaker Coulombic interactions in larger anions, which coincides with
previously reported results.\textsuperscript{[60, 62]} \( T_g \) reveals the energy required to separate associated ion pairs that forms physical cross-links in polymer matrix.

![Figure 3-9. Background-subtracted SAXS intensity as a function of scattering vector for polymer 3 and 6.](image)

The thermal stability of the block polymers was investigated by TGA under N\(_2\) atmosphere. It appears that all of the polymers have two onset decomposition temperatures (\( T_{d1} \)):

\( T_{d1} \) is related to decomposition of IL component, while \( T_{d2} \) is attributed to decomposition of P(VDF-HFP). Higher \( T_{d1} \) of the polymers with TFSI\(^-\) counterions results from the weaker nucleophilicity of TFSI\(^-\) versus BF\(_4^-\), as one of the proposed decomposition mechanisms of ILs is associated with an S\(_{N2}\) dealkylation reaction by nucleophilic anions.\textsuperscript{[74]} It was observed that \( T_{d1} \) decreases and \( T_{d2} \) increases slightly with the increase of the amount of IL in the polymer chains. The reduced \( T_{d1} \) may be ascribed to larger content of the anions for degradation with high tendency. The increase of \( T_{d2} \) probably originates from the influence of the ionic interactions of IL acting on P(VDF-HFP) as physical cross-links. This observation again supports the ability of P(VDF-HFP) to solvate ILs, which helps mix the two blocks and prevents the microphase separation in the triblock structures.
Fig. 3-11 shows the $\alpha$-relaxation peak frequency as a function of inverse temperature. The $\alpha$ relaxation is related to cooperative motions of polymer segments at temperatures above the glass transition. Notably, only a single $\alpha$ relaxation was observed in the DRS measurements, indicative of the absence of microphase separation in the triblock copolymers; this is consistent with the DSC and SAXS results. In addition, it is clearly seen that the polymers with larger anions (ie. TFSI) show faster $\alpha$-relaxation, as a consequence of the weaker association of ion pairs with each other. The frequency increases with the increase of IL content in the polymers.
Temperature dependence of DC ionic conductivity is plotted in Fig. 3-12, where the conductivity increases exponentially with increasing temperature. As expected, the DC conductivity at a given temperature increases steadily with IL segment content for both the BF$_4^-$ and TFSI series, apparently due to the increase of the volume fraction of the ion containing species. Interestingly, the polymers with TFSI anions exhibit higher ionic conductivities than the corresponding polymers with BF$_4^-$ counterions. A VFT function was fit to the conductivity data shown in Table 3-3.

$$\sigma(T) = \sigma_0 \exp\left(\frac{B}{T-T_0}\right)$$  \hspace{1cm} (3-3)

where $\sigma_0$ is the infinite temperature DC conductivity, $T_0$ is the Vogel temperature, and $B$ is a parameter related to the rate of change in the slope of the curve. In agreement with the DSC

---

Figure 3-11. The $\alpha$ relaxation relaxation process as a function of inverse temperature.
results, $T_o$ follows the same trends as $T_g$ determined by DSC. The VFT dependence of ion mobility reflects the coupling of segmental motion of polymers and ion motion.

![Figure 3-12. The DC conductivity of the polymers as a function of temperature.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_o$ (S/cm)</th>
<th>$B$ (±10 K)</th>
<th>$T_o$ (±3 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer 1</td>
<td>$10^{0.8}$</td>
<td>2990</td>
<td>-103</td>
</tr>
<tr>
<td>Polymer 2</td>
<td>$10^{0.9}$</td>
<td>2530</td>
<td>-93</td>
</tr>
<tr>
<td>Polymer 3</td>
<td>$10^{1.4}$</td>
<td>2030</td>
<td>-79</td>
</tr>
<tr>
<td>Polymer 4</td>
<td>$10^{0.1}$</td>
<td>2950</td>
<td>-99</td>
</tr>
<tr>
<td>Polymer 5</td>
<td>$10^{0.9}$</td>
<td>1980</td>
<td>-72</td>
</tr>
<tr>
<td>Polymer 6</td>
<td>$10^{0.5}$</td>
<td>1850</td>
<td>-69</td>
</tr>
</tbody>
</table>
3.3 Summary

Fluoropolymer based triblock copolymers with pendant imidazolium cations were synthesized for the first time. The synthetic approach involves radical polymerization of VDF and HFP using a functional initiator to yield the telechelic (PVDF-HFP) as the macro-CTA for subsequent RAFT polymerization of the methacrylate imidazolium monomer. The method reported herein provides facile synthetic access to incorporation of IL segments into fluoropolymers, which would significantly broaden the family of the IL-containing polymers. It was found that the compatibility of IL and fluoropolymer matrix likely prevents discrete microphase separation in the triblock copolymers. The polymers with TFSI counterions display higher ionic conductivities than their BF$_4^-$ analogs due to the reduced $T_g$ and enhanced polymer segmental mobility. The temperature dependence of the ion mobilities of the triblock copolymers is well described using a VFT equation, indicating a strong correlation between ion conduction and polymer segmental dynamics.

3.4 Experimental Section

3.4.1 Materials. All reagents were used without further purification. 4-(chloromethyl)benzoyl chloride, lithium peroxide, 2-[2-(2-chloroethoxy)ethoxy]ethanol, sodium iodide, methacryloyl chloride, 1-butylimidazole, 2,6-di-tert-butyl-4-methylphenol, sodium tetrafluoroborate, lithium bis(trifluoromethane sulfonyl)imide (LiTFSI), 3-mercapto propionic acid, potassium phosphate, carbon disulfide, sodium sulfate, 2,2’-azobis(2-methylpropionitrile), anhydrous acetonitrile, anhydrous dimethyl formamide were purchased from the Aldrich Chemical Co. Vinylidene fluoride (VDF) and hexafluoropropylene (HFP) were purchased from SynQuest Laboratory Inc. and used as received.
3.4.2 Synthesis of 4-chloromethyl benzoyl peroxide (2). To a 20 mL aqueous solution of Li₂O₂ (1.38 g, 30 mmol), 4-(chloromethyl)benzoyl chloride (4.44 g, 23.5 mmol) in Et₂O/hexane (40 mL, 1:1) was added slowly at 0 °C. The reaction mixture was stirred at 0 °C for 5 h. The reaction mixture was diluted by addition of chloroform (100 mL), and filtered and washed with water (2×30 mL). The organic phase was separated, and the aqueous phase was extracted with chloroform (2×20 mL). The combined organic phases were dried over MgSO₄. Removal of solvent yielded a white solid (1.8 g, 45%). ^1H NMR (CDCl₃, ppm): δ 8.12 (d, ArH), 7.56 (d, ArH), 4.67 (s, –CH₂Cl).

3.4.3 Synthesis of the telechelic P(VDF-HFP) with benzyl chloride terminal groups. 4-Chloromethyl benzoyl peroxide (350 mg, 1.6 mmol), and acetonitrile (30 mL) were added into 70 mL Parr reactor with a magnetic stir. The gas-condense transfer of VDF (6 mL, 0.06 mol) and HFP (21 mL, 0.22 mol) were carried out with rigorous exclusion of oxygen and moisture through a dual-manifold Schlenk line with 10⁻⁶ Torr high vacuum. The reactor was immersed in oil bath at 90 °C for 5 h. After residual gases were discharged, the solvent was evaporated, and the residue was dissolved in acetone and precipitated from chloroform. P(VDF-HFP) was collected and dried in vacuo at 60 °C. ^1H MMR (acetone-d₆, ppm): δ 8.10 (d, ArH), 7.70 (d, ArH), 4.83 (s, –CH₂Cl), 3.2 (–CF₂CH₂–CF₂CH₂–, head-to-tail structure), 2.5 (–CF₂CH₂–CH₂CF₂–, tail-to-tail structure). ^19F NMR (acetone-d₆, ppm): δ -70.0 to -80.0 (-CF₂CF(CF₃), -88.0 to -95.0 (-CH₂CF₂–CH₂CF₂–), -110.0 (-CH₂CF₂–CF₂CF(CF₃)), -113.0 to -116.0 (-CH₂CF₂–CF₂CH₂–), -179 to -185 (-CF₂CF(CF₃)). Mₙ (NMR) 16 kDa.

3.4.4 Synthesis of P(VDF-HFP) macro-CTA. To a suspension of K₃PO₄ (3.89 g, 11.5 mmol) in acetone (15 mL), 3-mercapto propionic acid (0.5 mL, 5.75 mmol) was added and the reaction
mixture stirred for 20 min. After adding carbon disulfide (0.66 mL, 10.9 mmol), the mixture was stirred overnight. The telechelic P(VDF-HFP) (2 g) was dissolved in 5 mL acetone, added to the reaction mixture and stirred overnight at 80 °C. After the resulting solids were filtered off and the solvent was evaporated, the residue was dissolved in acetone and precipitated from chloroform.

$^1$H MMR (acetone-d$_6$, ppm): $\delta$ 8.10 (d, ArH), 7.70 (d, ArH), 4.83 (s, –CH$_2$Cl), 3.2 (–CF$_2$CH$_2$–CF$_2$CH$_2$–, head-to-tail structure), 2.5 (–CF$_2$CH$_2$–CH$_2$CF$_2$–, tail-to-tail structure).

