The Pennsylvania State University

The Graduate School

Department of Materials Science and Engineering

POLYETHYLENE BASED ION CONDUCTORS

A Thesis in

Materials Science and Engineering

by

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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Master of Science

May 2012
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ABSTRACT

In this thesis, new ion conductive polymeric membranes were synthesized and studied for potential fuel and electrolysis cell applications. Polyolefin was used as the polymer backbone that provides the membrane with a stable and hydrophobic matrix, and some ionic groups were introduced in random or graft microstructure fashion to provide ionic channels for conductivity. The random copolymers were prepared by direct copolymerization and the graft copolymers were obtained by graft-onto reaction.

In Chapter 1, general background and theory for ion conductive membrane are introduced. It covers the principles of fuel cells, synthesis of functional polyolefins, and fabrication of membranes. In Chapter 2, new cationic exchange membranes are discussed, which is the main topic of this thesis. This chapter covers the procedures to prepare new polyethylene-graft-poly(arylene ether sulfone) graft copolymers, their structure characterization and membrane fabrication, and evaluation for fuel cell applications. Some PE-based PEMs show promising results with the desirable properties for proton exchange membrane and direct methanol fuel cells. Chapter 3 discusses a new polyethylene-based anionic exchange membrane, containing ammonium chloride (NR₃⁺Cl⁻) groups and cross-linkers. The chemistry was successfully developed to prepare a broad range of copolymer compositions for a systematic structure-property relationship study. Some cross-linked anionic membranes, with high IEC value and moderate water swelling, outperform all commercial membranes with exceptionally high ionic conductivity. In Chapter 4, conclusion and future work are included with the suggestions for further developing this class of polyolefin-based membranes. At the end of the thesis, appendix are provided, related to more detail information about measurements including proton conductivity and methanol permeability.

Overall, this thesis is devoted to develop a new chemical route to prepare ion conductive polyolefins (PE, PP, etc.) that are semi-crystalline, ductile, good chemical stability, excellent
hydrophobicity in the matrix, and cost-effective. The resulting polyolefin-based ion exchange membranes may show advantages in other areas, including electrodialysis, desalination etc.
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ACKNOWLEDGEMENTS

I would like to use this space to thank many people who helped me while I did research in polymer science and fuel cell areas at Pennsylvania State University (PSU). First, I am grateful to my advisor, Dr. Chung and his advices for the research. He taught me how to think scientifically and gave me a right direction to go for the research. Whenever I had difficulties and hardships during experiments and analysis, he was really helpful to find solutions and answers. Without his advices, I would not make it possible to do research in consistence. I would like to thank Dr. Lvov to be my co-advisor and provide substantial comments and advices for doing research as well as writing this thesis. His big favor on correcting this thesis moved me quite a lot. I also express my thankfulness to Dr. Hickner to be my committee for the defense and give me very useful advices for many measurements including proton conductivity and methanol permeability. My group members also deserve my acknowledgements. Dr. Jeong, who is the previous group member in my group, helped me a lot when I joined the group in many ways. Her specialty in chemistry and polymer synthesis let me even more interested in making materials and thinking logically and creatively. I really want to say thanks to her. Dr. Yuan’s funny joke and his optimistic thinking were always happy to enjoy with. However, his research skills and responsibilities were more than that, which I really learned from while I am in this group. Dr. Zhang helped me in building skills and know-how of organic synthesis, which were greatly useful for my research. I would like to take this opportunity to thank him. Dr. Fedkin in Dr. Lvov’s group was a good counselor in that he teaches me how to use humidifier and cells for proton conductivity measurements and let me use those equipments without any hustles. I am also thankful to Dr. Chunmei Wang to help me figure out the method that she utilized for proton conductivity measurement at various relative humidity conditions.
I have my family in South Korea. They always have concerns about me and want me to be a good man. In many times, I didn’t fulfill their expectations but they still love me. Taking this opportunity, I want to thank them with my full heart. Without their love, I wouldn’t endure many challenges in USA. Finally, I would like to thank my fiancée, Sunmi. She always encouraged me whenever I am in trouble and have no confidence in me. She always thinks me first before her, so I could entirely focus on my research projects in the lab. Sincerely thanks to her with all my heart.
Chapter 1.

Introduction

1.1. Fuel Cells

Fuel cells are the device to convert chemical energy of fuel sources to electric energy, thus can be utilized as an energy source to generate power. After the discovery of Welsh Physicist William Grove in 1839, fuel cells have been continuously and gradually studied and developed into various types, including polymer electrolyte membrane fuel cells, solid oxide fuel cells, alkaline fuel cells and molten carbonate fuel cells. Among these types, polymer electrolyte membrane fuel cells have received great deal of attention from academia to industry because of its enormous advantages, including small size, low power generation, high fuel efficiency and simple structure. More importantly, there have been many efforts made to use polymer electrolyte membrane fuel cells, especially proton exchange membrane fuel cells (PEMFCs) in automobiles to replace petroleum. In some countries in Europe, PEMFCs are equipped into buses and partly replaced diesel as a fuel source.

Figure 1.1 shows the assembly of a typical PEMFC, which is composed of electrodes, bipolar plates, catalyst layers, and proton exchange membrane (PEM). By inserting fuels such as hydrogen, electricity is generated through the cells and used for operating the intended devices. The thin polymeric membrane (usually less than 200 μm) is currently utilized as a solid electrolyte in the system. In this PEMFC operation, hydrogen gas is injected into anode and split into two protons and two electrons by platinum catalyst at catalyst layer in the anode. The released electrons pass through the external circuit to provide the energy and power, and the protons solvate with water molecules.
and diffuse through the membrane to the cathode to react with the O\textsubscript{2} while picking up electrons and forming water.

Figure 1.1. An example of using polymer ion exchange membrane as a solid electrolyte:
Fuel Cell Diagram by Ballard Power System, Inc.

Proton conductivity in PEM is crucial in determining the fuel cell performance. It is well-known that the most efficient mechanism for proton diffusion is associated with water molecules, via the formation of H\textsubscript{3}O\textsuperscript{+} species that move between water molecules. With a large amount of water, protons will have “enough vehicles” to go through the electrolyte membrane thus increasing
its mobility and conductivity. On the other hand, under a small amount of water condition, protons have to jump from one acid site to the other with high activation energy, which hinders the efficient transport. However, too much water in PEM has an adverse effect to the fuel cell. With a large amount of water, polymer membrane swells much more than it can maintain its mechanical properties. In addition, the excess water in PEM dilutes acid concentration, which reduces proton conductivity. Thus, water management is essential for PEMFCs to maximize the proton conductivity and long term durability. For fluoropolymer, such as Nafion discussed later, it is known that water content should be more than 6 water molecules per sulfonic acid group in order to have sufficient proton conductivity.$^{2,3}$

Chemical stabilities of PEMs are also very important to design good candidates for applications in fuel and electrolytic cells. There are many types of radical species such as •OH, •OOH generated during operations of the cells. Those radicals possibly attack polymer backbone and side chains thus causing degradation of PEMs.$^{4,5}$ If potential polymers are weak to the attack of radicals, they should not be utilized as PEMs. For example, tertiary carbon easily reacts with radicals and chain scission takes place from the carbon. Polystyrene is the most well known PEMs facing the issues.$^{6}$ On the other hand, Nafion is relatively resistant to the attack and shall not be degraded in a short time period. Mechanical properties of PEMs have been also studied by many research groups. In fuel cell applications, the properties should be especially good because operating conditions in PEM stacks are harsh. Dimensional changes due to hydration, dehydration, shrinking and expansion happen very frequently thus membranes whose mechanical properties are weak would easily fail to endure the conditions for a long period of time. Under chemical aging or attacks, mechanical properties of PEMs are significantly decreased due to probably degradation of PEMs as discussed above.$^7$
1.2. Electrolytic cells

Electrolytic cells are tools or devices which generate or increase chemical energy by the process called ‘electrolysis’. Chemical compounds are decomposed by electricity in electrolytic cells and it undergoes reverse mechanism to fuel cells. The typical electrolytic cell for water electrolysis is shown in Figure 1.3. By having external energy sources, it is possible to collect hydrogen and oxygen gas from hydrolysis in the cell. Electrolytic cells are very useful in generating hydrogen gas using the source of energy such as electricity and heat. Especially, if waste heat from nuclear power plant is used for the electrolytic cells, the efficiency of hydrogen generation will be dramatically increased.
Figure 1.3. Water electrolysis using electrolytic cell

Dr. Lvov’s group at the Pennsylvania State University has studied and developed the electrolytic cells for this purpose\textsuperscript{9}. The cell with an ion exchange membrane in its center is heated up to 80 to 100 °C and the rate of hydrogen generation is recorded by home-made system. In the system, membrane electrolyte assembly (MEA) or simply the cell is crucial because it has several roles such as facilitation of protons which are produced during electrolysis and prevention of copper migration through membrane. By using the most suitable ion exchange membrane in electrolytic cells, hydrogen can be generated at a high rate. Membrane should have a good barrier property to copper ions and high proton conductivity.
1.3. Ion Exchange Membranes

Ion conductor is a material that is able to conduct ions instead of electrons. In general, hydrocarbon polymer is a good candidate as an ion conductor because it is usually an electronic insulator yet can conduct ions by possessing counter ionic groups in its structure. This polymeric ion conductor in the film form is called ion exchange membranes (IEM), which has been in the center of intense investigation for decades in many important fields, including fuel cells, electrolysis, batteries, desalination, and so forth. In the electrochemical devices, ion exchange membrane serves as a solid electrolyte to facilitate the movement of ions from one electrode to the other electrode, as well as the separator between two electrodes. As discussed in PEMFCs, proton
can be transported through the proton exchange membrane. Depending on the membrane used, performance of the fuel cell is varied.

Ion exchange membranes can be categorized into two groups; one is cationic exchange membrane (CEM) and the other is anionic exchange membrane (AEM). For CEM membranes, strong sulfonic acid group\textsuperscript{11-12} is usually employed to facilitate the movement of the cations in the membranes from anode to cathode. On the other hand, anions like hydroxide ion (OH\textsuperscript{-}) and chloride ion (Cl\textsuperscript{-}) transport from cathode to anode through AEM membrane. In this case, ammonium (NR\textsubscript{3}\textsuperscript{+}) groups\textsuperscript{13-15} are normally responsible for the transport of the anions in the system. As shown in Figure 1.5, cationic or anionic groups are attached in main or pendant chains.

There are several ways of preparing ion exchange membranes by introducing ionic groups in the polymer or membrane. First, monomer with ionic group can be employed with the other monomer to produce copolymers\textsuperscript{13}. In this case, content of ionic groups in the copolymer is controlled by the feed ratio of monomer with and without ionic groups. Second, after the synthesis of polymer, ionic groups can be introduced by modification such as sulfonation\textsuperscript{16-17} and amination\textsuperscript{14-19}. The content of ionic groups in the copolymer is controlled by the relative ratio of repeat units of the copolymer to the used amount of modification reagent.
It is well known that ionic conductivity in membrane is a critical property for high efficiency of the fuel cell. Ionic conductivity is defined by the following equation, \[ \sigma = \mu z n \] where, \( \sigma \) is ionic conductivity, \( \mu \) is ion mobility, \( z \) is ionic charge, \( n \) is charge density. From this equation, ionic conductivity can be enhanced by high ion mobility, high ionic charge and high charge density. Among these three factors, ion mobility can be controlled by designing polymer structure and morphologies. According to previous publications, it is known that with very well defined and phase separated morphology, ions transport faster, increasing the ionic conductivity. If the continuous channel exists in the polymeric film, ions move even faster through the channel thus enhancing its conductivity even higher.

In general, it is very difficult to control the morphology of a random copolymer because components in the copolymer are randomly (or statistically) distributed along the polymer chain. Including Nafion, almost all of statistically random copolymers do not show distinctive morphology. Instead, the morphology is not well defined and often blurred in micrograph. In the
case of graft and block copolymers, morphologies are much more discernible than random counterparts and phase separation appears very clear\textsuperscript{20,26}. Hydrocarbon aromatic polymers including poly(arylene ether sulfone) (PAES), polycarbonate (PC) have been commonly used for synthesis of block or graft copolymers because those polymers can be readily modified and chemically stable. By controlling molecular weight of each block, it is possible to tune the ionic content of the copolymers. Ionic blocks contribute to hydrophilic character of the whole polymers and facilitate the movement of ions. On the other hand, non-ionic blocks play a supportive role to maintain the structural integrity and durability of the membrane. Due to this reason, block or graft copolymers are favored to control the morphology of the polymer more precisely than random copolymers in various applications.

1.3.1. Proton Exchange Membranes

As mentioned above, it is necessary to have an appropriate amount of ionic groups in ion exchange membranes, which should be tuned to balance ionic conductivity and water-swelling in the membrane. Cost for manufacturing PEM also cannot be ignored. Mechanical properties are important consideration for the design of a good polymer electrolyte for applications. If methanol is used as a fuel source, permeability should not be overlooked. Based on these requirements, a great amount of researches have been devoted to develop new polymeric membranes for fuel cells. Fluoropolymers such as Nafion were first commercialized, accelerating the fuel cell researches. Especially, high conductivity, ductility, chemical and physical resistance of Nafion made it benchmark membrane since it has been spotlighted as a candidate for fuel cell membranes. Nafion\textsuperscript{®}, invented and manufactured by Dupont (Figure 1.6) is currently the best known PEM for fuel cells. Nafion is a random copolymer and synthesized by free radical polymerization. It is known that Nafion has a certain crystalline of about 15 to 20% although it is random copolymer. Due to this
crystallinity, Nafion possesses good mechanical properties, that is, large elongation and high tensile strength. With flexible side chains and large amount of sulfonic acid group (~7 mol% for Nafion 117), its conductivity is up to 0.1 S/cm, which is high enough for fuel cell applications.

However, it is known that Nafion is very expensive and its conductivity is abruptly decreased at low humidity (<50 %) and high temperature (>120 °C) conditions. Methanol crossover is also severe when Nafion is used as an electrolyte for direct methanol fuel cells (DMFCs) thus significantly reducing the fuel cell efficiency.

Concerning all of these merits and demerits of it, many other polymers were studied to replace Nafion. One example is aromatic hydrocarbon polymer\textsuperscript{12} including poly(arylene ether sulfone) (PAES), poly(ether ether ketone) (PEEK), polyether sulfone (PES). These polymers can be produced at a low price and possess a good mechanical, chemical properties as Nafion does. However, the membranes from those polymers also suffered from low conductivity and high water swelling. Although they failed to replace Nafion for fuel cell membranes, designing polymer
structure and morphologies opened the possibilities that properties of the polymer can be readily controlled to employ the polymer in specific applications.

1.3.2. Anion Exchange Membranes

Anion exchange membranes (AEMs) are used in fuel cells, electrolysis and other applications. Recently, AEMs have been paid attention to many research groups\textsuperscript{15, 18, 29} because of its potential and practical uses in alkaline fuel cells. In this type of fuel cell, hydroxide ions are transported through the AEM to generate electricity in the system. Because hydrogen gas does not have to be split in anode, platinum is not necessary anymore, thus significantly reducing the price for catalysis. In the past, low mobility of hydroxide ions prevented its wide use in fuel cells. However since it is now generally accepted that the development of a new catalyst to replace platinum seems very difficult, although mobility of hydroxide ions is not as high as protons, alkaline fuel cells using hydroxide ions as conducting ions have drawn attention due to its potential in lowering the price of manufacturing fuel cells.