3.4.5 Synthesis of 1 - [2 - methacryloyloxy) - 3, 6 - dioxa-octyl] - 3 - butylimidazolium tetrafluoroborate (MDBIm-BF$_4$).

To 1-butyl imidazole (4.96 g, 0.040 mol), and 8-iodo-3,6-dioxa-octyl methacrylate (13.12 g, 0.05 mol) was added triethylamine (15.2 g, 0.15 mol). While cooling with ice, methacryloyl chloride (15.7 g, 0.15 mol) in 50 ml ether was added slowly. The mixture was stirred overnight, filtered, and extracted with water, then dried over MgSO$_4$, and evaporated to produce the product as yellow oil. Yield: 40.3 g (82%). $^1$H NMR (CDCl$_3$, ppm): $\delta$ 1.96 (s, =C-CH$_3$), 3.27 (t, -CH$_2$-I), 3.5-3.9 (m, CH$_2$O-CH$_2$-CH$_2$O-CH$_2$-), 4.31 (t, -COO-CH$_2$-), 5.59 (s, CH=I=C-COO-trans), 6.14 (s, CH=C-COO-cis).

8-Iodo-3,6-dioxa-octyl methacrylate. 8-Iodo-3,6-dioxaoctan-1-ol (39 g, 0.15 mol) was dissolved in 400 mL of dry ether, and added triethylamine (15.2 g, 0.15 mol). While cooling with ice, methacryloyl chloride (15.7 g, 0.15 mol) in 50 ml ether was added slowly. The mixture was stirred overnight, filtered, and extracted with water, then dried over MgSO$_4$, and evaporated to produce the product as yellow oil. Yield: 40.3 g (82%) yellow oil. $^1$H-NMR (CDCl$_3$, ppm: $\delta$ 1.96 (s, =C-CH$_3$), 3.27 (t, -CH$_2$-I), 3.5-3.9 (m, CH$_2$O-CH$_2$-CH$_2$O-CH$_2$-), 4.31 (t, -COO-CH$_2$-), 5.59 (s, CH=I=C-COO-trans), 6.14 (s, CH=C-COO-cis).
g, 0.040 mol), 0.1 g of 2,6-di-tert-butyl-4-methylphenol was added. The reaction mixture was stirred at 40 °C for 48 h. The mixture was dissolved in 24 mL of anhydrous acetonitrile and was added to a suspension of NaBF₄ (5.27 g, 0.048 mol) in 50 mL of anhydrous acetonitrile. After the mixture was stirred for 48 h at room temperature, the sodium bromide precipitate was removed by filtration, and the filtrate was concentrated. The concentrated filtrate was diluted with methylene chloride (200 mL) and filtered through a silica gel column. The removal of methylene chloride yielded the imidazolium-containing monomer as a yellow viscous liquid. \(^1\)H NMR (DMSO-d₆, ppm): 9.21 (s, -N=CH-N-), 7.80 (d, -N-CH=CH-N-), 6.01 (s, CH=C-COO-trans), 5.70 (s, CH=C-COO-cis), 4.37 (t, -COO-CH₂-), 4.20 (t, -CH₂-N-), 3.5-3.9 (m, CH₂-O-CH₂-CH₂-O-CH₂-), 1.87 (s, =C-CH₃), 1.78 (m, -CH₂-CH₂-CH₃), 1.25 (m, -CH₂-CH₂-CH₃), 0.89 (t, -CH₃). \(^{13}\)C NMR (DMSO-d₆, ppm): 14.1, 18.6, 19.6, 32.4, 49.7, 64.6, 69.6, 70.5, 122.8, 123.4, 126.7, 136.6, 137.1, 167.3. MS: [C₁₇H₂₉O₄N₂]⁺ calcd. 325, found 325.

3.4.6 Synthesis of the triblock copolymers. Different compositions of the triblock copolymers were prepared in the RAFT polymerization. Typical procedure: A reactor charged with AIBN (6.76 mg, 4×10⁻⁵ mol), P(VDF-HFP) macro-CTA (Mₙ = 23 kg/mol; 950 mg, 4×10⁻⁵ mol), MDBImBF₄ (0.82 g, 2×10⁻³ mol, 1.64 g, 4×10⁻³ mol, 2.46 g, 6×10⁻³ mol, respectively), and DMF (30 mL) was carried out with rigorous exclusion of oxygen and moisture through a dual-manifold Schlenk line with 10⁻⁶ Torr high vacuum. After the reactor was immersed in oil bath at 70 °C for 24 h, the reactor was rapidly cooled in cold water. The solvent was evaporated, and the residue was dissolved in acetone and precipitated in chloroform. The polymer was collected and dried in vacuo at 60 °C.
3.4.7 Anion-exchange reaction. Anion-exchange reaction of the triblock copolymer was conducted in acetonitrile at room temperature. Polymers 1-3 (0.5 g) and an excess amount of LITFSI were dissolved in acetonitrile (10 mL) and stirred for 48 h. The triblock copolymers was precipitated in deionized water, washed with deionized water several times and then dried in vacuo at 60 °C to obtain the triblock copolymers with TFSI counter-anion (Polymers 4-6).

3.4.8 Characterizations

The chemical compositions of the polymers were determined from $^1$H and $^{19}$F NMR on a Bruker AM-300 spectrometer. The thermal transition data were obtained by a TA Instruments Q100 differential scanning calorimeter (DSC) at a heating and cooling rate of 10 °C/min. The measurement temperature range was -80 to 150 °C. The glass transition temperature $T_g$ was determined by the midpoint of total heat flow curve in the thermal transition region. The thermogravimetric analysis (TGA) measurement was performed on a TA Instrument model Q50 at a heating rate of 10 °C/min under N$_2$ from room temperature up to a maximum of 800 °C.

Broadband Dielectric Relaxation Spectroscopy (DRS). DRS measurements were performed on a Concept 40 system from Novocontrol GmbH, and measured over the frequency range 10 mHz to 10 MHz. Temperature was controlled by a Quatro temperature control system with a precision of greater than ±0.1 °C. All copolymers were measured over the temperature range from -140 °C to 150 °C, well above the calorimetric $T_g$. Samples were prepared for DRS measurements by solution casting thin films, typically 60-70 µm thick, from a good solvent directly onto brass electrodes, 15 mm in diameter. A smaller, 5 mm diameter upper electrode was pressed onto each film. Samples were dried under vacuum (2-3 µbar) at room temperature (T >$T_g$) prior to measurement, and were transferred from the oven to the spectrometer as quickly as possible to
avoid moisture absorption. The effects of water on glassy state dynamics are well known, so great care was taken to minimize the sample exposure to moisture.

Small-angle X-ray scattering (SAXS) was performed on a Molecular Metrology SAXS, using Cu Kα radiation (wavelength = 1.5418 Å). The SAXS is equipped with a 2-D detector, and the scattering vector (q) range was calibrated with silver behenate.

Wide angle X-ray scattering (WAXS) was performed on a Rigaku DMAX-Rapid Microdiffraactometer equipped with a 2-D detector, also using CuKα radiation. For both SAXS and WAXS, software routines were used to evaluate the scattering intensity as a function of the diffraction angle of, 2θ, or q, defined as \( q = \frac{4\pi \sin(\theta)}{\lambda} \). Depending on the scattering intensity, samples were exposed from twenty minutes to two hours.

The same samples used for DRS measurements were used for scattering experiments. After DRS measurements were complete, samples were carefully removed from the brass electrodes and mounted in the SAXS or WAXS sample holder.
Chapter 4

Synthesis and Characterization of Lithium Ion Conducting Polymer Electrolytes Based on Comblike Polysiloxane with Ionic Liquid Branches

4.1 Introduction

Ionic liquids (ILs) have been of interest for the last few decades due to their unique properties, such as low-volatility, non-flammability, large electrochemical window, and high ion conductivity.\[^{19, 32, 55, 75}\] Polymerized ionic liquids (PILs) have been studied for use as single-ion polymer electrolytes.\[^{37, 60, 66, 76}\] Although PILs are of great interest as solid-state polymer electrolytes, they still have a major drawback: insufficient low ionic conductivity. To overcome these obstacles, many factors which can impact ionic conductivity in PILs have been determined, such as polymer chemistry, glass transition temperature, and polymer morphology.

Poly(ethylene oxide) (PEO) was the first solid polymer electrolyte used in lithium ion batteries.\[^{18}\] Even though it has the ability to solvate lithium ions, the room temperature (RT) ionic conductivity of PEO is low. It is a semicrystalline polymer, and ionic conduction occurs mostly in the amorphous phase. Since ion mobility should increase with a reduction in Tg and low content of amorphous phase. The increasing in the number of chain ends is expected to enhance conductivity by reducing Tg. Therefore, one approach to increasing the RT conductivity of PEO-based polymer electrolytes is by grafting short chain PEO oligomers as side chains to form comb or branched polymer structures.\[^{77-80}\] Moreover, when these ends are anchored to a flexible backbone, such as polysiloxanes, it may further increase the chain mobility which helps to improve the ionic conductivity.