AEMs are also commonly used in electrolysis to generate hydrogen gas. As shown in Figure 1.7, chloride ions should be continuously removed in cathode and transported to anode. In this system, conductivity of chloride ions is important because depending on it, efficiency of electrolysis can be increased.
For AEM fuel and electrolytic cells, the positively charged ionic groups should be attached in the copolymer so that anions can be coordinated with them. Typically, amine groups are used in AEMs because they are basic and easily modified to have methyl group or butyl group near the nitrogen in the group. However, amine groups are known to be degraded chemically under a certain condition\textsuperscript{31-32}, so that durability is very important issue in developing AEMs. By eliminating possible sources (e.g. β-hydrogen elimination) for degradation, AEMs will show a good durability for a long period of time\textsuperscript{15}. Commercial AEMs using cross-linked polystyrene are now available but their conductivities are significantly lower than PEMs.

1.3.3. Other Membrane Technologies

Ion exchange membrane is commonly found in many other fields (Figure 1.8), including desalination of sea water and brackish water, biosensors, actuators, and dialysis.\textsuperscript{33} By having cation and/or anion exchange membranes in desalination, it is possible to exclude solutes or salts effectively, thus allowing purification of water without having heavy metal ions\textsuperscript{34}. Same sign of ions from sea water by ion exchange membrane may deposit on its surface\textsuperscript{35}. With high ionic...
contents (high ion exchange capacity), electrodialysis or desalination is more favored thus, removing salts from sea water more effectively.

Figure 1.8. Schematic diagram of ion conductor (or ion exchange membrane) for various applications

Sensor and actuator also require ion exchange membranes for its operation. For example, in amperometric sensor, Nafion film is used to conduct protons produced from chemical reaction of oxygen, carbon dioxide and nitric oxide with water. In this case, high conductivity of Nafion film allows fast response of the sensor although the sensor is only operable under water. In actuator, ion exchange membranes including poly(arylene ether sulfone), Nafion and Flemion are utilized as electro-active polymer. As shown in Figure 1.9, ion conductor (ionomic membrane) is sandwiched between electro-conductive membrane (very thin ~20 μm) and used as actuator.
Ion conductive membrane also can be used in lithium-ion battery applications. These days, a very intensive research for replacing liquid organic electrolyte with solid polymer electrolyte in lithium-ion battery is undergoing in many research groups\textsuperscript{40-42}. In this application, ion conductive membrane is responsible for transporting lithium ions in the battery under dried or ionic liquid swollen condition. Dynamics in the ion conductive membrane for lithium ion battery is importantly concerned because mechanism of lithium transport is more or less dependent on the movement and/or flexibility of polymer chains.

1.4. Functionalization of Polyolefin

Polyolefins, especially polyethylene and polypropylene, are used in a wide range of applications, since they incorporate an excellent combination of mechanical, chemical properties and processability as well as cost effectiveness. These polymers are greatly influencing our day-to-day life ranging from minor items like milk bottles, containers, hoses, carpets to major engineering applications such as tires, car parts and aircraft accessories. So, polyolefins are
considered the most inexpensive high performance polymers. Their monomers are mainly produced from the catalytic cracking of hydrocarbons obtained during petroleum processing. Moreover, due to their excellent chemical and physical properties, and the ease of processability and recyclability, polyolefins are considered the most preferred choice among other commercial polymers. Unfortunately, because of their inert nature and limit available functionalization chemistry which significantly limits their end uses, especially for high-end applications.

Theoretically, there are two processes in the functionalization chemistry, as illustrated in Figure 1.10. One is the direct process by introducing functional group containing monomers during copolymerization reactions. The other involves chemical modification of pre-formed polymers. Ziegler-Natta and metallocene catalysts, using early transition metals, are the most important methods for preparing polyolefins. But the direct polymerization of functional monomers by these catalysts is normally very difficult, because of catalyst poisoning and other reactions. The Lewis acid components (Ti, V, Zr and Al) of the catalyst will tend to complex with nonbonded electron pairs on N, O, and X (halides) of functional monomers, in preference to complexation with the \( \pi \)-electrons of the double bonds. The net result is the deactivation of the active polymerization sites by formation of stable complexes between catalysts and functional groups, thus inhibiting polymerization. On the other hand, the post-polymerization processes have also faced many difficulties. Polyolefins with saturated hydrocarbon bonds are inert to most of reagents under normal reaction conditions. Much attention has been focused on the free radical reactions involving various free radical production mechanisms, such as thermal, flame, shock waves, UV and \( \gamma \)-radiations. Many attempts were carried out by mixing polyolefin with a free radical sensitive reagent, such as maleic anhydride, maleic acid and methacrylate, with the presence of peroxide initiator in melt or solution at high temperature. Despite the extensive research efforts to tune the reaction conditions and reagents, the free radical chemistry suffer from many undesirable side
reactions, such as the crosslinking and degradation of the polyolefin backbone and homopolymerization of monomers. Overall, the composition and structure of functionalized polyolefins were difficult to control.

Our group has developed third approach called reactive process. The basic idea is to circumvent the chemical difficulties in both direct and post-polymerization processes by designing a reactive copolymer “intermediate” that can be effectively synthesized and subsequently interconverted to the desirable functional polymer. This approach has benefited greatly from metallocene technology, especially due to its superior capability in the copolymerization reactions. Several new reactive comonomers have been identified, including borane monomers, p-methylstyrene, and divinylbenzene. With the suitable metallocene catalysts, they have shown effective incorporation into polyolefins with narrow molecular weight and composition distributions, similar to those of commercial polyolefin copolymers, such as m-LLDPE and poly(ethylene-co-styrene). As will be discussed later, this approach has opened up the opportunity
to prepare a broad range of new functional polyolefin with compositions and structures that would be very difficult to prepare by other methods.

It is very interesting to note that the reactive polyolefin approach has been broadened to prepare a polymer containing only a reactive group at the polymer chain end. The well-defined polymerization mechanism of metallocene catalysis leads to a precise control of chain transfer reaction. With the design of a chain transfer agent containing a reactive group, the \textit{in situ} chain transfer reaction produces the polymer having a terminal reactive group. In turn, the reactive groups located at the chain ends or in the side chains open up a lot of possibility to produce new polyolefin products, including block and graft copolymers and cross-linked polyolefin structures. Some polyolefin graft and block copolymers exhibit the morphologies with clear phase separation between hydrophobic and hydrophilic domains. The domain structures are basically controlled by block/graft copolymer composition.

1.5. Scope of research

In this thesis, two newly developed polyolefin-based cationic and anionic exchange membranes are intensively studied for two applications; fuel and electrolytic cells. Among polyolefins, polyethylene is used to demonstrate the unique features of new ion conductive membranes. Since the main purpose of this research is to develop new ion-conductive membranes, the thesis is more focused on synthesis of polymer membrane and characterization of the developed membranes. Functionalization of polyethylene is discussed in details because it is essential for systematic synthesis of the functional polymers in this study. Some important properties including conductivity, permeability and morphology for fuel cells and electrolysis are characterized to show the usefulness of these membranes. If readers are interested in electrolysis, catalyst, membrane fabrication, many literatures\textsuperscript{1, 43-44} are available.
Proton exchange membranes for fuel cells are introduced in Chapter 2. This chapter covers the procedures to prepare new polyethylene-graft-poly(arylene ether sulfone) graft copolymers, their structure characterization and membrane fabrication, and evaluation for fuel cell applications. Some PE-based PEMs show promising results with the desirable properties for proton exchange membrane and direct methanol fuel cells. Chapter 3 discusses a new polyethylene-based anionic exchange membrane, containing ammonium chloride (NR₃⁺Cl⁻) groups and cross-linkers. The chemistry was successfully developed to prepare a broad range of copolymer compositions for a systematic structure-property relationship study. Some cross-linked anionic membranes, with high IEC value and moderate water swelling, outperform all commercial membranes with exceptionally high ionic conductivity. Chapter 4 includes conclusion and future work with several suggestions.
Chapter 2.

Synthesis of Polyethylene-based Proton Exchange Membranes Containing PE Backbone and Sulfonated Poly(arylene ethersulfone) Side Chains for Fuel Cell Applications

2.1. Introduction

Since the discovery of Nafion, it has been extensively studied and applied in proton exchange membrane (PEM) fuel cells. Due to its high acidity, flexible side chains, chemical and thermal stability, Nafion became a benchmark material for fuel cell applications. However, Nafion could never be utilized as an alternative to petroleum for automotive applications because in such harsh condition in an automobile, water is readily evaporated and leached out of it, causing significant decrease of proton conductivity of Nafion at high temperature and low relative humidity conditions. The high manufacturing price of Nafion cannot be also compensated from its good properties for PEMs. Furthermore, high methanol crossover in Nafion was detrimental to utilize it as an electrolyte for direct methanol fuel cells (DMFCs).

As an alternative to Nafion, several families of hydrocarbon polymers such as poly(arylene ether sulfone), poly(etherketone), poly(etheretherketone) were extensively studied for PEMs in the past two decades. These polymers were advantageous because of their good thermal stability, easiness of synthesis and fabrication, high ion exchange capacity and less expensive manufacturing cost, compared to Nafion. However hydrocarbon polymers for PEMs could not replace Nafion because of low performance at low humidity and excessive swelling with relatively low proton conductivity.
In the past decade, morphology control of the ion conductive membranes was a hot issue in fuel cell researches because it is known that the control of morphology is an effective strategy to tune properties of the electrolyte membranes. Random copolymers such as Nafion are impossible to have a disenable morphology and hydrophilic-hydrophobic components are distributed randomly through the polymer chain. By synthesizing block copolymers, graft copolymers or tapered block copolymers, it is possible to have a wide variety of morphologies including spheres, cylindrical, lamellar structures\textsuperscript{20, 52-53}. At a certain ratio of hydrophilic to hydrophobic blocks, copolymer has a co-continuous channel through the membrane\textsuperscript{54-55}, which is ideal morphology for the proton conductivity.

Polyolefin is commonly and widely used in various applications because of its unique advantages such as superior chemical and physical stability, good processability and relatively cheap manufacturing cost. With these fruitful merits, it has been used as plastic bottles, containers, tires, bumpers and so forth. Porous polyethylene or polypropylene film is used as a separator between two electrodes in batteries because its hydrophobic structure not only is stable in electrochemical condition but also physically and effectively prevents direct contact of two electrodes and/or support solid electrolyte\textsuperscript{56-57}. However, since it is composed of C-C and C-H bonds, polyolefin is inherently hydrophobic, resulting in some shortcomings of it like poor adhesion and incompatibility with other class of materials or polymers. Also, it is barely used for ionic conductive materials where hydrophilic character is essentially needed. For the sake of compensating incompatibility with other materials and/or having hydrophilic component in polyolefin, it is usually functionalized with some functional groups such as borane group\textsuperscript{58-60}, para methyl styrene group\textsuperscript{61-62}, divinyl benzene group\textsuperscript{63} and further functionalized depending on a final application. Among these diverse routes for polyolefin functionalization, para methyl styrene is often selected to modify and/or functionalize polyolefin due to its easy purification or preparation,
cheap price, effective incorporation with various catalytic condition and more importantly, facile fabrications for further functionalization such as halogenation and metalation.\textsuperscript{64-66}

Grafting hydrophilic component onto polyethylene was technically challenging due to its inert chemical structure. In some previous publications\textsuperscript{67-69}, radiation-induced technique was used to graft hydrophilic units in polyolefin. In this method, free radicals generated by radiation initiated polymerization of styrene. The resulting polyethylene-g-polystyrene was postsulfonated by using concentrated sulfuric acid or chlorosulfuric acid. However, radiation generally caused several problems such as degradation of backbone chain, poor control of polymer structure and decrease of mechanical strength. Chemical approaches to graft polar side chains in polyolefin have been made\textsuperscript{70-72}. Polyethylene-graft-poly(methyl methacrylate) or polyethylene-graft-poly (propylene glycol), polyethylene-graft-poly(ε-caprolactone) could be synthesized with these routes but their properties were not intended for PEMs.

In this chapter, a new proton exchange membrane is introduced, which has completely hydrophobic polyethylene backbone that serves as a matrix and promisingly provides mechanical strength to very thin films. Polyethersulfone is connected onto polyethylene backbone by graft-onto coupling reaction and subsequently sulfonated. The resulting hydrophilic side chains provide the pathway of protons and water for high proton conductivity in the membrane. Synthetic method and various properties of the membranes for fuel cell applications are studied and investigated.

2.2. Experimental Section

2.2.1. Materials and Instrumentation

All oxygen and moisture sensitive manipulations were carried out inside of an argon-filled Vacuum Atmosphere dry box. Highly purified ethylene gas of chemical grade 3 was used for polymerization. Toluene was refluxed by Na and kept in dry box for use. Para methyl styrene was
dried by CaH₂ and distilled under reduced pressure. Constrained geometric catalyst (CGC) was synthesized according to the published procedure. Methylaluminoxane (MAO), benzoyl peroxide and n-bromosuccinimide were purchased from Sigma-Aldrich and used as received. Bisphenol A and dichlorodiphenyl sulfone (DCDPS) were recrystallized by hot toluene and dried under vacuum at 100 °C before use. Potassium carbonate was dried at 330 °C under nitrogen. N-methylpyrrolidinone (NMP), anisole and 1,1,2,2-tetrachloroethane were dried by CaH₂ and distilled under reduced pressure. Iron (II) persulfate heptahydrate and hydrogen peroxide was used as received.

All ¹H NMR spectrum were recorded on a Bruker AM 300 instrument either in 1,1,2,2-tetrachloroethane-d₂ or dimethylsulfoxide (DMSO)-d₆ at 110 °C. DSC thermograms were obtained by using TA Q100 instrument. Temperature range for heating and cooling cycle was from -30 °C to 200 °C with a heating rate of 10 °C/min. Second heating cycle was used to determine melting, crystalline temperature and heat of fusion. Thermal properties were investigated by using TA SDT Q600 instrument. Small amount of polymer was placed in ceramic cell and temperature was increased from 30 °C to 700 °C with a heating rate of 20 °C/min. Fourier transform infrared spectroscopy (FTIR) was recorded on a PE-1710 spectrometer from 4500 to 500 cm⁻¹ with a 4 cm⁻¹ resolution in 16 scans using polymer thin film (10–15 µm). Wide-angle X-ray scattering patterns (WAXS) were collected on a PANalytical X’Pert Pro MPD system using CuKα radiation (λ = 0.15406 nm) and a PXcel detector. Mechanical properties of the membranes were investigated at 50 % humidity at room temperature by pulling dumbbell shape thin polymer film in opposite direction at a rate of 2 mm/min using Instron 5866 Universal Test Instrument. Samples of interest were tested at least three times to confirm the validation of the results. In-plane and through-plane conductivity were measured by electrochemical impedance spectroscopy (EIS) with a Solartron 1260 frequency response analyzer (in-plane) or Gamry electrochemical measurement system.
(through-plane) in the frequency range from 10 Hz to 1 MHz. Methanol permeability was measured by in house setup equipped with Waters 1515 pump and RI dector. Contact angle measurement was performed by using Perkin Elmer contact angle goniometer.

### 2.2.2. Copolymerization of ethylene and p-methyl styrene

In a typical ethylene copolymerization condition, a Parr 450 ml stainless autoclave was pre-dried under vacuum line and toluene, MAO (10 wt % in toluene), p-methylstyrene and CGC were sequentially introduced into the autoclave under high pressure of ethylene gas. After the addition of CGC, copolymerization was conducted by extensive stirring at 60 °C for 20 mins. Additional ethylene was fed continuously into the autoclave to maintain a constant ethylene pressure and copolymerization was terminated by stopping ethylene feed, followed by pouring polymer solution into acidic methanol solution. Polymer was filtered and washed with THF and methanol thoroughly and dried under vacuum at 70 °C for 12 h.

### 2.2.3. Bromination of PE-co-p-MS

Bromination was performed in heterogeneous condition using NBS and BPO as bromine source and free radical initiator, respectively. In a typical reaction condition, 2 g of polymer was suspended in 100 ml 1,1,2,2-tetrachlorethane and temperature was elevated up to 75 °C. With the protection of nitrogen gas and stirring, 2 g of NBS and 0.04 g of BPO were added, and the reaction took place at 75 °C for 3 h, leading to deep yellow solution. After bromination, the polymer solution was cooled down to room temperature and poured into large amount of acetone. Light yellow polymer was filtered, washed with water and acetone several times to remove any residual NBS and BPO and dried under vacuum at 50 °C for 12 h.
2.2.4. Synthesis of poly(arylene ether sulfone) (PAES)

Poly(arylene ethersulfone) was synthesized by nucleophilic aromatic substitution polymerization\textsuperscript{74-75}. In a typical reaction, 18 g of bisphenol A (78.8471 mmol), 22.392 g of dichlorodiphenol sulfone (DCDPS, 77.9757 mmol) and 13.077 g of potassium carbonate (94.6165 mmol, 20 mol % excess to bisphenol A) were placed in 500 ml three neck round bottom flask with magnetic stirrer, condenser, argon inlet/outlet and dean stark trap. 240 ml of dried NMP and 120 ml of toluene (half volume of NMP) were injected into the flask at room temperature and kept for 1 hour. Temperature was elevated to 80 °C for 2 hours and 150 °C for 4 hours to dehydrate the reaction. After most toluene was trapped into dean stark trap, reaction temperature was increased to 175 °C for polycondensation. Out of a certain reaction time, viscous polymer solution was cooled down to room temperature, filtered, precipitated in isopropyl alcohol, filtered, washed with water and methanol, filtered again and dried at 110 °C for at least 24 hours under vacuum to give 96 % yield.

2.2.5. Graft-onto Reaction between Brominated PE-co-p-MS and Poly(arylene ethersulfone)

Graft-onto reaction was carried out in a homogeneous solution. In a typical reaction, to a 500 ml three neck round-bottom flask equipped with magnetic stirrer and condenser, 3.6 g PAES polymer (M\textsubscript{n}: 20 kg/mol and OH content: 0.36 mmol) and 0.05 g of potassium carbonate were added at 150 °C. Anisole (200 ml) was then introduced into flask with syringe to dissolve PAES completely. In a 100 ml one neck round-bottom Schlenk flask with a magnetic stirrer, 0.5 g of brominated PE-co-p-MS (M\textsubscript{v}: 320 kg/mol and Br content: 0.09 mmol) was dissolved into 50 ml of anisole at 120 °C. With the aid of cannula, homogeneous brominated PE-co-p-MS/anisole solution was transferred into the reactor that contains PAES/anisole solution. The coupling reaction was carried out at 150 °C with agitation for a specific time. After cooling down to room temperature, the
solution was centrifuged and washed with THF. Residual un-grafted PAES was completely
removed by Soxlet extraction with THF solvent. The resultant PE-g-PAES graft copolymer was
washed with de-ionized water and methanol, and then dried at 60 °C under vacuum for 12 h.

2.2.6. Membrane preparation and sulfonation

About 0.1 g of PE-g-PAES graft copolymer was dissolved in 6 ml anisole at an elevated
temperature. The homogeneous viscous solution was filtered through glass wool to remove any
impurities (particles) and cast onto a clean glass plate. The cast solution was dried for 2 days at
room temperature and another 12 h at 80 °C in vacuum. The resulting film (thickness: 20-40 μm)
was annealed under pressure at 110 °C for 12 h in vacuum. Sulfonation was then conducted on the
PE-g-PAES thin film under heterogeneous condition. Typically, the film was immersed in 50 ml
1,1,2,2-tetrachloroethane solution in a sealed container. Trimethylsilyl chlorosulfonate (1 ml) was
then added into the sealed container at room temperature. After 24 h of sulfonation, the resulting
sulfonated film was washed with methylene chloride, acetone and de-ionized water several times to
remove any residual reagents. The film was then acidified by soaking it into 1 mol/L HCl aqueous
solution for 24 h at room temperature, and then washed with de-ionized water thoroughly to remove
any residual HCl before drying at 70 °C under vacuum for 12 h. The resulting PE-g-g-PAES
membrane was usually kept in de-ionized water for use.

2.2.7. Measurements and Characterization

Water uptake (%) was calculated by [(W_{wet} - W_{dry})/W_{dry}] × 100%; wherein W_{wet} is the weight
of fully hydrated membrane, and W_{dry} is the weight of completely dried membrane. The membrane
was dried under vacuum for 12 h at 70 °C and stored in a desiccator before measuring the weight in
"dry" state (W_{dry}). The membrane was then equilibrated in de-ionized water for 24 h at room
temperature. After blotting the surface of the film quickly, the weight in "wet" state ($W_{\text{wet}}$) was measured. IEC was determined by back-titration using 0.01 mol/L NaOH aqueous solution. The PE-g-s-PAES membrane was soaked into 1 mol/L NaCl aqueous solution to release proton from the membrane. The solution was replaced every 4 h. After 24 h, the collected NaCl (aq) solution was titrated with 0.01 mol/L NaOH (aq) using phenolphthalein as an indicator. Colorless NaCl(aq) solution was changed to purple when a certain amount ($V_{NaOH}$) of NaOH(aq) was added. As a reference, the pure 1 M NaCl aqueous solution was titrated using the same condition to obtain the reference amount ($V_{\text{pure}}$) of NaOH(aq). IEC (mmol/g) was calculated by $\frac{[\text{NaOH}] \times (V_{NaOH} - V_{\text{pure}})}{W_{\text{dry}}}$. With the obtained water uptake and IEC value, the hydration number ($\lambda$) was calculated by $\frac{\text{water uptake ( m) } \times 10}{\text{IEC value } \times 18}$. In-plane conductivity in water phase was measured by a home-made 2 probe electrode conductivity cell and Solartron 1260 Gain/Phase Analyzer in the frequency range of $10-10^6$ Hz and calculated by $\frac{l}{(R \times \delta \times w)}$, where $l$ is the width between two electrodes (0.65 cm), $R$ is the ohmic resistance, $\delta$ is the thickness of the membrane (~40 µm), and $w$ is the width of the membrane (~1.0 cm). Through-plane conductivity in water phase was measured by a home-made 2 probe cell and Gamry Electrochemical Measurements system and calculated by $\frac{b}{\Delta R \times A_S}$, where $\Delta R$ is the difference of the cell resistance with and without membrane, $b$ is the thickness of the membrane, and $A_S$ is the surface area of the electrode (0.74 cm$^2$). In the measurement of conductivity at various humidity levels, relative humidity was controlled by setting up temperatures in the humidification saturator and the cell differently. Relative humidity was calculated by the equation, $\text{RH(\%)} = \frac{P(T_h)}{P(T_c)} \times 100^{10}$, where $\text{RH(\%)}$ is relative humidity and $P(T_h)$ is the pressure of saturated water vapor at humidification saturator and $P(T_c)$ is the pressure of saturated water vapor at conductivity cell. Before the measurement of conductivity, at least 2 hours were allowed to equilibrate the sample with the environment. At first, relative humidity was set up to 70 %, decreased to 50 % and 30 % and then increased up to 95 %. More detailed information is
found in the references\textsuperscript{10, 76}. Nafion 117 membrane was measured before all the conductivity measurements to confirm the validity of experimental condition. Measurement was conducted at least 5 times to obtain consistent resistance value over 2 hours. Methanol permeability was calculated\textsuperscript{77} by the equation \[
\ln \frac{M_{R,t} - M_{L,t}}{M_{R,0} - M_{L,0}} = -DH \chi t,
\] where \(M_{R,t}\) is the concentration of MeOH in methanol solution chamber at time \(t\), \(M_{L,t}\) is the concentration of MeOH in DI water chamber at time \(t\), \(M_{R,0}\) is the concentration of MeOH in methanol solution chamber at \(t = 0\), \(M_{L,0}\) is the concentration of MeOH in DI water chamber at \(t = 0\), \(D\) is diffusion coefficient, \(H\) is partition coefficient, \(DH\) is permeability and \(\chi\) is the geometric parameter (\(= A/\delta [1/V_R + 1/V_L]\), where \(A\) is surface area, \(\delta\) is thickness of membrane, \(V_R\) & \(V_L\) are the volume of methanol solution chamber and DI water chamber, respectively). Full descriptions and information about the conductivity cells and methanol permeability cells/equipments are found in Appendix at the end of the thesis.

Electrochemical stability was investigated by Fenton test. Polymer membrane was placed in the Fenton reagent (2 ppm FeSO\textsubscript{4} in 3 wt % H\textsubscript{2}O\textsubscript{2} aqueous solution). The membrane was heated in the solution for an hour. By weighing the membrane before and after the test and dividing the difference by the weight before test, the electrochemical stability was estimated. Three polymer membranes and Nafion 117 were tested at 80 °C and 95 °C.

2.3. Results and Discussion

A new material that is based on PE-g-s-PAES graft copolymers with a well-controlled molecular structure (i.e. backbone molecular weight, graft density, graft length, sulfonation level, etc.) was studied. The copolymer contains a high molecular weight PE backbone and several highly sulfonated poly(arylene ethersulfone) (s-PAES) side chains. With two extremely different polymer properties, the crystalline hydrophobic PE backbone and amorphous hydrophilic s-PAES side chains shall be micro-phase separated into a well-defined morphology that contains a robotic (water
non-swelling) PE matrix and some stable embedded s-PAES continuous ion conductive channels through the PE film. The combination may provide a PEM with a high IEC value without water over-swelling, therefore achieving high proton conductivity\(^3\). For a systematic study to identify suitable graft copolymer structures and compositions, the investigation involves several steps, including (i) the development of a chemical route to prepare a well-defined graft copolymer, (ii) utilizing the most suitable process to prepare PEM membranes, and (iii) a systematic comparison of structure-property relationships in conductivity, water-swelling, surface, and mechanical properties.

2.3.1. Synthesis of PE-g-PAES Graft Copolymer

Scheme 1 illustrates the synthesis steps in the preparation of PE-g-PAES graft copolymer (III), which involves a graft-onto reaction between poly(ethylene-co-p-bromomethyl styrene) (PE-co-p-MS-Br) (I) and poly(arylene ethersulfone) (PAES) (II). Both precursor polymer structures were pre-determined before the coupling reaction. In this research, the synthesis of PAES polymers (II) was extensively studied and reported in many publications\(^20, 74, 78\). Three PAES polymers with various molecular weight have been prepared with \(M_n = 13k, 20k, \) and \(26k \) g/mol, respectively. Molecular weight of PAES polymers was estimated by \(^1\)H-NMR and viscometry. First, by \(^1\)H-NMR molecular weight of PAES was determined by comparing the peak intensity of aromatic groups at the end group of PAES with the peak intensity of aromatic group at the repeat unit of PAES. The number of repeat units was calculated by dividing the peak intensity at 7.7 ppm by the peak intensity at 6.8 ppm. For example, in the case of PAES with 20,000 g/mol, repeat unit is about 45, which means that the peak intensity at 7.7 ppm is 45 times larger than the peak intensity at 6.8 ppm. By this method, the number average molecular weight of PAES was calculated. Second, in order to measure molecular weight using the intrinsic viscosity, a relationship between molecular weight
and intrinsic viscosity (IV) was obtained in advance. NMP was used as a solvent (medium) and LiBr (0.05M) was added to remove the polyelectrolyte effect.

As shown in the Figure 2.1, by testing several PAES whose molecular weight is already known by $^1$H-NMR, the relationship between the intrinsic viscosity and molecular weight can be obtained. Thus, by measuring the intrinsic viscosity, molecular weight of an unknown PAES can be obtained.

In our group, we had investigated the copolymerization of ethylene and styrenic comonomers, including p-methylstyrene (p-MS), using various metallocene catalysts $^{61,63,79}$. Several constrained geometry metallocene catalysts (CGC) showed comparative comonomer reactivity.
ratios and we obtained various copolymers, including ethylene/p-MS copolymers, with narrow molecular weight and composition distributions.

Table 2.1 summarizes several ethylene/p-MS copolymerization conditions and results. They are prepared by the \([\text{C}_5\text{Me}_4(\text{SiMe}_2\text{NtBu})]\text{TiCl}_2/\text{MAO CGC-metallocene catalyst system. All resulting PE-co-p-MS copolymers show a sharp } T_m \text{ transition and narrow molecular weight distribution (PDI} \sim 2\text{). Comparing runs I to IV, the p-MS content in the PE-co-p-MS copolymer proportionately increases with the monomer feed, and a copolymer with more than 6 mol } \% \text{ of p-MS (run IV) was observed. Although the catalyst maintains high catalyst activity, the copolymer molecular weight systematically decreases with the p-MS content. However, the copolymer}
molecular weight is also strongly depending on ethylene pressure. High molecular weight PE-co-p-MS copolymers (runs V and VII) can be easily obtained with high catalyst activity and desirable p-MS content. As will be discussed later, these PE-co-p-MS copolymers with [p-MS] <2 mol % were used in this study to maintain high PE crystallinity, melting temperature ($T_m$), and molecular weight.

Table 2.1. Summary of metallocene-mediated copolymerization of ethylene and p-methylstyrene

<table>
<thead>
<tr>
<th>Run</th>
<th>Reaction Condition</th>
<th>Polymerization Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ethylene (psi)</td>
<td>p-MS (mmol)</td>
</tr>
<tr>
<td>I</td>
<td>125</td>
<td>7.6</td>
</tr>
<tr>
<td>II</td>
<td>125</td>
<td>19</td>
</tr>
<tr>
<td>III</td>
<td>125</td>
<td>38</td>
</tr>
<tr>
<td>IV</td>
<td>125</td>
<td>76</td>
</tr>
<tr>
<td>V</td>
<td>220</td>
<td>19</td>
</tr>
<tr>
<td>VI</td>
<td>220</td>
<td>38</td>
</tr>
<tr>
<td>VII</td>
<td>320</td>
<td>38</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: 75 ml toluene, [Ti]= $4 \times 10^{-6}$ mol, [MAO]/[Ti] = 2250, Temp.= 60$^\circ$C, and Time = 20 mins.

$^b$Catalyst activity: Kg of PE/[mol of catalyst × hour].

$^c$Determined by $^1$H NMR.