Herein, we report the synthesis and characterization of the new polymer electrolyte. We chose polysiloxanes as the polymer backbone for the following reasons: 1) siloxane structures are
flexible, offering very low Tg, which helps to obtain the final polymers which have low Tg. 2) many chemical derivatives can be readily prepared via hydrosilation of poly (hydromethylsiloxane) (PHMS) with appropriate terminal olefins. We sought to prepare the polymers with long ethylene glycol side chain, which is hexethylene glycol in an attempt to increase ion mobility and to promote anion-cation dissociation, leading to enhance ionic conductivity via an increase in free ion concentration. In addition, we produced tripodand molecules with ionic liquids in order to increase ion concentration for the polymers and studied how the anion structures affecting the transport properties.

4.2 Results and Discussion
4.2.1 Synthesis

The comblike polysiloxanes with ionic liquid branches were synthesized in three steps: hydrosilylation, quaternization of 1-butyl imidazole, and anion exchange reaction as shown in Scheme 4-1. The addition of silicon-tripodand centers by hydrosilylation was confirmed from $^1$H NMR spectra as shown in Fig. 4-3. The proton resonance at 4.9 ppm of Si-H bond disappeared indicating the completion of the reaction. Also, no trace of double bonds, which is around 5.9-6.1 ppm exist in the $^1$H NMR spectra of the polymer.
Scheme 4-1. Synthesis of the combike polymer.
Figure 4-1. $^1$H NMR spectra of PHMS.

Figure 4-2. $^1$H NMR spectra of viny tris-17-bromo-3,6,9,12,15-pentaoxaheptadecan-1-ol silane.
Figure 4-3. $^1$H NMR spectra of the comblike polysiloxanes.

Fig. 4-4 shows the Attenuated total reflectance infrared (ATR-IR) spectra for the PSHG_TFSI and PHSG_Tf. As shown in Fig. 4-4a the IR spectrum of PSHG_TFSI shows asymmetric stretching band of S-N-S (790 cm$^{-1}$), symmetric bending band of CF$_3$ (762 cm$^{-1}$), symmetric stretching band of S-N-S (740 cm$^{-1}$), SO$_2$ stretching bands (asymmetric 1351, 1332 cm$^{-1}$; symmetric 1054 cm$^{-1}$) and CF$_3$ stretching bands (asymmetric 1132 cm$^{-1}$; symmetric 1185 cm$^{-1}$).[81] For PSHG_Tf, Fig. 4-4b. shows symmetric bending band of CF$_3$ (760 cm$^{-1}$), SO$_3$ stretching bands (asymmetric 1251, 1294 cm$^{-1}$; symmetric 1030 cm$^{-1}$) and CF$_3$ stretching bands (asymmetric 1228 cm$^{-1}$; symmetric 1158 cm$^{-1}$).[82,83]
4.2.2 Thermal Analysis. The Tg values of the polymers are reported in Table 4-1. The comblike polysiloxanes with ionic liquid branches are amorphous; the polymers do not display crystallization or melting in the temperature range of -100 to 150 °C as shown in DSC thermograms. Different anions affect the Tg; the polymer with TFSI has a Tg of -23 °C which is lower than the polymer with Tf, which has a Tg of -5 °C because of the plasticizing effect of the TFSI counterion on the polymers.\textsuperscript{84, 85} The anion structure also effect on thermal stability of the polymers. The decomposition of the polymer with TFSI takes place at 310 °C, while in the polymer with Tf takes place at 288 °C. The decomposition temperature of the ILs strongly depends on the anion types.\textsuperscript{86, 87} The higher thermal stability of the polymer with TFSI is due to the weaker nucleophilicity of TFSI versus Tf. As the main decomposition mechanisms of ILs is an $S_N2$ dealkylation reaction by nucleophilic anions.\textsuperscript{88} In addition, the TFSI anion is a weak or non-nucleophilic anion. Thus, it can undergo the decomposition process via sulfur dioxide release instead of dealkylation or proton transfer,\textsuperscript{89} which makes it more difficult to thermally degrade.
Table 4-1. DSC, TGA thermal analysis and ionic conductivity of PSHG_TFSI and PSHG_Tf.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tg (°C)</th>
<th>Td (°C)</th>
<th>( \sigma ) (25 °C, S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSHG_TFSI</td>
<td>-23</td>
<td>310</td>
<td>( 3.5 \times 10^{-5} )</td>
</tr>
<tr>
<td>PSHG_Tf</td>
<td>-5</td>
<td>288</td>
<td>( 3.6 \times 10^{-7} )</td>
</tr>
</tbody>
</table>

Figure 4-5. TGA thermogram of PSHG_TFSI and PSHG_Tf.

4.2.3 **Ionic conductivity.** The ionic conductivity at 25 °C was performed by Solatron 1260. The conductivity of PSHG_TFSI is higher than PSHG_Tf, which is the reverse order of Tg shown in Table 4-1. These results suggest that polymer chain relaxation plays a dominant role in ion transport. Also, the differences in conductivity may be attributed to the symmetry and size of the anions and the dissociation energy of the ion pairs. Fig. 4-5 shows the measured ionic conductivities of PILs as a function of temperature measured from DRS. With increasing temperature, the difference in ionic conductivity between PILs with different anions decreases.
For a solid polymer electrolyte system, the temperature dependent ionic conductivity is well described by VFT equation.

\[
\sigma(T) = \sigma_0 \exp\left(\frac{B}{T-T_0}\right)
\]  

(4-1)

Figure 4-6. The DC conductivity of the polymers as a function of temperature.

4.2.4 Ion Concentration. Fig. 4-6 shows the mobile ion concentration determined using EP model. The ion concentration increases with increasing temperature and it is well described by Arrhenius equation:

\[
p = p_\infty \exp\left(-\frac{E_a}{kT}\right)
\]

(4-2)

where \(p_\infty\) is the ion mobility as \(T \to \infty\), \(E_a\) is an activation energy. The activation energy is \(E_a = 6.6\) kJ/mol for PSHG_TFSI and \(E_a = 7.3\) kJ/mol for PSHG_Tf. The lower activation in PSHG_TFSI indicates a lower interaction strength of the larger TFSI anions to the imidazolium cations compared to the Tf anions.\(^{[90]}\)
4.2.5 Ion Mobility. The ion mobility was determined from EP model is shown in Fig. 4-7. The data are well described by VFT equation

\[
\mu = \mu_\infty \exp \left( \frac{-B}{T - T_0} \right)
\]  \hspace{1cm} (4.3)

where \(\mu_\infty\) is the ion mobility as \(T \to \infty\), \(B\) is a constant, and \(T_0\) is the Vogel temperature, at which the mobility extrapolates to zero. The VFT temperature dependence of ion mobility reflects the coupling of polymer segmental motion and ion motion. Like ionic conductivity, the ion mobility of PSHG_TFSI is higher than PSHG_Tf at the same temperature range. The lower ion mobility in PSHG_Tf can be understood in terms of the higher dissociation energy of the large TFSI anions to the imidazolium cations compared to the Tf anions,\textsuperscript{[90]} which results in a lower energy barrier for anion motion.
4.2.6 Morphology. To study the morphology of PSHG_TFSI and PSHG_Tf, WAXD and SAXs were performed on the polymer samples at room temperature. As shown in Fig. 4-8, WAXD patterns for the samples display two amorphous halos: at \( q \approx 0.8 \) Å arising from phase-separated polysiloxane segments and at \( q \approx 1.5 \) Å arising non-polysiloxane segments.\[^{91,92}\] PSHG_TFSI and PSHG_Tf exhibited the broad peaks at \( q \approx 0.017 \), and 0.024 Å, respectively. This suggests a microphase-separation between hydrophobic PMHS main chains and hydrophilic hexaethylene glycol-ionic liquid side chains with the aggregate size 37 nm in PSHG_TFSI and 26 nm in PSHG_Tf.
4.2.7 Electrochemical Stability. The electrochemical stability windows were determined for both samples using linear sweep voltammetry (LSV) at stainless steel electrode as a working and lithium electrode as a counter and reference electrode. Linear voltammograms of the polymer electrolytes are shown in Fig. 4-9. The region where the current as a function of voltage was nearly constant was taken as the region that shows the electrochemical stability of these ionic liquids. Based on this method, PSHG_TFSI has an electrochemical window of 5.8 V whereas
PSHG_Tf has the electrochemical window of 4.1 V. This suggests that PSHG_TFSI is somewhat more electrochemically stable than PSHG_Tf. In addition, the better anodic stability (relatively higher anodic potential limits) for the TFSI\(^-\) based polymer may be explained by better resistance of the TFSI\(^-\) anion towards oxidation.

![Sweep voltammetry graphs](image)

Figure 4-10. Linear sweep voltammetry of PSHG_TFSI and PSHG_Tf at RT, on a stainless steel electrode, with a platinum counter electrode with a sweep rate of 1 mV/s.
4.2.8 Effect of Adding Lithium Salts on the Properties of the Polymers. A series of lithium salts was added to the polymers: to a sample of PSHG_TFSI was added LiTFSI 50, 100, 150 mol%, and PSHG_Tf was added LiTf 50, 100, 150 mol%. All samples showed only Tg as shown in Fig. 4-10, and as summarized in table 4-2. The Tg of the PSHG_TFSI decreases from -23 to -26, -28 and -34 °C as the LiTFSI content is increased from 0 to 50, 100 and 150 mol%, respectively, which is explained by the plasticity effect of TFSI anion.\cite{85} This result is contrast to the PSHG_Tf where the incorporated LiTf increases the ion agglomeration and leads to an increased Tg. Fig. 4-11 shows the effect of the concentration of salts on the ionic conductivity as a function of temperature. The ionic conductivity of the PSHG_TFSI improves as the LiTFSI content is increased from 0 to 50, and 100 mol%, respectively. This result is attributed to an increase of number of ions and lowered Tg value. A further increase of the LiTFSI content from 100 to 150 wt% lowers the conductivity, which is attributed to the formation of ion aggregates. Generally, with the increase of salt concentration, aggregated ions increased and number of free ions decreased. The increasing of LiTf content causes the formation of ion aggregation, which leads to the small increase of Tg and the decrease of number of effective carrier ions and ionic conductivity. The conductivity increases exponentially with increasing temperature. A VFT function was fit to the conductivity data and the parameter as shown in table 4.3.

\[
\sigma(T) = \sigma_0 \exp \left( \frac{B}{T - T_0} \right) \quad (4.1)
\]

where \(\sigma_0\) is the infinite temperature DC conductivity, \(T_0\) is the Vogel temperature, and B is a parameter related to the rate of change in the slope of the curve.
Figure 4-11. DSC thermograms of the polymers at different concentrations of Li salts.
Table 4-2. Tg of the polymers at different concentrations of Li salts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tg (°C)</th>
<th>Samples</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSHG_TFSI</td>
<td>-23</td>
<td>PSHG_Tf</td>
<td>-5</td>
</tr>
<tr>
<td>PSHG_TFSI_50 mol% LiTFSI</td>
<td>-27</td>
<td>PSHG_Tf_50 mol% LiTf</td>
<td>-1</td>
</tr>
<tr>
<td>PSHG_TFSI_100 mol% LiTFSI</td>
<td>-28</td>
<td>PSHG_Tf_100 mol% LiTf</td>
<td>0</td>
</tr>
<tr>
<td>PSHG_TFSI_150 mol% LiTFSI</td>
<td>-34</td>
<td>PSHG_Tf_150 mol% LiTf</td>
<td>2</td>
</tr>
</tbody>
</table>
Figure 4-12. Effect of lithium salts on the ionic conductivity.
Table 4-3. Conductivity VFT fitting parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_0$ (S/cm)</th>
<th>B (±10 K)</th>
<th>$T_o$ (±1 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSHG_TFSI</td>
<td>$10^{0.2}$</td>
<td>1270</td>
<td>192</td>
</tr>
<tr>
<td>PSHG_TFSI_50mol%LiTFSI</td>
<td>$10^{0.2}$</td>
<td>1320</td>
<td>189</td>
</tr>
<tr>
<td>PSHG_TFSI_100mol%LiTFSI</td>
<td>$10^{0.4}$</td>
<td>1350</td>
<td>186</td>
</tr>
<tr>
<td>PSHG_TFSI_150mol%LiTFSI</td>
<td>$10^{0.1}$</td>
<td>1250</td>
<td>196</td>
</tr>
<tr>
<td>PSHG_Tf</td>
<td>$10^{0.1}$</td>
<td>1410</td>
<td>208</td>
</tr>
<tr>
<td>PSHG_Tf_50mol%LiTf</td>
<td>$10^{0.2}$</td>
<td>1440</td>
<td>207</td>
</tr>
<tr>
<td>PSHG_Tf_100mol%LiTf</td>
<td>$10^{0.3}$</td>
<td>1600</td>
<td>207</td>
</tr>
<tr>
<td>PSHG_Tf_150mol%LiTf</td>
<td>$10^{0.2}$</td>
<td>1500</td>
<td>216</td>
</tr>
</tbody>
</table>

4.2.9 Lithium Transference Number. The transference number of an ion is the fraction of the total current that is carried by the respective ion across a given medium. The lithium transference number ($T_{Li^+}$) of the polymer electrolyte was evaluated by DC polarization and AC impedance spectroscopy using the technique described by Evans.\(^{[93]}\) From the technique, Li/polymer electrolyte/Li cell was polarized by a constant potential difference between the electrodes and monitored until the current eventually reached to the steady state as shown in Fig. 4-12. The fall in current may result from: (i) a growth of passivating layers at the electrodes up to some limiting thickness, and (ii) a concentration gradient in the polymer electrolyte which affects the motions of ions. Fig. 4-13 shows Cole-Cole plots measured by impedance measurement before and after applying constant potential. The plots have two semicircles that can be fit to find out: (i) the bulk resistance ($R_e$) which intercepts the $Z_{real}$ axis at high frequency ($\omega \rightarrow \infty$), (ii) the interfacial resistance ($R_i$) which is the semicircle at low frequency, and (iii) the charge transfer resistance ($R_{ct}$) which is the semicircle at high frequency.\(^{[94, 95]}\) We chose PSHG_TFSI_100mol%LiTFSI to
find $T_{Li^+}$, since it has the highest ionic conductivity among the samples. The $T_{Li^+}$ of the polymer was calculated from Eq. 4-4.

$$T_{Li^+} = \frac{I_s(\Delta V - I_0R_0)}{I_0(\Delta V - I_sR_s)}$$

Where $I_0$ and $I_s$ are current at initial and steady state, $\Delta V$ is a constant potential (25 mV), $R_0$ and $R_s$ are the resistance of the passivating layer on the interface of lithium electrode at the initial and steady state, respectively. Table 4-4 lists $T_{Li^+}$ and other parameters, a value of $T_{Li^+} = 0.62$ was obtained which is higher than a value of 0.05 of 1-ethyl-3-methylimidazolium tetrafluoroborate adding LiBF$_4$ from the study of Hayamizu.$^{[96]}$ It is believed that the improvement in $T_{Li^+}$ may come from the immobility of the imidazolium cations on the polymer structure. Generally, in a lithium battery electrolyte, a small value of $T_{Li^+}$ is not desirable. Since only the lithium ion can be oxidized/reduced on the electrodes and other ions are only polarized near the electrode under potential gradient, low conductivity can be expected from a small $T_{Li^+}$.

Figure 4-13. Current vs time profile of PSHG_TFSI_100 mol% LiTFSI at RT under a 25 mV DC bias.
4.2.10 Interfacial Stability. The stability of the polymer electrolyte towards the lithium electrode is one of the important properties in applications of lithium batteries. To evaluate the stability of PSHG_TFSI_100 mol% LiTFSI with respect to lithium, the interfacial resistance of Li/polymer electrolyte/Li cell was monitored by electrochemical impedance spectroscopy. Fig. 4-14 shows the Cole-Cole plot, the diameter of the semicircle gives the overall interfacial resistance. The interfacial resistance of the sample gradually increases due to the growth of a passivation layer on the lithium electrode. Then, the $R_i$ reaches a stability value of 19.6 kΩ in 3 days.
Figure 4-15. Cole-Cole plots of a Li/PSHG_TFSI_100 mol% LiTFSI/Li cell. Evolution of the R, at RT is shown in the inset.

4.2.11 Cyclic Voltammetry. CV of Li/PSHG_TFSI_100 mol% LiTFSI/Li cell was carried out at RT with a sweep rate at 1 mV/s. Cyclic voltamograms as shown in Fig. 4-15 exhibit well defined anodic peaks between 0.5 to 0.7 V vs. Li/Li$^+$ and reduction peaks between -0.6 to -0.7 V vs. Li/Li$^+$. On cycling, the cathodic and anodic peak current values slowly decrease may due to the slowly increasing in forming of passivation layer on the lithium surface that prevents further redox reaction.
4.2.12 Mechanical Property. A solid polymer electrolyte is preferred in the view point of safety which prevents leaking and dendritic growth of lithium that occurs in liquid electrolyte. The dynamic shear moduli was measured as a function of shear strain. Under a fixed frequency (\( \omega = 10 \text{ rad s}^{-1} \)) we applied strain and measured the storage modulus (\( G' \)) and loss modulus (\( G'' \)). Fig. 4-16 shows dynamic moduli (\( G', G'' \)) and tan delta (\( G''/G' \)) as a function of shear stain. It was found that at low strains, \( G' \) is higher than \( G'' \) which is the characteristic of a solid-like elastic material. The highest elastic modulus of PSHG_TFSI is found to be \( 2.1 \times 10^5 \) Pa. When increasing in shear strain, \( G'' \) increases until maximum then subsequently dominates \( G' \) or tan \( \delta \) (\( G''/G' \)) becomes greater than 1, which indicates a strain-induced transition to fluid-like state.
Figure 4-17. The dynamic shear moduli ($G'$, $G''$) and tan delta of PSHG_TFSI as a function of applied strain at RT.

### 4.3 Summary

The new polymer structures containing tripodant hexaethylene ionic liquid moiety with TFSI and Tf counterions have been synthesized and their properties have been characterized. Introducing tripodant hexaethylene imidazolium cations on the polymer structure leads to createcomb-like polymer electrolytes, which is completely amorphous. Anion structures had a significant effect on glass transition temperature, ionic conductivity, thermal and electrochemical stability. PSHG_TFSI had lower glass transition temperature and a significantly higher ionic conductivity than with PHSG_Tf. The polymer electrolytes based on TFSI anion has higher thermal and electrochemical stability than the polymer based Tf anion due to the higher stability of TFSI anion when compared with Tf anion. Adding LiTFSI and LiTf also affected Tg and ionic conductivity. PSHG_TFSI with 100 mol% TFSI showed stability with a lithium electrode and
lithium transference number of 0.62 which indicates a potential as a solid polymer electrolyte in lithium battery application.