$^d$Determined by intrinsic viscosity in decalin at 135$^\circ$C with $[\eta] = KM_\alpha$, K=62 $\times$ 10$^{-3}$ ml/g, $\alpha$=0.7.$^{70}$

Bromination of the PE-co-p-MS copolymer (fine powder) was carried out in a 1,1,2,2-tetrachloroethane suspension solution using benzoyl peroxide (BPO) as a free radical initiator and N-bromosuccinimide (NBS) as a bromination reagent. The heterogeneous reaction was performed at 75 $^\circ$C under a nitrogen atmosphere in a dark environment, and the excess amount of NBS to p-MS in mol % was used. A light yellow polymer powder was obtained. Figure 1 compares the $^1$H NMR spectra of a PE-co-p-MS copolymer (run VII) before and after the bromination reaction. The
chemical shift at 2.35 ppm, corresponding to the benzyl proton $\Phi$-CH$_3$ in PE-co-p-MS, significantly reduces its intensity, and a new split peak around 4.54 ppm, corresponding to the protons in benzylbromide ($\Phi$-CH$_2$Br), are observed. It clearly shows that the bromination reaction predominantly takes place at the p-CH$_3$ position. The degree of bromination estimated from the integrated peak areas between p-bromomethyl protons at 4.54 ppm and aromatic protons at 7.0-7.4 ppm is 53%.

Figure 2.2. $^1$H NMR spectra of (top) PE-co-p-MS and (bottom) brominated PE-co-p-MS-Br.

Table 2.2 summarizes several comparative sets of the bromination reaction using three PE-co-p-MS copolymers (runs II, V, and VII in Table 2.1) with ~1.5 mol % p-MS content and various
molecular weights (220k, 320k, and 390k g/mol). The bromination reaction of PE-co-p-MS is very selective on p-MS moieties at 75°C, and the efficiency of bromination is controlled by the reaction time and mole ratio of [NBS]/[p-MS], as well as by polymer molecular weight (kinetic reasons). With 3 h of reaction time at 75 °C, more than 50 % of p-MS groups in the copolymer are brominated without showing any significant change in polymer molecular weight. However, with a further increase of the reaction temperature to 90 °C, we did observe some reduction in polymer molecular weight. It is interesting to note that the heterogeneous reaction condition may be beneficial to enhance this selective free-radical induced bromination reaction on p-MS moieties. The bulky p-MS groups in the PE-co-p-MS copolymer shall reside in the amorphous phase. With the solution swelling, the p-MS groups will have a good chance to come in contact with BPO/NBS reagents. On the other hand, the PE chains in the crystalline phase may have a lower chance of meeting the chemical reagent (solution), therefore delaying potential side reactions. Although there is a low Br concentration in the resulting PE-co-p-MS-Br, they provide more than sufficient coupling sites for the preparation of PE-g-PAES graft copolymers.

Table 2.2. Summary of the bromination reaction\(^a\) in forming PE-co-p-MS-Br copolymers.

<table>
<thead>
<tr>
<th>Run</th>
<th>Starting PE-co-p-MS</th>
<th>Reaction Condition</th>
<th>PE-co-p-MS-Br Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(M_v) (g/mol)</td>
<td>p-MS content (mol%)</td>
<td>[NBS]/[p-MS] (mole ratio)</td>
</tr>
<tr>
<td>II-1</td>
<td>220k</td>
<td>1.8</td>
<td>10.5</td>
</tr>
<tr>
<td>II-2</td>
<td>220k</td>
<td>1.8</td>
<td>10.5</td>
</tr>
<tr>
<td>II-3</td>
<td>220k</td>
<td>1.8</td>
<td>10.5</td>
</tr>
<tr>
<td>II-4</td>
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<td>1.8</td>
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<tr>
<td>VII-2</td>
<td>390k</td>
<td>1.5</td>
<td>10.5</td>
</tr>
</tbody>
</table>
Reaction conditions: 100 ml 1,1,2,2-tetrachloroethane, 2g PE-co-p-MS copolymer, 0.04 g BPO, temp. = 75°C.

Determined by $^1$H NMR.

Bromination efficiency: % of p-MS reacted to form p-MS-Br.

The graft-onto reaction between PE-co-p-MS-Br (I) and PAES polymers (II) was carried out under a similar condensation polymerization condition as was used in the preparation of PAES polymers, with the exception of applying a common anisole solvent to maintain both polymers in solution throughout the coupling reaction. After the coupling reaction, the un-reactive PAES polymer was carefully removed by Soxlet extraction. Figure 2.2 compares the $^1$H NMR spectra between the starting PE-co-p-MS-Br (run VII-2 in Table 2.2) and the resulting PE-g-PAES graft copolymer (run A-1 in Table 2.3). In addition to a major PE peak at 1.35 ppm, there are several new peaks shown in the PE-g-PAES graft copolymer, including a methyl peak at 1.67 ppm, corresponding to two methyl groups in bisphenol A units and several aromatic peaks between 6.9 and 7.9 ppm. The composition of the PE-g-PAES graft copolymer (i.e. the mole ratio between ethersulfone units in the side chains and ethylene units in the backbone) was determined by comparing the peak intensity between the 1.35 and 1.67 ppm peaks and the protons involved in each monomer unit. Since there is a huge difference between ethylene and arylene ethersulfone unit molecular weights (28 vs. 442 g/mol), the mole ratio between these two cannot adequately reflect the structure of the graft copolymer (III). The PE-g-PAES graft copolymer in Figure 2.3 (bottom) contains only 2.7 mol % of ethersulfone units, but has 30 weight % and 25 volume % to that of PAES in the graft copolymer.
Figure 2.3. $^1$H NMR spectra of (top) PE-co-p-MS-Br and (bottom) PE-g-PAES graft copolymer.

The FT-IR spectroscopy was also applied to confirm the graft copolymer. As shown in Figure 2.4, the PE-g-PAES graft copolymer exhibits several new absorption bands, including 1006 cm$^{-1}$ for diphenyl ether, 1030 cm$^{-1}$ for sulfonic acid (sym), 1100 cm$^{-1}$ for SO$_2$ (sym), and 1310 cm$^{-1}$
for $SO_2$ (asym), corresponding to PAES side chains.

Figure 2.4. FT-IR spectrum of a) PAES, b) PE-g-PAES c) PE-g-s-PAES
Table 2.3 Summary of PE-g-PAES graft copolymers and their coupling reaction condition

<table>
<thead>
<tr>
<th>Run</th>
<th>$M_n$ of PE (g/mol)</th>
<th>Br in PE (mol%)</th>
<th>$M_n$ of PAES (g/mol)</th>
<th>Reaction Temperature (°C)</th>
<th>Reaction Time (h)</th>
<th>PAES (wt%)</th>
<th>PAES (vol%)</th>
<th>Ave. # of PAES chains per PE Graft</th>
<th>Graft Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>390k</td>
<td>0.8</td>
<td>20k</td>
<td>110</td>
<td>6</td>
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<td>42</td>
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<td>1.0</td>
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<td>1.2</td>
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<tr>
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<td>0.8</td>
<td>20k</td>
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<td>20k</td>
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<td>46</td>
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<td>1.2</td>
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<tr>
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<td>20k</td>
<td>150</td>
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<td>43</td>
<td>8.7</td>
<td>1.4</td>
</tr>
<tr>
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<td>0.8</td>
<td>20k</td>
<td>150</td>
<td>24</td>
<td>63</td>
<td>58</td>
<td>15.1</td>
<td>2.4</td>
</tr>
<tr>
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<td>20k</td>
<td>150</td>
<td>24</td>
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<td>37</td>
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<tr>
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<td>13k</td>
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<td>24</td>
<td>55</td>
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</tr>
<tr>
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<td>20k</td>
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<td>24</td>
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</tr>
<tr>
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<td>26k</td>
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<td>37</td>
<td>5.1</td>
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<td>20k</td>
<td>110</td>
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<td>2.4</td>
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<tr>
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<td>20k</td>
<td>110</td>
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<td>39</td>
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<tr>
<td>E-3</td>
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<td>20k</td>
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<td>46</td>
<td>6.7</td>
<td>1.6</td>
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<tr>
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<td>20k</td>
<td>110</td>
<td>18</td>
<td>58</td>
<td>51</td>
<td>8.2</td>
<td>1.9</td>
</tr>
</tbody>
</table>


$^b$ Determined by $^1$H NMR.

$^c$ Calculation based on PE density = 0.95 g/cm$^3$ and PAES density = 1.25 g/cm$^3$

$^d$ PAES side chains per 1000 ethylene units in the backbone.

$^e$ % of Br in PE-co-p-MS-Br involved the coupling reaction with PAES.
Table 2.3 compares five sets of graft-onto reactions involving four PE-co-p-MS-Br copolymers with $M_w = 220k, 250k, 320k$, and $390k$ g/mol and three PAES polymers with $M_w = 13k, 20k$, and $26k$ g/mol, respectively. In each coupling (graft-onto) reaction, the mole ratio of two active sites ($[\text{p-MS-Br}] / [\text{phenol}]$) was maintained at $\frac{1}{4}$, with excess PAES side chains. In sets A and B we compare two reaction temperatures ($110$ and $150^\circ C$) and four reaction times (6, 9, 12, and 24 h), using the same PE-co-p-MS-Br (run VII-2 in Table 2.2 with molecular weight: $390$ kg/mol and Br content: $0.8$ mol %) and PAES (molecular weight: $20$ kg/mol). The grafting efficiency significantly increases with the increase of both reaction temperature and time, and the gap between low and high temperature conditions become smaller with the sufficient reaction time. In run B-4 (under $150$ °C and $24$ h), the resulting PE-g-PAES graft copolymer contains about $18$ PAES side chains along the PE backbone. In set C (runs C-1, C-2, and C-4), we investigated the molecular weight effect of PE-co-p-MS-Br using three PE-co-p-MS-Br copolymers (runs II-5, V-1, and VII-1 in Table 2.2) that have the same Br content ($0.5$ mol %) but different molecular weight ($220k, 320k$, and $390k$ g/mol, respectively). The side-by-side coupling reactions were conducted under the same reaction condition ($150$ °C for $24$ h) and PAES (molecular weight: $20$ kg/mol). Evidently, high molecular weight PE-co-p-MS-Br (with high solution viscosity) clearly slowed down the coupling reaction with the PAES polymer. In Set D, we focused on the effect of the poly(arylene ethersulfone) molecular weight to the coupling reaction. The comparative study involved three PAES polymers with molecular weights of $13k, 20k$, and $26k$ g/mol, respectively, and the same PE-co-p-MS-Br copolymer (run V-1 in Table 2.2) at $150$ °C for $24$ h. The graft efficiency is strongly affected by the molecular weight of PAES—higher molecular weight means lower efficiency. This reverse molecular weight effect indicates the importance of PAES mobility to the coupling (graft-onto) reaction, due to the fact that the PAES polymer chain only contains two active terminal groups. Overall, the graft efficiency seems dependent on four factors: reaction temperature, reaction time,
and the molecular weights of both PE-co-p-MS-Br (I) and PAES (II) polymers. High molecular weight polymers require higher temperatures and longer reaction times in the coupling reaction. With the proper selection of reaction conditions, there should be no problem to prepare a broad range of well-defined PE-g-PAES graft copolymers with controlled molecular structures (i.e. backbone molecular weight, graft density, and graft length).

Figure 2.5 compares DSC curves of a PE-g-PAES graft copolymer (run B-4 in Table 2.3) with the corresponding PE-co-p-MS-Br (run VII-2 in Table 2.2) and the starting PE-co-p-MS copolymer (run VII in Table 2.1). Both PE-co-p-MS and PE-co-p-MS-Br, having less than 2 mol % of comonomer units, show a sharp melting temperature peak ($T_m$) at 125 °C and heat of fusion ($\Delta H$) of about 116.6 J/g, both are slightly below those in high density polyethylene (HDPE). The low concentration of comonomer units (branch points) has only little effect on the PE chain crystallization. In Figure 2.5(c), in addition to a melting peak at 120 °C and $\Delta H$ of about 47.5 J/g (41% of PE-co-p-MS-Br), the PE-g-PAES graft copolymer also exhibits a $T_g$ at 175 °C, corresponding to the $T_g$ of PAES homopolymer (A1 in Appendix). Despite the incorporation of high molecular weight PAES side chains, the PE-g-PAES graft copolymer shows only a small decrease (~7 °C) in PE melting temperature and a decrease of heat of fusion ($\Delta H$) mainly due to the dilution effect. Considering the PE backbone is only contributing to 43 % of the weight to the PE-g-PAES graft copolymer, the PE backbone maintains its high crystallization ability despite the presence of the PAES side chains. Evidently, in the PE-g-PAES graft copolymer with graft density <1 mol %, a clear micro-phase separation was developed in the morphology that includes a highly crystalline and hydrophobic PE phase and an amorphous (high $T_g$) and more hydrophilic PAES phase.
2.3.2. PE-g-s-PAES PEMs and Mechanical Properties

The resulting PE-g-PAES copolymers are completely soluble in organic solvents, such as anisole, at an elevated temperature. As illustrated in scheme 2, the homogeneous viscous polymer solution was solution-cast into films, and then dried to form uniform membranes with thicknesses of 20-40 μm. The formed light brown transparent and ductile membranes, as shown in Figure 2.6 (left), were suspended in 1,1,2,2-tetrachloroethane solution for carrying out the sulfonation reaction using a trimethylsilyl chlorosulfonate reagent\textsuperscript{78, 81} under a heterogeneous condition. The films
gradually deepen in color, maintaining their transparency. Figure 2.6 (right) shows a typical PE-g-s-PAES PEM with a higher sulfonation (DS) level, showing brown and transparent. It is interesting to note that the sulfonation level reported in the poly(arylene ethersulfone)\textsuperscript{81}, including the commercial ones (such as UDEL-P1700)\textsuperscript{78, 82-83}, was usually less than 1 sulfonic acid per arylene ethersulfone unit. The higher sulfonation level leads to extensive swelling or dissolution by water and polar solvents. McGrath et al.\textsuperscript{20, 23, 49, 84-86} reported the control of water swelling by direct copolymerization of bi-sulfonated sulfone monomers with the hydrophobic sulfone units in both random and block copolymers. As will be discussed later (Table 2.5), most of the PE-g-PAES graft copolymers achieved a higher degree of sulfonation with 1.6-1.7 sulfonic acid per arylene ethersulfone unit in this post-sulfonation reaction, despite the heterogeneous reaction condition. In addition, the resulting PE-g-s-PAES PEMs still maintain very good mechanical properties and well-controlled water swelling. The DSC curve of PE-g-s-PAES PEM (curve d in Figure 2.5) reveals that PE crystalline phase remains intact during the sulfonation reaction. There were no significant change in melting temperature and heat of fusion. Evidently, the hydrophobic and crystalline PE backbone provides a stable matrix and allows the sulfonated PAES (s-PAES) side chains in forming highly hydrophilic (acidic) ion-conductive channels across the PEM film.
Scheme 2

Solution casting

PE-g-PAES Film
(thickness 20-40 μm)

Sulfonation reaction

Sulfonated PE-g-s-PAES PEM Film
Figure 2.6. Photograph of (left) an unsulfonated PE-g-PAES membrane (run B-4) and (right) the corresponding sulfonated PE-g-s-PAES membrane (run s-B-4).

Figure 2.7 compares strain-stress curves of a set of polymers that are formed during the preparation of the PEM sequence, including the starting PE-co-p-MS, PE-co-p-MS-Br, PE-g-PAES (run B-4 in Table 2.3), and PE-g-s-PAES (run s-B-4 in Table 2.5). In general, the graft copolymers containing PAES (or s-PAES) side chains exhibit very different mechanical profiles than the starting PE-co-p-MS and PE-co-p-MS-Br copolymers, which behave like a typical PE thermoplastic with a yield curve showing relatively low tensile strength, low modulus, and high elongation. The high $T_g$ PAES in the PE-g-PAES graft copolymer abruptly increases tensile strength and modulus and decreases the elongation, resembling a high performance engineering plastic. After the subsequent heterogeneous sulfonation reaction, the sulfonated PE-g-s-PAES PEM film absorbs some water (discussed later), however it still maintains very good mechanical strength with similar stiffness with PE-g-PAES film and high tensile strength (~35 Mpa).
Figure 2.7. A comparison of strain-stress curves for a set of (a) PE-co-p-MS, (b) PE-co-p-MS-Br, (c) PE-g-PAES, and (d) PE-g-s-PAES during the PEM preparation.

Table 2.4. Summary of mechanical properties of the polymers during the PEM preparation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Structure Information(^a)</th>
<th>Tensile Strength [MPa]</th>
<th>Young’s Modulus [MPa]</th>
<th>Elongation at Break [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE-co-p-MS</td>
<td>(390k/0/0/0)</td>
<td>15.3±1.0</td>
<td>196±38</td>
<td>225±41</td>
</tr>
<tr>
<td>PE-co-p-MS-Br</td>
<td>(390k/0/0/0)</td>
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<td>135±23</td>
<td>171±19</td>
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<tr>
<td>Nafion117</td>
<td>--</td>
<td>13.7±1.5</td>
<td>117±13</td>
<td>208±13</td>
</tr>
<tr>
<td>PE-g-PAES (run B-4)</td>
<td>(390k/20k/63/0)</td>
<td>48.0±7.3</td>
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<tr>
<td>PE-g-s-PAES (run s-B-4)</td>
<td>(390k/20k/63/1.54)</td>
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<td>5.8±0.3</td>
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<tr>
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<td>(320k/20k/63/0)</td>
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<td>3.2±0.1</td>
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<tr>
<td>PE-g-s-PAES (run s-C-3)</td>
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<td>1120±121</td>
<td>6.6±0.7</td>
</tr>
<tr>
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<td>3.1±0.1</td>
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<tr>
<td>PE-g-s-PAES (run s-C-1)</td>
<td>(250k/20k/64/1.60)</td>
<td>24.7±2.3</td>
<td>957±86</td>
<td>5.2±0.3</td>
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</tbody>
</table>

\(^a\) (PE backbone molecular weight/PAES side chain molecular weight/PAES wt%/degree of sulfonation)
Table 2.4 compares the mechanical properties of three graft copolymer sets with various PE backbone molecular weights (390k, 320k, and 250k g/mol), before and after sulfonation. They have the same PAES side chains, similar high PAES content (63wt%), and a degree of sulfonation (number of sulfonic acids per arylene ethersulfone unit in the s-PAES side chains). Three references, including PE-co-p-MS, PE-co-p-MS-Br, and Nafion 117 random copolymers, were also measured and compared side-by-side. In general, all PE-g-PAES and PE-g-s-PAES graft copolymers show a dramatic modulus increase and elongation reduction from the corresponding PE copolymers. They behave like rigid and strong engineering plastics. The higher the PE molecular weight in PE-g-PAES graft copolymers (before sulfonation), the higher the tensile strength and Young’s modulus. However, the differences were reduced in the sulfonated PE-g-s-PAES graft copolymers. Sulfonic acids, with the associated water molecules (plasticizer) in the s-PAES phase (discussed later), somewhat reduce the overall mechanical strength. However, the high molecular weight PE-g-s-PAES graft copolymers (runs s-B-4 and s-C-3) still maintain very high tensile strength (~35 MPa) and Young’s modulus (10 times that of Nafion 117). All mechanical results are consistent with a morphology that has continuous PAES domains imbedded in a highly crystalline PE matrix. In the fuel cell applications, high modulus PEM with low elongation is highly desirable, which provides long-term stability of MEA assemblies that are usually operated under harsh environments—strong acids, free radicals, and continuous fluctuation of pressure, temperature, humidity, etc. The weak PEMs also lead to the fuel crossover from anode to cathode or vice versa\(^87\). It is interesting to note that the combination of chemical and electrochemical stability with high crystallinity and hydrophobicity of the PE matrix may offer a unique (stable) framework for the water-swelled PEM containing many proton-conductive micro-channels.

2.3.3. Proton Conductivity and Water Swelling
Table 2.5 shows ion exchange capacity (IEC), degree of sulfonation (DS), proton conductivity (in-plane and through-plane), water swelling (WS), and the hydration number ($\lambda$) for two sets of PE-s-PAES membranes that are prepared from two corresponding sets of PE-g-PAES graft copolymers (B and E sets in Table 2.3), with PE molecular weights of 390k and 220k g/mole, respectively, and the same PAES graft length (20k g/mol) but different graft density. All PE-g-PAES graft copolymers were sulfonated to a high degree of sulfonation (DS ranging from 1.48-1.62). As expected, both PEM sets show an increase in water uptake and proton conductivity proportional to the IEC value. Most of the PE-s-PAES membranes achieve high proton conductivity (in the same range or higher than Nafion 117). It is quite unexpected to see such a big effect on the PE backbone molecular weight to the water uptake and hydration number, as well as the significant higher through-plane conductivity than in-plane conductivity in all PE-s-PAES membranes, which is quite opposite to many reported PEMs\textsuperscript{21, 26, 88}.

Table 2.5. Summary of IEC, water uptake, hydration number, and the in-plane and through-plane conductivities of two sets of PE-g-s-PAES PEMs and Nafion 117.

<table>
<thead>
<tr>
<th>Sample</th>
<th>IEC [mmol/g of PE-g-s-PAES]</th>
<th>IEC [mmol/g of s-PAES]</th>
<th>Degree of Sulfonation$^a$</th>
<th>Water Uptake [%]</th>
<th>Hydration Number$^b$ [l]</th>
<th>In-plane Conductivity [mS/cm]</th>
<th>Through-plane Conductivity [mS/cm]</th>
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<td>83</td>
</tr>
<tr>
<td>s-E-4</td>
<td>1.78</td>
<td>3.36</td>
<td>1.50</td>
<td>93</td>
<td>29</td>
<td>70</td>
<td>104</td>
</tr>
<tr>
<td>s-E-5</td>
<td>1.91</td>
<td>3.29</td>
<td>1.48</td>
<td>104</td>
<td>30</td>
<td>78</td>
<td>144</td>
</tr>
<tr>
<td>Nafion117</td>
<td>0.91</td>
<td>-</td>
<td>-</td>
<td>24</td>
<td>15</td>
<td>77</td>
<td>81</td>
</tr>
</tbody>
</table>

$^a$ Degree of sulfonation: # of sulfonic acid per arylene ethersulfone unit in the s-PAES side chains.

$^b$ Hydration number: # of H$_2$O molecules per sulfonic acid by $^1$H NMR.
Figure 2.8. (left) Comparison of water uptake (%) and hydration number ($\lambda$) and (right) in-plane and through-plane conductivities vs. IEC values for two sets of PE-s-PAES PEMs (B & E) and Nafion117.
Figure 2.8 shows the side-by-side comparisons of water uptake and conductivity between two sets of PE-g-s-PAES PEMs (B and E samples in Table 2.5) and Nafion 117. Figure 2.8 (left) shows both water uptake (%) and hydration number (λ) vs. IEC value (in s-PAES phase) for both sets of PE-g-s-PAES PEMs and Nafion 117. Considering the extensive water swelling (water uptake >160% and λ >50) in the sulfonated poly(arylene ethersulfone) with DS value ~1.2, all PE-g-s-PAES PEMs (with DS value >1.4) show significantly smaller water swelling. In fact, the water uptake of PE-g-s-PAES PEM is strongly dependent on the PE backbone molecular weight, even in such a high molecular weight range (390k vs. 220k g/mol). Comparing similar IEC values (s-B-1 vs s-E-3; 1.64 vs. 1.67), the B set graft copolymers with a 390k g/mole PE backbone show less than half of the overall water swelling than those in the E set graft copolymers with a 220k g/mol PE backbone. Evidently, the water pressure in the PE-g-s-PAES with a high IEC value is so high that some extra high molecular weight and high crystallinity PE polymer is needed to contain the water over-swelling. In set B (the 390k case), although the water uptake still linearly increases with the IEC value, the hydration number only shows a moderate increase. With regards to PE-g-s-PAES PEM (s-B-4) and its IEC value (more than double that of Nafion 117), the hydration number for each acid (λ = 14) in PE-g-s-PAES is almost the same with that of Nafion 117 (λ = 15). The high molecular weight PE backbone, with the combination of high hydrophobicity and crystallinity, forms an exceptionally strong hydrophobic matrix (water prohibited zone) in PE-g-s-PAES PEM to resist water swelling in the hydrophilic phases even with very high acid content. It may form some well-protected (robotic) hydrophilic ion-conductive channels in PE-g-s-PAES PEMs, which are not very sensitive to acid contents. Therefore, it is possible to continuously increase the IEC value and proton conductivity (set B), without the penalty of the dilution effect, due to excessive water swelling that also weakens the membrane strength and stability.
Figure 2.8 (right) compares in-plane and through-plane conductivities for the same two sets of PE-g-s-PAES PEMs and Nafion 117. The conductivity essentially proportionately increases with the IEC value. The PE molecular weight appears to be not particularly sensitive to the conductivity. However, good control of water swelling in PE-g-s-PAES (Set B), with higher PE molecular weight, allows the preparation of PEMs with higher IEC values while still maintaining high mechanical strength. Therefore, the PEMs in the high molecular weight B set can reach very high proton conductivity. After the IEC value reaches 1.4, both in-plane and through-plane conductivities accelerate with higher slopes. This turning point (from the s-E-2 sample in Table 2.5) implies that the morphology in PE-g-s-PAES changes from not fully connected ionic domains to a complete network structure with many ionic channels across the PEM film. In fact, this PEM sample was originated from the PE-g-PAES graft copolymer (run E-2 in Table 2.3) that contains 33 vol % of PAES, which is consistent with the expected percolation threshold\(^{54,55,89}\). It is a pleasant surprise to observe the through-plane conductivity of s-B-4 sample reaching 167 mS/cm (double that of Nafion 117) and significantly higher through-plane conductivity than in-plane conductivity in all PE-g-s-PAES graft copolymers with percolated ionic channels (IEC value >1.4). The difference becomes larger as the IEC increases. All results indicate a significantly improved connectivity between ion channels, especially in the through-plane direction. Since the through-plane conductivity is directly relative to the fuel cell performance, this is a positive surprise, and it deserved a further study to understand the structure causing this anisotropy in conductivity.

Proton conductivity of membranes was measured at various relative humidity levels and temperatures. Relative humidity (RH) level and temperature varied from 30 % to 95 % and from 30 ºC to 80 ºC, respectively. Figure 2.9 shows the proton conductivity at various relative humidity level and temperature ranged above. Like proton conductivity in liquid phase (100 % relative humidity level), through-plane proton conductivity was higher than in-plane proton conductivity at
a whole range. When compared with Nafion 117, at high humidity level (95 %), proton conductivity of PE-g-s-PAES is shown to be higher than that of Nafion 117. However as relative humidity lowers, the proton conductivity of PE-g-s-PAES and Nafion 117 were collapsed together thus no advantages for PE-g-s-PAES were observed at 30 % RH. It is well known that at low humidity condition, proton conductivity decreases abruptly due to low water contents in polymer membrane. Based on the proton conductivity at various temperatures, it was possible to calculate activation energy by Arrhenius equation for a temperature range of 50–80 °C as shown in Table 2.6.

Table 2.6. Activation energy of Nafion 117 and PE-g-s-PAES; In-plane and Through-plane (unit – kJ/mol)

<table>
<thead>
<tr>
<th></th>
<th>In-Plane</th>
<th>Through-Plane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nafion 117</td>
<td>PE-g-s-PAES</td>
</tr>
<tr>
<td>RH 30%</td>
<td>18</td>
<td>15.6</td>
</tr>
<tr>
<td>RH 50%</td>
<td>11.2</td>
<td>10.9</td>
</tr>
<tr>
<td>RH 70%</td>
<td>7.3</td>
<td>5.9</td>
</tr>
<tr>
<td>RH 95%</td>
<td>6.7</td>
<td>3</td>
</tr>
</tbody>
</table>

At all relative humidity levels, activation energy of PE-g-s-PAES was lower than that of Nafion 117, indicating that better co-continuous channels are developed in PE-g-s-PAES\(^3\). Nonetheless, proton conductivity was not higher than Nafion 117 thus it is speculated that for PE-g-s-PAES, there are many other factors to determine proton conductivity including acidity of acid groups, side chain flexibilities\(^21,91\). Compared with Nafion 117, PE-g-s-PAES has a low acidity and less flexible chains (aliphatic fluorine side chains vs. rigid PAES chains for proton conduction).
It is known that under electric field, protons transport through the electrolyte by hopping, vehicle and surface mechanisms\(^{92}\). At high water contents, all these three mechanisms are responsible for the proton conduction. However, at low humidity condition, the proton conductivity in a polyelectrolyte becomes difficult because of low hopping capability of protons between active sides in PEMs and absolutely reduced water contents (vehicles). In other words, protons are less solvated by water and associated with sulfonic acids nearby and polymer chains are aggregated thus making the sites for proton hopping to be much farther each other. As a result, activation energy becomes higher and proton conductivity is greater as relative humidity drops.
from 95 to 30 % as shown in Table 2.6. Likewise, less amount of water does not efficiently convey solvated protons from one to the others thus proton conduction by vehicle mechanism is greatly diminished as well\textsuperscript{93}. Surface mechanism for proton conduction is not hindered as much as in these two mechanisms because due to low water contents, ratio of surface to bulk water is decreased, compensating proton conduction by the surface mechanism\textsuperscript{21}. Due to this reason, surface mechanism becomes a lot more important at low humidity condition. Flexible side chains of Nafion 117 may be benefited from this fact, letting it to have high proton conductivity at low humidity condition in spite of its low acid contents.

Through plane conductivity had shown higher than in plane conductivity like liquid phase condition as shown in Figure 2.9. However, advantage of having high conductivity in PE-g-s-PAES is leveled off as relative humidity decreases probably due to longer and insufficient time for the equilibrium of membranes with humidified environment.