### 4.4 Experimental Section

#### 4.4.1 Materials. All reagents were used without further purification. Poly(methylhydrosiloxane) (PMHS, Mn = 1,700-3,200), Hexaethylene glycol, triphenyl phosphate, tetrabromomethane (CBr₄), trichlorovinylsilane, 1-butyl imidazole, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), Lithium trifluoromethanesulfonate (LiTf), 2% Karstedt catalyst solution in xylene, anhydrous acetonitrile, DMF, and anhydrous benzene were purchased from Sigma-Aldrich. THF, chloroform, and methanol were purchased from VWR.

#### 4.4.2 Synthesis of 17-bromo-3,6,9,12,15-pentaoxaheptadecan-1-ol (2). To a solution of hexaethylene glycol (10 g, 35.42 mmol) in THF (10 ml) was added triphenyl phosphine (4.65 g, 17.71 mmol), then added CBr₄ (5.87 g, 17.71 mmol). The reaction mixture is stirred for 4 h at RT. Then the reaction mixture is concentrated and purified by column chromatography with 95:5 Chloroform/methanol to give 17-bromo-3,6,9,12,15-Pentaoxaheptadecan-1-ol as colorless oil: ¹H NMR (CDCl₃) δ: 3.16 (s, -OH), 3.43 (t, -CH₂-Br), 3.58-3.68 (m, -O-CH₂-), 3.78 (t, -CH₂-CH₂-Br); ¹³C NMR (CDCl₃) δ: 30.1, 61.6, 70.2-70.7 (br), 73.0 (-CH₂-CH₂-Br).

#### 4.4.3 Synthesis of vinyl tris17-bromo-3,6,9,12,15-pentaoxaheptadecan-1-ol silane (3). To a solution of 17-bromo-3,6,9,12,15-pentaoxaheptadecan-1-ol (5.6 g, 0.016 mol) in toluene (50 ml) is added triethylamine (3.2 g, 0.032 mol) followed by trichlorovinylsilane (0.873 g, 5.33 mmol). The reaction mixture is stirred for 3 h at RT, then diluted with EtOAc (50 ml), washed with water and dried over anhydrous Na₂SO₄. The organic layer is concentrated to give product 3: ¹H NMR
(CDCl3) δ: 3.43 (t, -CHBr), 3.58-3.68 (m, -O-CH2), 3.79 (-O-CH2-CH2Br), 3.89 (t, -Si-O-CH2) 5.9-6.1 (m, CH=CH-Si), 13C NMR (CDCl3) δ: 30.1, 62.4 (-Si-O-CH2, 70.8-71.9 (signal overlap), 72.7 (-CH2-CH2-Br), 137.4 (CH=CH-Si).)

4.4.4 Synthesis of comblike polysiloxane with ionic liquid branches (PSHG_TFSI, PSHG_Tf). 900 mg of poly(methylhydrosiloxane) (PMHS, average molecular weight 2450 g/mol) was dissolved in anhydrous benzene (20 ml), then vinyl tris-17-bromo-3,6,9,12,15-pentaoxahexadecan-1-ol silane (4.05 g, 3.73 mmol) and 2 drops of Karstedt catalyst solution in xylene were added. The mixture was stirred at 50 °C for 48 h. The solvent was evaporated in vacuum to give the polymer 5. Then dissolve polymer 5 in DMF (20 ml), added 1-butyl imidazole (1.39 g, 11.19 mmol) and stirred at 40 °C for 24 h. After removal of solvent, the obtained product was mixed with LiTFSI (3.21 g, 11.19 mmol), or LiTf (1.75 g, 11.19 mmol) in anhydrous acetonitrile (20 ml). The mixture was stirred for 24 h at RT and then filtered. The solvent was remove, the final products were purified by washing with diethyl ether several times and repeated precipitated into a 90/10 (v/v) mixture of hexane and acetone to remove unreacted compounds, then the products were dried under vacuum to give products PSHG_TFSI, PSHG_Tf. 1H NMR (DMSO-d6) δ: 0.90 (t, -CH3), 1.26 (m, -CH2-CH2-CH3), 1.78 (m, -CH2-CH2-CH3), 3.42-3.60 (m, -O-CH2), 4.20 (t, O-CH2-CH2-N), 4.35 (t, -N-CH2-CH2-N), 7.78 (d, -N-CH=CH-N), 9.18 (s, -N=CH-N)

4.4.5 Sample preparation. 200 mg of the PSHG_TFSI or PSHG_Tf was dissolved in anhydrous DMF (5 mL). LiTFSI or LiTf (50, 100 and 150 mol% of tripodant hexaethylene tripodant molecule) were introduced to obtain the varied lithium salt content in the polymer electrolytes. After stirring overnight at room temperature, the solution was cast on a substrate. The electrolyte
was dried under atmospheric pressure at 50 °C for 12 h, and then the temperature was increased to 75 °C for 6 h. Afterwards, increasing temperature to 100 °C for 3 days in vacuum to remove residual solvent and anneal the films.

### 4.4.6 Characterizations

The chemical compositions of the polymers were determined from $^1$H and $^{13}$C on a Bruker AM-300 spectrometer. The thermal transition data were obtained by a TA Instruments Q100 differential scanning calorimeter (DSC) at a heating and cooling rate of 10 °C/min. The measurement temperature range was -130 to 150 °C. The glass transition temperature $T_g$ was determined by the midpoint of total heat flow curve in the thermal transition region. The thermogravimetric analysis (TGA) measurement was performed on a TA Instrument model Q50 at a heating rate of 10 °C/min under N$_2$ from room temperature up to a maximum of 800 °C.

Broadband Dielectric Relaxation Spectroscopy (DRS). DRS measurements were performed on a Concept 40 system from Novocontrol GmbH, and measured over the frequency range 10 mHz to 10 MHz. Temperature was controlled by a Quatro temperature control system with a precision of greater than ±0.1 °C. All polymers were measured over the temperature range from -115 °C to 115 °C, well above the calorimetric $T_g$. Samples were prepared for DRS measurements by solution casting thin films from DMF as a solvent onto stainless steel electrodes. Samples were dried under vacuum at 100 °C prior to measurement, and were transferred from the oven to the spectrometer as quickly as possible to avoid moisture absorption.

Small-angle X-ray scattering (SAXS) was performed on a Molecular Metrology SAXS, using Cu K$_\alpha$ radiation (wavelength = 1.5418 Å). The SAXS is equipped with a 2-D detector, and the scattering vector (q) range was calibrated with silver behenate.
Wide angle X-ray scattering (WAXS) was performed on a Rigaku DMAX-Rapid Microdiffractometer equipped with a 2-D detector, also using CuKα radiation. For both SAXS and WAXS, software routines were used to evaluate the scattering intensity as a function of the diffraction angle of, 2θ, or q, defined as \( q = \frac{4\pi \sin(\theta)}{\lambda} \).

A Solartron 1260A was used to carry out the lithium transference number \( (T_{Li^+}) \) and interfacial resistance \( (R_i) \) experiments. The testing parameters were controlled by ZPlot software, while the resulting data were analyzed using ZView. The \( T_{Li^+} \) and \( R_i \) of the solid electrolyte were measured using Li/polymer/Li cells, where electrolyte samples were mounted between two non-blocking lithium metal electrodes. The \( T_{Li^+} \) was evaluated according to the procedure described by Evans et al.[93] Potentiostatic measurements were carried out to determine the initial \( (I_o) \) and final steady-state \( (I_s) \) currents by applying a DC polarization voltage of 25 mV across the samples. Impedance spectroscopy at frequency range from 1 MHz to 1 Hz was used to determine the film initial state resistance \( (R_0) \) and steady-state resistance \( (R_s) \). Transference numbers \( (T_{Li^+}) \) of the electrolyte samples were calculated from the following equation:

\[
(T_{Li^+}) = \frac{I_s(\Delta V-I_oR_0)}{I_o(\Delta V-I_sR_s)}
\]

Where \( \Delta V \) is the DC polarization voltage (10mV) applied to the cell. The \( R_0 \) and \( R_s \) are determined from Cole-Cole plots measured by impedance measurement before and after applying constant potential.

Linear sweep voltammetry was used to determine the electrochemical stability window of the electrolyte material in SS/polymer/Li coin cells, where stainless steel disk was used as the working electrode while a lithium disk served as the counter and reference electrode. A voltage sweep was carried out on the material between -3 and 6 V at a constant scan rate of 1 mV/s.
Cyclic voltammetry was used to determine the electrochemical stability of electrolyte in Li/polymer/Li coin cell with the voltage range from -3 to 3 V at a scan rate of 1 mV/s.