**2.3.4. Surface properties of PE-g-s-PAES PEMs**

The unusual phenomenon of higher through-plane conductivity than in-plane conductivity prompted us to investigate the surfaces of PE-g-s-PAES membranes. It is logical to speculate that the low surface energy of the PE chain in the graft structure may be favorable to diffuse and stay on the surface of the PEM membrane. To verify this assumption, a contact angle measurement was performed using a water drop on PEM surfaces. Figure 2.10 shows the photographs of the water drop on the membrane surface (vs. time) for both PE-g-PAES (run B-4 in Table 2.3) and PE-g-s-PAES (sample s-B-4 in Table 2.5), as well as for Nafion 117. Upon the water drop coming in contact with the Nafion 117 PEM surface, the water drop immediately diffused into the matrix. After 3 minutes, the water drop almost disappeared from the PEM surface, with the contact angle at $38.03^\circ$. On the contrary, the water drop was quite stable on the PE-g-PAES surface with the contact
angle change less than 1 degree from 100.34° to 99.97°, which is significantly higher than the 83.84° of pure poly(arylene ethersulfone). The corresponding sulfonated PE-g-s-PAES PEM also retained the water drop very well, only allowing the water drop to slowly diffuse into the matrix. Its contact angle changed from 98.41° to 86.61° after 3 minutes. Evidently, the surfaces of both PE-g-PAES and PE-g-s-PAES are significantly more hydrophobic than the surface of Nafion 117. A very thin layer of PE must cover their surfaces. The detailed contact angle comparison is presented in Table 2.7.

Table 2.7. Summary of contact angle measurement of polymers and Nafion 117

<table>
<thead>
<tr>
<th></th>
<th>PE-co-p-MS</th>
<th>PE-co-p-MS-Br</th>
<th>PE-g-PAES(B-4)</th>
<th>PE-g-s-PAES(s-B-4)</th>
<th>Nafion117</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact Angle (°)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 min</td>
<td>103.95</td>
<td>100.89</td>
<td>100.34</td>
<td>98.41</td>
<td>80.27</td>
</tr>
<tr>
<td>Contact Angle (°)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 mins</td>
<td>--</td>
<td>--</td>
<td>99.97</td>
<td>86.61</td>
<td>38.03</td>
</tr>
</tbody>
</table>

Figure 2.10. Comparison of water drops on PE-g-PAES, PE-g-s-PAES, and Nafion 117 PEMs.
2.3.5. Methanol permeability and selectivity of PEMs

From the contact angle study, we knew that a thin PE hydrophobic layer is on the surface of the membrane and postulated that the thin layer will prevent or at least hinder the methanol crossover to a great extent. Based on this hypothesis, it was interesting to investigate methanol permeability of the membranes and using Waters 1515 Pump and refractive index (RI) detector, concentration variation before and after methanol permeation through the membrane was measured, as in literatures. As introduced in experimental section, the equation allowed us to calculate methanol permeability by monitoring the change of methanol concentration. Figure 2.11 and Table 2.8 show the results of methanol permeability test and comparison with well known commercial and home-made copolymers.

Table 2.8. Summary of various properties of studied membranes, well-known random copolymers and commercial membrane

<table>
<thead>
<tr>
<th>Entry</th>
<th>Degree of Sulfonation [%]</th>
<th>IEC [mmol/g]</th>
<th>Water Uptake [%]</th>
<th>Hydration number (λ)</th>
<th>In-plane Conductivity [mS/cm]</th>
<th>Through-plane Conductivity [mS/cm]</th>
<th>Methanol permeability (*10^-8 cm²/s)</th>
<th>Selectivity a</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>sA1-1 (30wt%)</td>
<td>81</td>
<td>1.1</td>
<td>21</td>
<td>11</td>
<td>30</td>
<td>34</td>
<td>9.02</td>
<td>3.33</td>
<td>This work</td>
</tr>
<tr>
<td>sA2-1 (42wt%)</td>
<td>77</td>
<td>1.44</td>
<td>30</td>
<td>12</td>
<td>42</td>
<td>57</td>
<td>9.87</td>
<td>4.26</td>
<td>This work</td>
</tr>
<tr>
<td>sA3-1 (47wt%)</td>
<td>77</td>
<td>1.62</td>
<td>35</td>
<td>12</td>
<td>63</td>
<td>85</td>
<td>12.7</td>
<td>4.96</td>
<td>This work</td>
</tr>
<tr>
<td>sA4-1 (56wt%)</td>
<td>75</td>
<td>1.93</td>
<td>46</td>
<td>13</td>
<td>85</td>
<td>131</td>
<td>24.9</td>
<td>3.41</td>
<td>This work</td>
</tr>
<tr>
<td>BPSH30</td>
<td>30</td>
<td>1.3</td>
<td>24</td>
<td>10</td>
<td>30</td>
<td>--</td>
<td>20</td>
<td>1.5</td>
<td>ref 25</td>
</tr>
<tr>
<td>BPSH40</td>
<td>40</td>
<td>1.7</td>
<td>39</td>
<td>13</td>
<td>75</td>
<td>--</td>
<td>38</td>
<td>1.97</td>
<td>ref 24</td>
</tr>
<tr>
<td>Nafion 117</td>
<td>--</td>
<td>0.91</td>
<td>24</td>
<td>15</td>
<td>77</td>
<td>81</td>
<td>69.7</td>
<td>1.10</td>
<td>This work</td>
</tr>
</tbody>
</table>

a The number in parenthesis means selectivity when through plane conductivity is considered.
All the membranes of PE-g-s-PAES showed low methanol permeability than Nafion 117 and BPSH series except for sA4-1. We believe that the thin PE layer must cover the surface of PE-g-s-PAES, rendering the interference of methanol crossover in the membrane. Other membranes including Nafion 117 and BPSH series do not have this unique geometry thus methanol may go through the membranes without any hindrance within the time\textsuperscript{24-25}. Due to low methanol permeability of PE-g-s-PAES membranes, selectivity which is defined as proton conductivity divided by methanol permeability\textsuperscript{51} is much higher for PE-g-s-PAES than Nafion 117 and BPSH series as shown in Figure 2.12. High conductivity of sA4-1 made it possible to have relatively high selectivity compared to BPSH series although its methanol permeability was higher than BPSH series. However, selectivity has the maximum point by balance of proton conductivity and methanol
permeability thus it is inferred that the choice of appropriate percentage of PAES is important to obtain a high selectivity membrane. Due to this trade-off between proton conductivity and methanol permeability, as many other literatures\textsuperscript{22, 74} it is also shown that the maximum value of selectivity appears at a certain point and levels off beyond the point.

![Figure 2.12: Selectivity of studied PE-g-s-PAES membranes and Nafion117](image)

Figure 2.12. Selectivity of studied PE-g-s-PAES membranes and Nafion117, (through-plane selectivity of BPSH series was not available)

From the selectivity results, approximately 50 wt % PAES in the copolymer is most desirable for direct methanol fuel cells. We speculate that high amount of PAES certainly increases proton transports in the membranes, not sacrificing positive properties such as mechanical properties at this compositional range. However, both lower and higher PAES than 50 wt % gives some disadvantages in the membrane performance. Because molecular weight of PAES is fixed as
20k g/mol in this study, channel size of PAES in the copolymer may be almost the same for the studied samples. As a result, below a certain weight ratio of PE and PAES methanol is not permeated as proton is. However, when the PAES is incorporated enough to copolymer (~50 wt %) and makes a continuous channel, methanol can transport through the channel thus, methanol permeability abruptly increases.

2.3.6 X-ray Diffraction study

The high selectivity of PE-g-s-PAES can be attributed to two reasons. First, as discussed, it is speculated that PE is on the surface of the polymer film because of its low surface energy. Second, morphology of the PE-g-s-PAES is expected to have co-continuous channels. The evidence can be found from the fact that crystallinity of polyethylene is not destroyed by graft coupling reaction. Crystallizable polyethylene is microphase-separated during the film formation followed by crystallization. Both DSC in Figure 2.5 and X-ray diffraction (XRD) in Figure 2.13 results support this argument. As shown in Figure 2.13, it is obvious that the crystal structure of polyethylene is maintained after the coupling reaction with PAES. Although the peak intensity of PE-g-PAES and PE-g-s-PAES was decreased more than a half of the peak intensity of polyethylene, if weight percent of PAES (ca. 50 wt %) is taken into account, it is believed that the coupling reaction and incorporation of PAES in the copolymer do not affect on the crystallinity of polyethylene.
Figure 2.13. WAXS patterns of (a) PE-co-p-MS copolymer (with 1.5 mol% of p-MS units), and (b) PE-co-p-MS-Br copolymer (with 0.8 mol% of Br units) (c) the corresponding PE-g-PAES graft copolymer containing 63 wt% of PAES. (d) the corresponding PE-g-s-PAES graft copolymer.

From the peak intensity, crystallinity was quantitatively calculated\(^{95-97}\) by the equation \(X_c = \frac{I_c}{I_a + I_c} \times 100\%\), where \(X_c\) is degree of crystallinity, \(I_c\) is the area of crystalline peaks (\{110\} at \(2\theta=21.4^\circ\) and \{200\} at \(2\theta=23.6^\circ\)) and \(I_a\) is the area of amorphous hump at \(2\theta=19.8^\circ\) and summarized in Table 2.9. The crystallinity of four copolymers from XRD patterns was shown to be almost identical from DSC, thus confirming that the clear phase separation of PE-g-PAES and PE-g-s-PAES occurred in the copolymer.
Table 2.9. Summary and comparison of degree of crystallinity of polymers studied in this research

<table>
<thead>
<tr>
<th></th>
<th>$T_m$(°C)</th>
<th>$\Delta H_m$(J/g)</th>
<th>$X_c$(%) by DSC</th>
<th>$X_c$(%) by XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE-co-p-MS</td>
<td>125</td>
<td>132.2</td>
<td>67</td>
<td>64</td>
</tr>
<tr>
<td>PE-co-p-MS-Br</td>
<td>124</td>
<td>116.6</td>
<td>60</td>
<td>59</td>
</tr>
<tr>
<td>PE-g-PAES</td>
<td>118</td>
<td>47.5</td>
<td>24.2</td>
<td>26</td>
</tr>
<tr>
<td>PE-g-s-PAES</td>
<td>116.5</td>
<td>45.2</td>
<td>23.1</td>
<td>21</td>
</tr>
</tbody>
</table>

2.3.7. Electrochemical stability of PEMs

Electrochemical stability of PE-g-s-PAES was studied by Fenton test. As shown in Table 2.10, PE-g-s-PAES showed very high oxidative stability in the Fenton test. It is known that under ferrous ions, chemical attack by peroxide radicals (•OH and •OOH) is accelerated, leading to degradation of polymers\textsuperscript{46, 98}. Typically hydrophilic part is more easily degraded because of the sufficient amount of water which allows the oxidative reaction to occur at a faster rate than the hydrophobic counterpart. In the case of PE-g-s-PAES, the results show that with more than 50 wt % of sulfonated PAES and about 2 mmol/g IEC, oxidative stability was excellent and even better than Nafion 117, proving that PE-g-s-PAES is clearly phase separated and high amount of hydrophilic part is well surrounded and protected by the denser hydrophobic PE matrix. PE thin layer on the surface may also be responsible for the high electrochemical stability of PE-g-s-PAESs. The film was not changed in appearance at all and kept its dimensional stability as well out of the test.
Table 2.10. Electrochemical (oxidative) test of PE-g-s-PAESs and Nafion 117 with Fenton reagent

<table>
<thead>
<tr>
<th>Sample</th>
<th>IEC (mmol/g)</th>
<th>Residual weight after Fenton test (80 °C) (%)</th>
<th>Residual weight after Fenton test (95 °C) (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE-co-p-MS</td>
<td>--</td>
<td>100</td>
<td>100</td>
<td>This work</td>
</tr>
<tr>
<td>PE-co-p-MS-Br</td>
<td>--</td>
<td>100</td>
<td>100</td>
<td>This work</td>
</tr>
<tr>
<td>PE-g-s-PAES (sA1-1, 30 wt %)</td>
<td>1.1</td>
<td>100</td>
<td>99.6</td>
<td>This work</td>
</tr>
<tr>
<td>PE-g-s-PAES (sA3-1, 47 wt %)</td>
<td>1.62</td>
<td>98.7</td>
<td>96.9</td>
<td>This work</td>
</tr>
<tr>
<td>PE-g-s-PAES (sA4-1, 56 wt %)</td>
<td>1.93</td>
<td>97.5</td>
<td>95.2</td>
<td>This work</td>
</tr>
<tr>
<td>Nafion 117</td>
<td>0.91</td>
<td>96.4</td>
<td>93.7</td>
<td>This work</td>
</tr>
<tr>
<td>X30Y8</td>
<td>1.62</td>
<td>40</td>
<td>--</td>
<td>ref50</td>
</tr>
<tr>
<td>M4</td>
<td>1.99</td>
<td>93</td>
<td>--</td>
<td>ref99</td>
</tr>
<tr>
<td>2a</td>
<td>1.80</td>
<td>90</td>
<td>--</td>
<td>ref100</td>
</tr>
</tbody>
</table>

2.4. Conclusion

We have developed a new class of polyethylene-based proton exchange membranes (PE-PEMs) for fuel cell applications. The systematic study of the graft-onto (coupling) reaction between brominated PE and poly(arylene ethersulfone) allows us to prepare a broad range of graft copolymers with well-controlled molecular structures, including the PE backbone and PAES side chain molecular weights, and graft density. With the combination of selective and efficient sulfonation reaction on PAES side chains, we have prepared PE-based PEMs with very high IEC values (>3 mmol/g in sulfonated PAES domains) in addition to well micro-phase separated morphology with a highly hydrophobic and crystalline PE matrix and the imbedded continuous proton conductive channels. The high molecular PE backbone in the graft copolymer provides the stable separator function, which allows the incorporation of a high concentration of sulfonic acids.
(high IEC value) in the conductive s-PAES domains for conduction function. In addition to the control of water swelling and maintaining good mechanical properties, the PE-based PEMs possess a thin PE hydrophobic surface layer that is reflected in the water contact angle and the anisotropic ion conductivity. By this character, PE-based PEMS showed low methanol permeability and high selectivity compared to Nafion 117. Overall, this new class of PE-g-s-PAES PEMs offer a desirable set of properties, including conductivity, water uptake, mechanical strength, and cost-effectiveness for fuel cell applications. This unique combination of bulk and surface morphology may also affect fuel selectivity and humidity effects to the conductivity; they will be addressed in a future work.
Chapter 3.

New Polyethylene based Anion Exchange Membranes (PE-AEMs) with High Ionic Conductivity

3.1. Introduction

Anion exchange membranes (AEMs) have relatively short history compared to PEMs but its unique properties and applications accelerated research on it in the past decades. Typically, AEMs are used for electrolysis, alkaline fuel cells and desalination. Among those various usages, the research in developing new AEMs in our group has stemmed from a nuclear hydrogen production program using a Cu-Cl thermochemical cycle.\textsuperscript{10,101} This process involves an electrolysis reaction \((2\text{CuCl} + 2\text{HCl} \rightarrow 2\text{CuCl}_2 + \text{H}_2)\) in an aqueous solution at 25-80 °C. For producing \(\text{H}_2\) at the cathode of the CuCl-HCl electrolyzer, an efficient Cl\(^-\) conductive AEM is essential for selective Cl\(^-\) ion diffusion from cathode to anode, without any diffusion of the Cu\(^+\) and Cu\(^{+2}\) species through the membrane from the anode to the cathode. High ion conductivity shall be achieved by possessing a stable and hydrophobic matrix and embedded hydrophilic channels across the polymer membranes. It is important to have high IEC to achieve high ionic conductivity. At the same time, polymer membrane should be stable in harsh condition and water environment for its long term durability in AEM electrolytic cells. In order to meet those requirements as an AEM, various types of polymers have been studied and researched in the past decades.
Polysulfones\textsuperscript{102-103} and cross-linked polystyrenes\textsuperscript{18, 104-105} are commonly utilized as a backbone polymer for making AEMs. Those polymers show various advantages however also some drawbacks. For example, polysulfones are difficult to make high molecular weight because monomer purify is significantly affected on polycondensation polymerization. With a trace amount of impurities including moisture, it is almost impossible to obtain high molecular weight polysulfones. Cross-linked polystyrenes show moderate water swelling and simple methods for incorporating ionic groups. However, due to cross-linking nature, cross-linked polystyrenes are not soluble in solvents thus making it extremely difficult to control film fabrications or further modifications\textsuperscript{68, 105}. Coates et al.\textsuperscript{15, 106} recently reported a new synthetic approach to prepare cross-linked AEMs via ring-opening metathesis copolymerization of cyclo-olefins and their quarten-ammonium derivatives. One of the comonomers contains two olefin units that engage in double enchainment to form a cross-linked structure. Some resulting cross-linked AEMs exhibit high anion conductivity and good mechanical properties.
Polyolefins, such as high density polyethylene (HDPE) and isotactic polypropylene (PP), are known to be very stable in severe electrochemical environments. As a matter of fact, the microporous PE and PP are the most common separators in rechargeable Li\(^+\) ion batteries.\(^{29-31}\) They exhibit a unique combination of chemical stability, hydrophobicity, high crystallinity, negligible swelling, and good mechanical properties under demanding environments, and are inexpensive. The combination also positions the polyolefins to be a very interesting polymer matrix for IEMs. The introduction of some continuous ion conductive channels through the polyolefin film may form IEMs with a stable hydrophobic membrane matrix and well-defined hydrophilic ionic channels that may offer a high IEC value, controllable water swelling, and high ionic conductivity. In the past there have been several papers\(^{107-108}\) discussing the polyolefin based ion-exchange membranes with some success. Due to synthesis difficulties—catalyst poison\(^{109}\) by a functional group in the direct Ziegler-Natta mediated-olefin polymerization process, the most common functionalization routes have been based on the post-polymerization process, involving an irradiation-mediated free radical graft polymerization of a monomer-bearing ionic group or styrene followed by a functionalization reaction (sulfonation, alkaline hydrolysis, etc.) of benzyl groups. Unfortunately, the free radical process usually results in very complicated molecular structures\(^{110}\). The polymer structure and morphology have rarely been characterized. Recently, Coates et al.\(^{29}\) extended the ring-opening metathesis copolymerization with the subsequent hydrogenation reaction to prepare solution-processible PE-based alkaline AEMs (without cross-linking). A desirable AEM with 1.5 mmol HO\(^-\)/g IEC value, insoluble in both pure water and aqueous methanol at 50 °C, exhibits mechanical strength of 6 MPa at break and high hydroxide and carbonate conductivities (65 and 30 mS/cm at 50 °C, respectively).

In this chapter, I will discuss a new AEM preparation process, which involves a metallocene-mediated ethylene polymerization process to prepare soluble functional PE copolymers
that can be solution-casted and further derived into PE-based Cl⁻ ion conductive AEMs. The resulting PE-AEMs contain a wide range of ammonium chloride (\(-NR_3^+\text{Cl}^\) groups in the flexible methylene side chains and various degrees of cross-linking density (after thermal treatment). The effective chemical method to prepare functional polyethylene copolymers with well-controlled molecular structures allows us to carry out a systematic study to understand the structure-property relationship, including Cl⁻ ion conductivity, water uptake, and ion selectivity under various conditions. The main objective in this research is to identify the most suitable PE-AEM that can perform significantly higher Cl⁻ ion conductivity and ion selectivity than commercial ones, while maintaining good chemical, thermal, and mechanical stability.

3.2. Experimental section

3.2.1. Materials and Instrumentation

All O₂ and moisture sensitive manipulations were carried out inside an argon filled Vacuum Atmosphere dry box. Methylaluminoxane (MAO) (Ethyl) was purified by vacuum-pumping to remove trimethylaluminium (TMA) at 70-80 °C for 6 hours. \(\text{rac-CH}_2\text{CH}_2\text{(3-t-Butyl-Ind)}_2\text{ZrCl}_2\) catalyst\(^{111}\) and \(4\)-(3-butenyl)-styrene\(^{112}\) were prepared using the published procedures. Polymerization-grade ethylene (Matheson) was used as received. Toluene (Wiley Organics) was distilled over CaH₂ under argon. Allyl bromide (99 %), lithium bis(trimethylsilyl)amide (97 %), iodomethane (99 %) and 2-iodopropane (Sigma-Aldrich) were used as received.

All high-temperature \(^1\text{H}\) NMR spectra were recorded on a Bruker AM-300 instrument in 1,1,2,2-tetrachloroethane-\(d_2\) at 110 °C. The melting temperatures of the polymers were measured by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 instrument controller with a heating rate of 20 °C/min. All mechanical properties (tensile strength, tensile modulus, elongation at break, etc.) were measured according to the ASTM D-1708 method. The dog-bone specimens (38
mm x 15 mm overall size and 5 mm x 22 mm in the gauge area) were die cut and performed using an Instron 5866 universal tester, with a load cell of 100 N and a constant cross head speed of 1 mm/min. At least 5 samples were tested in order to minimize possible errors.

3.2.2. Synthesis of 6-bis(trimethylsilyl)amino-1-hexene

This monomer was prepared in two reaction steps. In a 500 mL flask equipped with a magnetic stirring bar, 50 g (0.299 mol) of lithium bis(trimethylsilyl)amide dissolved in 200 mL of THF was slowly added into a mixture of 25 mL (0.329 mol) of chloromethyl methyl ether and 50 mL of THF at 0 °C under a nitrogen atmosphere. Once the addition was complete, the solution was allowed to warm to room temperature for 2 h before evaporating the excess chloromethyl methyl ether and THF solvent. N,N-Bis(trimethylsilyl)methoxymethylamine (80 % yield) was isolated by distillation. In the second step, 6-bis(trimethylsilyl)amino-1-hexene was prepared by treating N,N-bis(tri-methylsilyls)methoxymethylamine with 4-pentenenemagnesium bromide. In a 500 mL flask equipped with a magnetic stirring bar and a condenser, 5.2 g magnesium powder (0.22 mol) was suspended in 200 mL dry ether, and 25 mL (0.21 mol) of 5-bromo-1-pentene diluted with 50 mL dry ether was then introduced dropwise through the condenser. The solution was refluxed overnight before adding 41 g (0.20 mol) of N,N-bis(trimethylsilyls)methoxymethylamine over a period of 2 h under room temperature. The reaction was allowed to proceed at room temperature for another 2 h before adding 100 mL of aqueous NaOH solution (30 %). The organic layer was then distilled over CaH2 to obtain 6-bis(trimethylsilyl)amino-1-hexene in 73 % yield.1H NMR (300 MHz, 25 °C, CDCl3): 5.81 (m, 1 H, -CH=CH2), 5.07 (m, 2 H, -CH=CH2), 2.77 (t, 2 H, -CH2-N-), 2.14 (m, 2 H, -CH2-CH≡CH2-), 1.38 (m, 4 H, -CH2-CH2-), 0.21 (s, 18 H, -NSi2(CH3)6).
3.2.3. Co- and ter-polymerization of ethylene, 6-bis(trimethylsilyl)amine-1-hexene and divinylbenzene

A typical copolymerization reaction was carried out in a 250 ml glass flask with a magnetic stirrer, which was charged with 50 ml toluene, 6-bis(trimethylsilyl)amine-1-hexene, dry MAO (Al/Zr = 1000), and ethylene (14 psi). Zirconium catalyst (1 μmol) in 3 ml of toluene solution was then injected into the reactor to initiate the copolymeriation. After 60 min of polymerization at constant temperature and ethylene pressure, the reaction solution was quenched by acetone and filtered, washed extensively with acetone to remove residual monomer and then dried under vacuum at room temperature for 12 h.

Terpolymerization of ethylene/6-bis(trimethylsilyl)amine-1-hexene/divinylbenzene was carried out under a similar condition. In a 250 ml glass flask with a magnetic stirrer, ethylene, 2-hex-5-enyl-1,1,3,3,3-hexamethyl-disilazane, divinylbenzene, and dry MAO (Al/Zr = 1000) were charged before injecting zirconium catalyst (1 μmol) in 3 ml toluene solution to initiate the terpolymeriation reaction. After 30 min of polymerization at 50 °C and constant ethylene pressure (0.14 Mpa), the reaction was quenched by acetone and filtered, washed extensively with acetone to remove residual monomer and then dried under vacuum at room temperature for 12 h.

3.2.4. Functional Group Interconversion

The incorporated bis(trimethylsilyl)amine (-N(SiMe₃)₂) groups in the co- and ter-polymers were further converted to the desired -NR₂ and -NR₃⁺Cl⁻ groups (R: H, CH₃, and C₃H₇). One example is to interconvert ethylene/C₆N(SiMe₃)₂ copolymer into various PE-NR₂ copolymers. About 1g of ethylene/C₆N(SiMe₃)₂ copolymer was suspended in 50 mL of THF at 50 °C before adding dropwise 2 mol/L methanolic hydrogen chloride solution. The mixture was stirred for 4 h at 50 °C, and then poured into 1 mol/L methanolic NaOH solution. The resulting polymer was
collected by filtration and washed with 1 mol/L aqueous ammonia and water under a nitrogen atmosphere. After drying at 50 °C under vacuum for overnight, the resulting PE-NH₂ copolymer was obtained with quantitative yield. The pendant NH₂ groups in PE were further alkylated to PE-N(CH₃)₂ and PE-N(iso-C₃H₇)₂ copolymers using various alkyl iodides. In a typical example, 1 g of PE-NH₂ copolymer was suspended in 50 mL of dry isopropyl alcohol in the presence of 2.76 g of potassium carbonate (0.02 mol) under N₂. The solution was refluxed for 1 h and then 1.51 g of 2-iodine propane (0.01 mol) was added and the whole solution was stirred under reflux for 5 days. The resulting polymer was collected by filtration and washed with THF, 1 mol/L aqueous ammonia and water subsequently under nitrogen atmosphere. After vacuum-drying at room temperature for overnight, the resulting PE-N(iso-C₃H₇)₂ copolymer was obtained with quantitative yield. Similar experimental procedures were carried out in ethylene/C₆N(SiMe₃)₂/diene terpolymer. However, the terpolymer was usually solution-casted into film, then thermally cross-linked to form the corresponding cross-linked terpolymer film, before carrying out amino group interconversion under solid state conditions. As will be discussed, the amino group reactions are also very efficient in film form.

3.2.5. Membrane Preparation and Evaluation

Membranes were prepared by casting a viscous xylene solution of ethylene/C₆N(SiMe₃)₂ copolymer or ethylene/C₆N(SiMe₃)₂/diene terpolymer onto a Teflon substrate using an Elcometer 4340 Automatic Film Applicator at an elevated temperature, assuring no precipitation of the polymer due to crystallization of the PE segments. To avoid air bubbles, films were casted several times by gradually increasing the film thicknesses. The resulting solution-casted films (size 4” x 6”') were heated at 110 °C for 2 h to remove the remaining solvent. Some films were further compressed at 150 °C under a pressure of 165 Mpa to remove any defects and obtain a uniform thickness. In the
ethylene/C_2N(SiMe_3)_2/diene terpolymer case, the membranes were further treated at 220 °C for 2 h under vacuum to complete the cross-linking reaction. The -N(SiMe_3)_2 groups in the resulting membranes were then converted to the desired -NR_2 groups (R: H, CH_3, and C_3H_7), following the previously discussed procedures. All films were soaked in 0.5 mol/L HCl solution for 24 h to transfer all amine groups to ammonium salt (-NR_3^+Cl^-).

All membranes were characterized with the degree of water swelling (DS), water content (λ), ion exchange capacity (IEC), and ionic conductivity, all measured at ambient temperature. The DS value (g H_2O/100 g dry film) was determined by \((W_w - W_d)/W_d\), where \(W_w\) and \(W_d\) are the weight of a wet (equilibrated with water) and dry membrane, respectively. The water content (λ) is calculated based on a molar ratio of water to ammonium chloride. The IEC value is based on Cl^- concentration that was measured by chloride precipitation using an AgNO_3 solution and AgCl precipitation, with K_2CrO_4 as an end-point indicator. The membrane conductivity was measured in a clip-type conductivity cell (Figure A2 in the Appendix). Two titanium disk electrodes are applied to both sides of the membrane. Both compartments of the cell were filled with various solutions of a desired concentration. The conductivity measurements were performed by a two-electrode electrochemical impedance spectroscopy using the Gamry Electrochemical Measurements system. The experimental details are discussed in the Supplemental Information.

3.3. Result and Discussion

A new material that is based on polyethylene based random copolymers with very high chloride ion conductivity was studied. The copolymer contains a moderately high polyethylene backbone and flexible side chain containing a hydrophilic amine group at the end. With two extremely different properties between backbone and side chain in a polymer chain, the hydrophobic PE backbone serves as a robust matrix to support the integrity of the made membranes.
and amorphous hydrophilic, flexible side chains shall make continuous channels through the PE film. Cross-linker such as divinyl benzene, p-(3-butenyl) styrene must be used to strengthen the film and provide a AEM with a high IEC value without water over-swelling, therefore achieving high chloride conductivity. For a systematic study, the investigation involves several steps, including (i) the development of a chemical route to prepare physically robust and high IEC random co- or terpolymers, (ii) finding the most suitable condition or process to prepare AEM membranes, and (iii) a systematic comparison of the obtained AEMs at various aqueous solutions.

### 3.3.1. Synthesis and Characterization of PE-NR$_3^+$Cl$^-$ and x-PE-NR$_3^+$Cl$^-$ Membranes

Scheme 1 illustrates two parallel synthesis routes to prepare PE-NR$_3^+$Cl$^-$ membranes (V) and their cross-linked counterpart x-PE-NR$_3^+$Cl$^-$ membranes (V’). The chemistry involves a metallocene-mediated polymerization of ethylene, bis(trimethylsilane)-protected-amino-olefins [C$_x$N(SiMe$_3$)$_2$] (I), with or without diene cross-linkers (II), to obtain the intermediate ethylene/C$_x$N(SiMe$_3$)$_2$ copolymer (III) and ethylene/C$_x$N(SiMe$_3$)$_2$/diene terpolymer (III’), respectively. The resulting PE copolymer (III) and terpolymer (III’) intermediates contain various concentrations of pendant silane-protected amino groups, and few percentages of styrene moieties (cross-linkers)$^{45,46}$ in the terpolymers. They are completely soluble in common organic solvents, and the silane-protected amino groups can be further modified into the desired -NR$_3^+$Cl$^-$ groups in solution or in solid state conditions with simple chemicals. However, due to the low solubility of PE polymers containing a high concentration of -NR$_3^+$Cl$^-$ groups (R: H, CH$_3$, iso-C$_3$H$_7$) both PE copolymer (III) and terpolymer (III’) intermediates were usually solution-casted into films with a thickness of 50-70 µm, followed by thermal cross-linking reaction in the PE terpolymer (III’) cases. A subsequent functional group transformation reaction occurs in a solid state to obtain the desired PE-NR$_3^+$Cl$^-$ (V) and x-PE-NR$_3^+$Cl$^-$ membranes (V’).
Scheme 1. Two parallel synthetic routes to prepare PE-NR₃⁺Cl⁻ and x-PE-NR₃⁺Cl⁻ membranes.