Dynamic shear moduli were measured by using RDS-IIE rheometer. The sample was placed between two parallel plates with a diameter 25 mm. The shear strain was varied to obtain storage modulus (G') and loss modulus (G'') at room temperature.
Chapter 5

Ionic Liquid Tethered Polyhedral Oligomeric Silsesquioxane

5.1 Introduction

Ionic liquids (ILs) have been interesting in applications in various electrochemical systems as high ion conductivity and non-volatile electrolytes, such as dye sensitised photoelectrochemical. Even though many attempts have developed to use ILs in lithium batteries due to their unique properties such as low vapor pressure, high thermal stability, wide electrochemical window, and high RT conductivity, ILs still have similar problems like other liquid electrolytes, such as they cannot suppress dendrite growth, have leaking problem, and have low lithium transference numbers (0.05). Therefore, gel or solid ionic liquid-based electrolytes that combine the unique properties of ionic liquids with the mechanical integrity of solid electrolytes and improving the disadvantages of ILs are preferable.

Recently, many attempts have studied a novel class of hybrid materials based on polyhedral oligomeric silsesquioxane (POSS). POSS is an inorganic Si₈O₁₂ core characterized by a cage-like structure, which can be functionalized by attaching functional groups. Through appropriate design of the structure, these POSS derivatives can be tailored for specific applications, such as electrochromic devices, liquid crystals, photoresists, electrolytes, and self-assembly structures.

In this chapter, octameric hexaethylene oxide-ionic liquid (POSS_IL) have been synthesized; first the star octuply-tripodant hexethylene oxide POSS was produced via hydrosilylation of octakis(dimethyldimethoxy)silsesquioxane (POSS) with vinyl tris-17-bromo-3,6,9,12,15-pentaoxaheptadecan-1-ol silane. Then, attaching 1-butyl imidazole by quaternization
to create ionic liquid chain ends. Two different lithium salts which are LiTFSI and LiPF$_6$ have been added to the electrolyte to study the effect of lithium salts on the properties of POSS_IL.

5.2 Results and discussion

5.2.1 Synthesis
Scheme 5-1. Synthesis of vinyl tris-17-bromo-3,6,9,12,15-pentaoxaheptadecan-1-ol silane, and hydrosilylation with POSS to form POSS_IL.

POSS_IL was synthesized through the hydrosilylation of viny tris-17-bromo-3,6,9,12,15-pentaoxaheptadecan-1-ol silane with octakis(dimethylsiloxy)silsesquioxane as shown in Scheme 5-1 and monitored by using $^1$H NMR. The peaks for the vinyl group: $\delta$ 5.9-6.0 ppm in Figure 5-2 and Si–H protons: $\delta$ 5.1 ppm in Figure 5-1 disappeared in the spectrum of POSS_IL in Figure 5-3, supporting the complete hydrosilylation reaction.
Figure 5-1. $^1$H NMR spectra of POSS.

Figure 5-2. $^1$H NMR spectra of viny tris-17-bromo-3,6,9,12,15-pentaaxadaheptadecan-1-ol silane.
5.2.2 Thermal Properties. Fig. 5-4 displays TGA thermograms of pure POSS and POSS_IL. It was found that when incorporating ionic liquid-hexaethyl glycol, the onset decomposition temperature is increased from 246 °C (pure POSS) to 257 °C (POSS_IL). The reason might be from the branched or dendritic PEOs wrapping around the POSS unit which helps to protect the thermal decomposition. Fig. 5-5 shows DSC thermograms of POSS_IL, POSS_IL_100% mol LiTFSI, and POSS_IL_100 mol% LiPF$_6$ during the second heating scan. The results are shown in Table 5-1. Tg was increased from -33 °C for POSS_IL to -31°C with 100% mol LiTFSI. The increase in Tg with addition of LiTFSI has been attributed to restriction in segmental mobility when the lithium cations complex with the ether oxygens of PEO, and possibly due to the transient Li-O bonds creating inter-chain and intra-chain crosslinks.$^{[109]}$ On the other hand, Tg
was decreased to -41°C with 100% mol LiPF$_6$. The decrease in Tg with addition of LiPF$_6$ may be caused by the presence of water molecules. It is known that LiPF$_6$ possesses a high capability to absorb water.\textsuperscript{[110]} Thus, the moisture is absorbed, which creates hydrogen bonds between ethylene oxide and water molecules and disrupts inter-chain and intra-chain linkages between ethylene oxide-imidazolium cation and ethylene oxide-LiPF$_6$. Then the mobility of PEO increases and reduces Tg in POSS_IL_100 mol% LiPF$_6$.

![TGA thermograms of pure POSS and POSS_IL.](image)

**Table 5-1.** Glass transition temperatures and ionic conductivity at 30°C of POSS_IL, POSS_IL_100% mol LiTFSI, and POSS_IL_100 mol% LiPF$_6$.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tg (°C)</th>
<th>$\sigma$ (S/cm, 30 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POSS_IL</td>
<td>-33</td>
<td>4.04×10$^{-5}$</td>
</tr>
<tr>
<td>100% mol LiTFSI</td>
<td>-31</td>
<td>1.14×10$^{-4}$</td>
</tr>
<tr>
<td>100% mol LiPF$_6$</td>
<td>-41</td>
<td>4.72×10$^{-4}$</td>
</tr>
</tbody>
</table>
5.2.3 Ionic Conductivity. The ionic conductivity data are shown in Fig. 5-6 and summarized in Table 5-1. The conductivity of the samples is increased when adding salts. This could be understood because adding lithium salt can increase the concentration of ions which leads to an increase in ionic conductivity. Conductivity can be affected by ion mobility, ion–ion interactions, anion size, lattice energies, salt dissociation, and anion polarization.\[^{[85]}\] In our system, the conductivity of POSS\_IL\_100 mol\% LiPF$_6$ is higher than POSS\_IL\_100 mol\% LiTFSI. This can be explained by the Tg of 100 mol\% LiPF$_6$ is lower than the Tg of 100 mol\% LiTFSI. Thus, LiPF$_6$ system has higher polymer segmental mobility than LiTFSI system, which helps to promote ion mobility and create the higher ionic conductivity.
5.2.4 Effect of Ionic Liquid on Ionic Conductivity. The POSS_PEO has been synthesized in order to study the effect of ionic liquid on the conductivity of the system. The different of the chemical structures between POSS_PEO and POSS_IL is POSS_PEO also has hexaethylene side chain but has methoxy end group (-OCH₃) instead of imidazolium cation in POSS_IL. The comparison of conductivity in both systems is shown in Fig. 5-7. By adding the same amount of LiPF₆, it was found that the POSS system with ionic liquid end group has higher conductivity than the POSS system without ionic liquid. The higher in conductivity is presumably due to a higher in number of charge carriers from imidazolium cation and TFSI anion.
5.2.5. Microstructural Characterization. Wide-angle X-ray diffraction (WAXD) pattern of the POSS_IL is shown in Fig.5-8. There are three characteristic diffraction peaks in the sample. The two diffraction peaks centered at d-spacing of 7 Å ($q = 0.9$ Å$^{-1}$) and 4.3 Å ($q = 1.46$ Å$^{-1}$) may be attributed to Van der Waals packing of the intermediate spacing corresponded to noninterdigitated packing and noninterdigitated packing of the branches.$^{[111, 112]}$ A third peak at a d-spacing of 10.7 Å ($q = 0.6$ Å$^{-1}$) is attributed to 101 reflection peak of POSS rhombohedral unit cell.$^{[113]}$
5.2.6 Electrochemical Stability. Fig. 5-9 shows the linear sweep voltamograms of the Li/POSS sample/Li cells at a scan rate of 1 mVs$^{-1}$ at room temperature. The sample with 100 mol% LiTFSI and 100 mol% LiPF$_6$ exhibit a cathodic limit at 0.78V and 0.74 (vs. Li/Li$^+$), respectively and both samples show an anodic limit over 7 V (vs. Li/Li$^+$). It can be seen that the electrolytes show high cathodic and anodic stability versus lithium. Due to the formation of the passivation film on the surface of Li electrode, ions can hardly contact the Li electrode. Consequently, ions might not be reduced on the surface of the lithium electrode and thus the electrochemical stability is improved.$^{[114]}$.$^{[115]}$
Figure 5.9. Linear sweep voltammograms of POSS_IL_100mol%LiTFSI, and POSS_IL_100 mol% LiPF₆ at a sweep rate of 1 mV/s at RT.

5.2.7 Mechanical Properties. Fig. 5-10 shows the strain-dependent dynamic moduli of POSS_IL measured in an oscillatory shear flow as a function of applied strain amplitude with fixed frequency (ω = 10 rad/s). At low shear strain, storage modulus (G′) is higher than loss modulus (G″) which is a characteristic of a solid-elastic material. The further increase in shear strain, G′
gradually increases and the concomitant appearance of a maximum in $G''$ which indicates a strain-induced transition to fluid-like state. The results can identify the sample in term of “soft glassy” materials. Soft glassy materials are individual elements trapped in tight cages produced by interactions with their neighbors as shown in a cartoon in Fig. 5-10.\textsuperscript{38,116} The maximum in $G''$ reflects the amount of mechanical energy dissipated when cages break apart. The sample shows elastic modulus of $1.2 \times 10^5$ Pa and can be casted to a film due to the high fraction of hexaethylene oxide which might be entangled.

Figure 5-10. The dynamic shear moduli ($G'$, $G''$) and tan delta as a function of applied strain at RT.
5.2.8 Lithium Transference Number. The lithium transference numbers ($T_{Li^+}$) were determined by the method reported by Bruce et al., $^{[93]}$ which is a DC polarization method based on the DC polarization technique.

$$ (T_{Li^+}) = \frac{I_0(\Delta V-I_0R_0)}{I_0(\Delta V-I_sR_s)} \quad (5-1) $$

From the technique, Li/POSS_IL_100 mol%PF$_6$/Li cell was polarized by a constant potential difference at 25 mV between the electrodes and monitored until the current eventually reached steady state as shown in Fig. 5-11. Fig 5-12 shows the impedance spectra of the cell before and after polarizing. By fitting the curve, the values of the current can be obtained at the initial polarization time, $I_0$ and under steady-state conditions, $I_s$. By inserting the values of $I_0$, $I_s$, $R_0$ and $R_s$ from Table 5-2 in Eq. 5-1, the lithium transference number was determined to be 0.69 which is a reasonable value for practical application in lithium batteries.

Figure 5-11. Current vs time profile of POSS_IL_100 mol% LiPF$_6$ at RT under a 25 mV DC bias.
Figure 5-12. Cole-Cole plot of the AC impedance at the initial and steady state of Li/POSS_IL_100 mol% LiPF₆/Li cell at RT, polarized with a potential difference of 25 mV.

Table 5-2. Parameters obtained from the application of a constant potential and impedance response to calculate the lithium transference number of POSS_IL_100 mol% LiPF₆.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$I_0$ (A)</th>
<th>$R_0$ (Ω)</th>
<th>$I_s$ (A)</th>
<th>$R_0'$ (Ω)</th>
<th>$\Delta V$ (mV)</th>
<th>$T_{Li^+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 mol% LiPF₆</td>
<td>$4.71 \times 10^{-6}$</td>
<td>1697</td>
<td>$3.11 \times 10^{-6}$</td>
<td>2821</td>
<td>25</td>
<td>0.69</td>
</tr>
</tbody>
</table>

5.2.9 Interfacial Resistance. The interfacial stability of POSS_IL_100 mol% LiPF₆ in contact with lithium electrode was measured from Cole-Cole plot, using Li/electrolyte/Li cells. Fig. 5-13 shows the impedance spectra of Li/POSS_IL_100 mol% LiPF₆/Li cell as a function of storage. The diameter of the semicircle is contributed to the resistance of the passivation film ($R_i$), with increasing with storage time $R_i$ increases and stabilizes after 3 days to a value of 3.5 kΩ.
5.2.10 Cyclic Voltammetry. Fig. 5-14 shows of Li/PSHG_TFSI_100 mol% LiTFSI/Li cell at RT with a scan rate at 1 mV/s. The cyclic voltammograms exhibit well defined anodic peaks between 0.6 to 0.8 V vs. Li/Li\(^+\) and reduction peaks between -0.5 to -0.8 V vs. Li/Li\(^+\). After first cycle, the system shows stability by considering in no substantial change in redox voltage and the cathodic and anodic peak current values are almost the same. The overlap of the curves of cyclic voltammograms indicates the occurrence of reversible redox process.
5.3 Summary

Hybrid polyoctahedral silsesquioxane (POSS)-based electrolytes have been synthesized by reaction of POSS with vinyl tris-17-bromo-3,6,9,12,15-pentaoxaheptadecan-1-ol silane. $^1$H NMR confirmed the completed hydrosylation reaction of attachment of vinyl molecules on POSS. The resulting hybrid electrolyte can form dimensionally stable sample due to the entanglement of hexaethylene oxide branches. When adding LiTFSI and LiPF$_6$, lithium ion was dissolve by hexaethylene oxide of POSS_IL, improving the conductivity of the hybrid electrolyte compared with POSS_IL without adding salt. The results have shown that the hybrid electrolytes exhibit good ionic conductivity, thermal stability, lithium transference number, interfacial stability, mechanical property, and wide electrochemical window.
5.4 Experimental Section

5.4.1 Materials. All reagents were used without further purification. Octasilane polyhedral oligomeric silsesquioxane (POSS) was purchased from Hybrid Plastics. Triphenyl phosphine, tetrabromomethane (CBr₄), trichlorovinylsilane, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), Lithium hexafluorophosphate (LiPF₆), 2% Karstedt catalyst solution in xylene, anhydrous acetonitrile, DMF, and anhydrous benzene were purchased from Sigma-Aldrich. Hexaethylene glycol, 1-butyl imidazole, THF, ethyl acetate, diethyl ether, chloroform, and methanol were purchased from VWR.

5.4.2 Synthesis of 17-bromo-3,6,9,12,15-pentaoxaheptadecan-1-ol (2). To a solution of hexaethylene glycol (10 g, 35.42 mmol) in THF (10 ml) was added triphenyl phosphate (4.65 g, 17.71 mmol), then added CBr₄ (5.87 g, 17.71 mmol). The reaction mixture is stirred for 4 h at RT. Then the reaction mixture is concentrated and purified by column chromatography with 95:5 Chloroform/methanol to give 17-bromo-3,6,9,12,15-Pentaoxaheptadecan-1-ol as colorless oil: ¹H NMR (CDCl₃) δ: 3.16 (s, -OH), 3.43 (t, -CH₂-Br), 3.58-3.68 (m, -O-CH₃), 3.78 (t, -CH₂-CH₂-Br); ¹³C NMR (CDCl₃) δ: 30.1, 61.6, 70.2-70.7 (br), 73.0 (-CH₂-CH₂-Br).

5.4.3 Synthesis of vinyl tris17-bromo-3,6,9,12,15-pentaoxaheptadecan-1-ol silane (3). To a solution of 17-bromo-3,6,9,12,15-pentaoxaheptadecan-1-ol (5.6 g, 0.016 mol) in toluene (50 ml) is added triethylamine (3.2 g, 0.032 mol) followed by trichlorovinylsilane (0.873 g, 5.33 mmol). The reaction mixture is stirred for 3 h at RT, then diluted with EtOAc (50 ml), washed with water and dried over anhydrous Na₂SO₄. The organic layer is concentrated to give product 3: ¹H NMR (CDCl₃) δ: 3.43 (t, -CH₂-Br), 3.58-3.68 (m, -O-CH₃), 3.79 (-O-CH₂-CH₂-Br), 3.89 (t, -Si-O-CH₃-).
5.9-6.1 (m, CH$_2$=CH-Si-), $^{13}$C NMR (CDCl$_3$) $\delta$: 30.1, 62.4 (Si-O-CH$_2$), 70.8-71.9 (signal overlap), 72.7 (-CH$_2$-CH$_2$-Br), 137.4 (CH$_2$=CH-Si-).

5.4.4 Synthesis of Ionic Liquid Tethered POSS (POSS_IL). Dissolved POSS (640 mg, 0.63 mmol) in anhydrous benzene (20 ml), then added vinyl tris-17-bromo-3,6,9,12,15-pentaoxaheptadecan-1-ol silane (5.48 g, 5.04 mmol) and 2 drops of Karstedt catalyst solution in xylene were added. The mixture was stirred at 50 °C for 48 h. The solvent was evaporated in vacuum to give the product 5. Then dissolve it in DMF (20 ml), added 1-butyl imidazole (2.04 g, 16.43 mmol) and stirred at 40 °C for 24 h. After removal of solvent, the obtained product was mixed with LiTFSI (4.72 g, 16.43 mmol) in anhydrous acetonitrile (20 ml). The mixture was stirred for 24 h at RT and then filtered. The solvent was remove, the final products were purified by washing with diethyl ether several times and repeated precipitated into a 90/10 (v/v) mixture of hexane and acetone to remove unreacted compounds, then the products were dried under vacuum to give product POSS_TFSI: $^1$H NMR (DMSO-d$_6$) $\delta$: 0.90 (t, -CH$_3$), 1.26 (m, -CH$_2$-CH$_3$-CH$_3$), 1.78 (m, -CH$_2$-CH$_2$-CH$_3$), 3.42-3.60 (m, -O-CH$_2$-), 4.20 (t, O-CH$_2$-CH$_2$-N-), 4.35 (t, -N-CH$_2$-CH$_2$-), 7.78 (d, -N-CH=CH-N-), 9.18 (s, -N=CH-N-).

5.4.5 Sample Preparation. 200 mg of POSS_IL was dissolved in anhydrous DMF (5 mL). LiTFSI or LiPF$_6$ 100 mol% of tripodant hexaethylene tripodant molecule was introduced to the polymer solution. After stirring overnight at room temperature, the solution was cast on a substrate. The electrolyte was dried under atmospheric pressure at 50 °C for 12 h, and then the temperature was increased to 75 °C for 6 h. Afterwards, increasing temperature to 100 °C for 3 days in vacuum to remove residual solvent and anneal the sample.
5.4.6 Characterizations

The chemical compositions of the polymers were determined from $^1$H and $^{13}$C on a Bruker AM-300 spectrometer. The thermal transition data were obtained by a TA Instruments Q100 differential scanning calorimeter (DSC) at a heating and cooling rate of 10 °C/min. The measurement temperature range was -100 to 150 °C. The glass transition temperature $T_g$ was determined by the midpoint of total heat flow curve in the thermal transition region. The thermogravimetric analysis (TGA) measurement was performed on a TA Instrument model Q50 at a heating rate of 10 °C/min under N$_2$ from room temperature up to a maximum of 800 °C.

Broadband Dielectric Relaxation Spectroscopy (DRS). DRS measurements were performed on a Concept 40 system from Novocontrol GmbH, and measured over the frequency range 10 mHz to 10 MHz. Temperature was controlled by a Quatro temperature control system with a precision of greater than ±0.1 °C. All polymers were measured over the temperature range from -115 °C to 115 °C, well above the calorimetric $T_g$. Samples were prepared for DRS measurements by solution casting thin films from DMF as a solvent onto stainless steel electrodes. Samples were dried under vacuum at 100 °C prior to measurement, and were transferred from the oven to the spectrometer as quickly as possible to avoid moisture absorption.

Wide angle X-ray scattering (WAXS) was performed on a Rigaku DMAX-Rapid Microdiffractometer equipped with a 2-D detector, also using CuK$_\alpha$ radiation. The software routines were used to evaluate the scattering intensity as a function of the diffraction angle of, 2\( \theta \), or q, defined as \( q = 4\pi \sin(\theta)/\lambda \).

A Solartron 1260A was used to carry out the lithium transference number experiments. The testing parameters were controlled by ZPlot software, while the resulting data were analyzed using ZView. The lithium-ion transference number of the solid electrolyte was measured using Li/polymer/Li cells, where electrolyte samples were mounted between two non-blocking lithium
metal electrodes. The transference number \( T_{\text{Li}^+} \) was evaluated according to the procedure described by Evans et al.[93] Potentiostatic measurements were carried out to determine the initial \( I_o \) and final steady-state \( I_s \) currents by applying a DC polarization voltage of 25 mV across the samples. Impedance spectroscopy at frequency range from 1 MHz to 1 Hz was used to determine the film initial state resistance \( R_o \) and steady-state resistance \( R_s \). Transference numbers \( T_{\text{Li}^+} \) of the electrolyte samples were calculated from the following equation:

\[
(T_{\text{Li}^+}) = \frac{I_s(\Delta V - I_o R_o)}{I_o(\Delta V - I_s R_s)}
\]

Where \( \Delta V \) is the DC polarization voltage (10mV) applied to the cell. The \( R_o \) and \( R_s \) are determined from Cole-Cole plots measured by impedance measurement before and after applying constant potential.

Linear sweep voltammetry was used to determine the electrochemical stability window of the electrolyte material in SS/polymer/Li coin cells, where stainless steel disk was used as the working electrode while a lithium disk served as the counter and reference electrode. A voltage sweep was carried out on the material between -3 and 6 V at a constant scan rate of 1 mV/s.

Cyclic voltammetry was used to determine the electrochemical stability of electrolyte in Li/polymer/Li coin cell with the voltage range from -3 to 3 V at a scan rate of 1 mV/s.

Dynamic shear moduli were measured by using RDS-IIE rheometer. The sample was placed between two parallel plates with a diameter 25 mm. The shear strain was varied to obtain storage modulus \( (G') \) and loss modulus \( (G'') \) at room temperature.
Chapter 6

Conclusions and Suggestions for Future Work

6.1 Summary

In this thesis, we have developed new chemistries for the synthesis of novel polymer electrolytes. Synthesis of well-defined polymer structures is very interesting due to the desirable properties of polymers which can be obtained by intelligently designing chemical structures. Fluoropolymers have been interesting due to the excellent thermal and mechanical properties. However, using them in further reactions to create new structures or advanced applications have been difficult because of poor solubility in common organic solvents and difficult to synthesis of functional groups in polymer chains. However, Using a telechelic fluorinated polymer synthetic approach with functional benzoyl peroxides, we can create $\alpha,\omega$-difunctional fluoropolymers.

We have used the telechelic fluorinated polymer synthetic approach to create P(VDF-PFSVE) nanocomposites membranes. The telechelic P(VDF-PSFVE) containing perfluorosulfonic acid side chains have been successfully prepared by radical polymerization using the functional initiator. The resulting triethoxysilane terminated P(VDF-PSFVE) underwent in-situ sol-gel reaction with TEOS and THSPSA to form proton conductive fluorinated polymer nanocomposites with uniform filler dispersion. It was found that the properties of the membranes highly dependent on the concentration and structure of the polysilsesquioxane fillers. The incorporation of the2 wt% THSPSA to the fluorinate polymer matrix results in the composite membranes has the proton conductivity value of 0.089 S/cm which is higher that Nafion with the value of 0.075 S/cm. In addition, the P(VDF-PSFVE) composite membranes with TEOS display suppressed methanol permeability without sacrificing the proton conductivity and thus achieve better electrochemical selectivity in comparison to Nafion.
We also used telechelic polymer approach to prepare the triblock copolymers composed of poly(VDF-co-HFP) and ionic liquid segments. We selected P(VDF-HFP) as a polymer backbone due to its flexibility and low Tg, which would help increase ion mobility and also utilize the natural characteristics of fluoropolymers which have high thermal, chemical, and mechanical properties. First, we have made the telechelic P(VDF-HFP) with benzyl chloride terminal groups. Then we changed the chlorine-end groups to trithiocarbonate end-groups as the macro-chain transfer agent for RAFT polymerization of the imidazolium methacryloyl monomer. This method provided facile synthetic access to incorporation of IL segments into fluoropolymers, which broadens the family of the IL-containing polymers.

Furthermore, we were interested in ILs because their unique properties especially in high ionic conductivity. We designed and synthesized new structures of ionic liquids based polymers. Based on previous studies, vinyl ionic liquids with ethylene oxide spacers have been prepared. The vinyl structure was created in order to use ionic liquids in reactions such as polymerization, and hydrosilation. A spacer between ionic liquid moiety and vinyl group has been introduced in order to increase mobility of ions and we specifically chose ethylene oxide unit because it can dissociate ions which would help to increase number of free ions in the system. We have successfully synthesized 1-[2-methacryloyloxy]-3, 6-dioxa-octyl]-3-butylimidazolium tetrafluoroborate (MDBIm-BF₄), imidazolium-containing monomer, then used it in RAFT polymerization for the triblock copolymers of poly(VDF-co-HFP) and ionic liquid segments. In order to increase ionic conductivity, concentration of ions is a major factor. Therefore, we have designed vinyl tripodand ionic liquid which contains three ionic liquid moieties in one repeating unit, vinyl tris17-bromo-3,6,9,12,15-pentaoxaheptadecan-1-ol silane. Then we have used it in hydrosilation of PHMS and POSS to create the new solid polymer electrolyte. It has been found that PSHG_TFSI_100 mol% with LiTFSI and POSS_IL with 100 mol% LiPF₆ have a conductivity value of 3.5×10⁻⁵ at 30 °C and 4.72×10⁻⁴ at 25 °C, respectively, which is one of the
best solid electrolytes. Additionally, they exhibit good thermal stability, dimensional and mechanical properties, electrochemical, and interfacial stability, and lithium transference number. Due to these factors, we can see their potential in lithium battery applications.

6.2 Suggestions for Future Work

In this thesis, we have focused on the development of synthetic chemistry for the synthesis of polymer electrolytes for advanced electrochemical energy devices. We have demonstrated that PSHG_TFSI_100 mol% with LiTFSI and POSS_IL with 100 mol% LiPF_6 have good properties and have potential as solid electrolytes in lithium ion battery. Thus, it would be worthy to study galvanostatic tests to see the cycling performance of the lithium battery cell with our electrolytes.

In POSS_IL study, we have not varied the concentration of lithium salts due to the limitation of time frame. Since the concentration of ions can affect the ionic conductivity, the concentration of lithium salts should be evaluated. We can systematically vary the amount of lithium to optimize properties of the electrolyte. The properties such as ionic conductivity, glass transition temperature, electrochemical stability, and lithium transference number can be investigated.

Ionic liquids are very interesting substances due to their many unique properties especially high ion conductivity. For fuel cell applications, other studies have shown that the polymer electrolytes with ionic liquid membranes can be performed under water-free conditions. The PEM having nanostructures of lamellae and hexagonal cylinders can be created ion-conducting channels from phase-separation of hydrophobic polymer backbone and hydrophilic –SO_3H with ionic liquid molecules. Protons can be transported via proton hopping mechanisms by –SO_3H groups function as proton-active sites, the protons transfer from –SO_3H sites to anions of ionic liquid which occur by the conversion of hydrogen bonds into covalent
bonds. Therefore, it would be very interesting to synthesize copolymers containing –SO$_3$H group with ionic liquids and try to induce phase separations to obtain ionic domains of –SO$_3$H groups with ionic liquids for transporting protons and study in water-free condition of fuel cell applications.

It would be worthwhile to use our tripodand ionic liquid in other reactions to synthesize new polymer electrolytes because our studies have shown that we could create solid polymer electrolytes with good properties. Our tripodand ionic liquid can undergo other reactions due to its vinyl group in its structure which can be used as a monomer in radical polymerization. A variety of polymers can be prepared from the tripodand such as homopolymers and copolymers with other components.

Although we successfully synthesized the comblike polysiloxane and dendritic POSS with ionic liquid branches, it was found that their lithium transference numbers were not close to one which is desirable for lithium battery application. Since our systems have mobile anions which can move and compete with lithium ions, the lithium transference number cannot reach to one. It would be very interesting to synthesize tripodand molecules with –SO$_3$Li groups or other anion moieties. By inhibiting migration of anions, lithium cations could be dominant mobile ions while makes the lithium transference number closer to one.
References


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