In the first step of metallocene-mediated polymerization reactions to prepare ethylene/CₓN(SiMe₃)₂ copolymers (III) and ethylene/CₓN(SiMe₃)₂/diene terpolymers (III'), the suitable metallocene catalysts shall be free from interacting with -N(SiMe₃)₂ group and exhibit good reactivity toward α-olefin moieties in all three monomers, as well as performing selective mono-
enchainment of diene monomers (II). In addition, it is essential to identify the most effective C₅N(SiMe₃)₂ and diene comonomers for obtaining PE copolymers (III) and terpolymer (III’) with high molecular weights and controllable amounts of amino groups and pendant styrenic moieties (cross-linkers). Table 1 summarizes four comparative reaction sets using rac-Et(Ind)₂ZrCl₂/MAO and rac-CH₂(3-t-Butyl-Ind)₂ZrCl₂/MAO catalysts that have been shown to have a good combination of free of catalyst poison, high reactivity toward α-olefin moieties, and selective mono-enchainment of 1,4-divinylbenzene (DVB) or 3-butenylstyrene (BSt). Sets A and B compare ethylene/α,ω-amino-olefin copolymerization using three functional comonomers, including 3-bis(trimethylsilyl)amino-propylene \([C₃N(SiMe₃)₂]\), 6-bis(trimethylsilyl)amino-hexene \([C₆N(SiMe₃)₂]\), and 11-bis(trimethylsilyl)amino-undecene \([C₁₁N(SiMe₃)₂]\), and two catalyst systems, respectively. The \([C₃N(SiMe₃)₂]\) comonomer, having only 1 methylene spacer, did not engage in the copolymerization reaction; the short spacer may not be sufficient to prevent the amino group from interfering with the metallocene-mediated α-olefin insertion. On the other hand, the \([C₁₁N(SiMe₃)₂]\) comonomer is too big to effectively compete with the small ethylene during the copolymerization. The maximum \([C₁₁N(SiMe₃)₂]\) content in the copolymer was 8.6 mol % (run B-6). It is interesting to note that there was a paper¹¹³ reporting a similar ethylene/C₁₁N(SiMe₃)₂ copolymerization by rac-Me₂Si(Benz[e]Ind)₂ZrCl₂/MAO catalyst, which produced only insoluble copolymer with a maximum 3.7 mol % \([C₁₁N(SiMe₃)₂]\) content.
Table 3.1. Summary of metallocene-mediated co- and ter-polymerization reactions between ethylene, \( \alpha, \omega \)-amino-olefins, and dienes.

<table>
<thead>
<tr>
<th>Run</th>
<th>Catalyst</th>
<th>Polymerization condition</th>
<th>Yield (g)</th>
<th>( M_v^d ) (Kg/mol)</th>
<th>Polymer composition</th>
<th>Ethylene (mol%)</th>
<th>( [C_x(N(SiMe_3)_2]^y) (mol%)</th>
<th>diene (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>A</td>
<td>14 (n=3)</td>
<td>0</td>
<td>3.0</td>
<td>153</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>A-2</td>
<td>A</td>
<td>14 (n=6)</td>
<td>0</td>
<td>1.5</td>
<td>89</td>
<td>85.8</td>
<td>14.2</td>
<td>0</td>
</tr>
<tr>
<td>A-3</td>
<td>A</td>
<td>14 (n=6)</td>
<td>0</td>
<td>1.0</td>
<td>73</td>
<td>77.9</td>
<td>22.1</td>
<td>0</td>
</tr>
<tr>
<td>A-4</td>
<td>A</td>
<td>14 (n=6)</td>
<td>0</td>
<td>0.6</td>
<td>58</td>
<td>72.8</td>
<td>27.2</td>
<td>0</td>
</tr>
<tr>
<td>A-5</td>
<td>A</td>
<td>14 (n=6)</td>
<td>0</td>
<td>0.4</td>
<td>46</td>
<td>69.0</td>
<td>31.0</td>
<td>0</td>
</tr>
<tr>
<td>B-1</td>
<td>B</td>
<td>14 (n=3)</td>
<td>0</td>
<td>3.0</td>
<td>271</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B-2</td>
<td>B</td>
<td>14 (n=6)</td>
<td>0</td>
<td>1.8</td>
<td>148</td>
<td>85.9</td>
<td>14.1</td>
<td>0</td>
</tr>
<tr>
<td>B-3</td>
<td>B</td>
<td>14 (n=6)</td>
<td>0</td>
<td>1.2</td>
<td>119</td>
<td>77.6</td>
<td>22.4</td>
<td>0</td>
</tr>
<tr>
<td>B-4</td>
<td>B</td>
<td>14 (n=6)</td>
<td>0</td>
<td>0.7</td>
<td>97</td>
<td>74.6</td>
<td>25.4</td>
<td>0</td>
</tr>
<tr>
<td>B-5</td>
<td>B</td>
<td>14 (n=6)</td>
<td>0</td>
<td>0.4</td>
<td>74</td>
<td>69.5</td>
<td>30.5</td>
<td>0</td>
</tr>
<tr>
<td>B-6</td>
<td>B</td>
<td>14 (n=6)</td>
<td>0</td>
<td>0.2</td>
<td>46</td>
<td>91.4</td>
<td>8.6</td>
<td>0</td>
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<tr>
<td>C-1</td>
<td>A</td>
<td>14 (n=6)</td>
<td>0.4 (DVB)</td>
<td>0.6</td>
<td>78</td>
<td>87.3</td>
<td>12.2</td>
<td>0.5 (DVB)</td>
</tr>
<tr>
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<td>A</td>
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<td>0.4 (DVB)</td>
<td>0.5</td>
<td>49</td>
<td>73.0</td>
<td>26.6</td>
<td>0.4 (DVB)</td>
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<tr>
<td>C-3</td>
<td>A</td>
<td>14 (n=6)</td>
<td>0.4 (DVB)</td>
<td>0.3</td>
<td>43</td>
<td>71.1</td>
<td>28.5</td>
<td>0.4 (DVB)</td>
</tr>
<tr>
<td>C-4</td>
<td>A</td>
<td>14 (n=6)</td>
<td>0.4 (BSt)</td>
<td>0.8</td>
<td>cross-linked polymer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-5</td>
<td>A</td>
<td>14 (n=6)</td>
<td>0.1 (BSt)</td>
<td>0.6</td>
<td>50</td>
<td>73.7</td>
<td>26.1</td>
<td>0.2 (BSt)</td>
</tr>
<tr>
<td>C-6</td>
<td>A</td>
<td>14 (n=6)</td>
<td>0.1 (BSt)</td>
<td>0.4</td>
<td>43</td>
<td>70.8</td>
<td>29.0</td>
<td>0.2 (BSt)</td>
</tr>
<tr>
<td>D-1</td>
<td>B</td>
<td>14 (n=6)</td>
<td>0.4 (DVB)</td>
<td>1.6</td>
<td>133</td>
<td>85.5</td>
<td>13.9</td>
<td>0.6 (DVB)</td>
</tr>
<tr>
<td>D-2</td>
<td>B</td>
<td>14 (n=6)</td>
<td>0.4 (DVB)</td>
<td>0.6</td>
<td>101</td>
<td>69.7</td>
<td>29.8</td>
<td>0.5 (DVB)</td>
</tr>
<tr>
<td>D-3</td>
<td>B</td>
<td>14 (n=6)</td>
<td>0.4 (DVB)</td>
<td>0.5</td>
<td>74</td>
<td>66.2</td>
<td>33.4</td>
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<td>D-4</td>
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<td>0.4 (BSt)</td>
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<td>cross-linked polymer</td>
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<tr>
<td>D-5</td>
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<td>14 (n=6)</td>
<td>0.1 (BSt)</td>
<td>0.5</td>
<td>78</td>
<td>68.3</td>
<td>31.5</td>
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<tr>
<td>D-6</td>
<td>B</td>
<td>14 (n=6)</td>
<td>0.1 (BSt)</td>
<td>0.6</td>
<td>97</td>
<td>71.7</td>
<td>28.1</td>
<td>0.2 (BSt)</td>
</tr>
</tbody>
</table>

\( ^a \) Catalyst A: rac-Et(Ind)\(_2\)ZrCl\(_2\)/MAO and catalyst B: rac-CH\(_3\)(3-t-Butyl-Ind)\(_2\)ZrCl\(_2\)/MAO.

\( ^b \) 3-bis(trimethylsilyl)amino-propylene (n = 3); 6-bis(trimethylsilyl)amino-hexene (n = 6); 11-bis(trimethylsilyl)amino-undecene (n = 11).

\( ^c \) 1,4-divinylbenzene (DVB); 4-(3-butenyl)-styrene (BSt).

\( ^d \) Estimated by intrinsic viscosity of polymer/decalin dilute solution at 135°C with the standard of polyether (K = 6.2x10\(^{-2}\) ml/g, and \( \alpha = 0.7 \)).
Evidently, the most suitable amino-comonomer is \([\text{C}_6\text{N(SiMe}_3\text{)}_2]\) having 4 methylene spacers. Although the catalyst activity systematically decreases with the increase of the \([\text{C}_6\text{N(SiMe}_3\text{)}_2]\) comonomer feed, the comonomer content in the copolymer increases correspondingly. We have prepared soluble ethylene/\([\text{C}_6\text{N(SiMe}_3\text{)}_2]\) copolymers (III) with up to 30 mol% \([\text{C}_6\text{N(SiMe}_3\text{)}_2]\) contents in both catalyst systems. In detail, by comparing every comparative run (A-2 vs. B-2, A-3 vs. B-3, A-4 vs. B-4, A-5 vs. B-5) between two catalyst systems, the \(\text{rac-CH}_2(3\text{-t-Butyl-Ind})_2\text{ZrCl}_2/\text{MAO}\) catalyst shows better performance with higher yields, higher \([\text{C}_6\text{N(SiMe}_3\text{)}_2]\) incorporation, and higher copolymer molecular weight.

Sets C and D show the results of ethylene/\([\text{C}_6\text{N(SiMe}_3\text{)}_2]/\text{diene}\) terpolymerization reactions using the same two catalyst systems. In addition to select the \([\text{C}_6\text{N(SiMe}_3\text{)}_2]\) functional comonomer, the focus was shifted to the mono-enchainment of diene comonomers (i.e. DVB and BSt), which shall result in soluble ethylene/\([\text{C}_6\text{N(SiMe}_3\text{)}_2]/\text{diene}\) terpolymers (III') containing pendant styrenic moieties (cross-linkers). It is interesting to note that both \(\text{rac-Et(Ind)}_2\text{ZrCl}_2\) and \(\text{rac-CH}_2(3\text{-t-Butyl-Ind})_2\text{ZrCl}_2\) catalysts prepare ethylene/\([\text{C}_6\text{N(SiMe}_3\text{)}_2]/\text{DVB}\) terpolymers with good solubility, but only forming soluble ethylene/\([\text{C}_6\text{N(SiMe}_3\text{)}_2]/\text{BSt}\) terpolymers with a relatively low BSt concentration (runs C-5, C-6, D-5, and D-6). With the increased BSt concentrations, both catalysts produce insoluble ethylene/\([\text{C}_6\text{N(SiMe}_3\text{)}_2]/\text{BSt}\) terpolymers (runs C-4 and D-4). The double-enchainment activity may be slightly higher in the BSt case than in the DVB case, which may be associated with the kinetic availability of the pendant styrene moieties after mono-enchainment. The flexible pendant styrene moieties in the BSt case may be more inviting to engage in a second enchainment reaction, especially in these soluble (completely amorphous) PE terpolymers with a high concentration of comonomer units. Note that our previous results\textsuperscript{114} showed no detectable cross-linking reaction in propylene/BSt copolymerization reactions, which form PP copolymers with high crystallinity that may prevent the second enchainment. However, the BSt asymmetric diene,
containing both α-olefin and styrenic olefin, shows a higher incorporation than the DVB symmetric diene, due to higher catalyst reactivity toward the α-olefin moiety. Furthermore, the flexible pendant styrene moieties in the polymer chain are essential to enhance an inter-chain cyclo-addition reaction\textsuperscript{115} that offers high cross-linking efficiency. With all experimental results and considerations, all cross-linked x-PE-NR₅⁵Cl membranes (discussed later) are based on ethylene/C₆N(SiMe₃)₂/BSt terpolymers with low BST contents, prepared by the \textit{rac}-CH₂(3-t-Butyl-Ind)₂ZrCl₂/MAO catalyst system.

Figure 3.2 compares three $^1$H NMR spectra between C₆N(SiMe₃)₂ functional comonomer, an ethylene/C₆N(SiMe₃)₂ copolymer (run A-2), and an ethylene/C₆N(SiMe₃)₂/DVB terpolymer (run C-1). Figure 3.2(a) exhibits the expected chemical shifts and intensities for a pure C₆N(SiMe₃)₂ comonomer (with the inserted chemical structure and chemical shift assignments). Figure 3.2(b) shows a major peak at 1.35 ppm, corresponding to ethylene units, and two chemical shifts at $\delta = 2.77$ ppm (t, 2 H, -CH₂-N) and $\delta = 0.21$ (s, 18 H, -NSi₂(CH₃)₆) indicating 14.2 mol % C₆N(SiMe₃)₂ content in the ethylene/C₆N(SiMe₃)₂ copolymer (run A-2). Figure 3.2(c) displaces the expected chemical shifts at $\delta = 2.77$, 1.35, and 0.21 ppm in the ethylene/C₆N(SiMe₃)₂/DVB (87.3/12.2/0.5 mole ratio) terpolymer (run C-1). In addition, the expanded spectrum (inserted) also show several minor chemical shifts at 5.2 and 5.7 ppm (doublet, CH=CH₂) and 6.7 ppm (doublet of doublet, CH=CH₂); aromatic proton peaks occur between 7.1 and 7.4 ppm (C₆H₄), corresponding to the incorporated DVB units (0.5 mol %). The peak intensity ratios indicate that the mole ratio of the vinyl group to the phenyl group is near unity, implying mono-enchainment of DVB units during the metallocene-mediated polymerization.
Figure 3.2. $^1$H NMR spectra of (a) C₆N(SiMe₃)₂ comonomer, (b) ethylene/C₆N(SiMe₃)₂ copolymer containing 14.2 mol % C₆N(SiMe₃)₂ units (run A-2), (c) ethylene/C₆N(SiMe₃)₂/DVB terpolymer having 12.2 mol % C₆N(SiMe₃)₂ and 0.5 mol % DVB contents (run C-1). (Inset: the chemical shift assignments for C₆N(SiMe₃)₂ comonomer).
The silane-protected amino groups in the ethylene/C₆N(SiMe₃)₂ copolymer were further interconverted to various amino groups. For the solution ¹H NMR study, polymer modifications
were carried out in solution, and all resulting polymers maintained good solubility in common organic solvents. Figure 3.3 shows $^1$H NMR spectra of two PE copolymers containing 3.2 mol % of -NH$_2$ groups and 14.2 mol % of -N(iso-C$_3$H$_7$)$_2$ groups, respectively. Due to strong polar group interactions, the PE-NH$_2$ copolymer with the higher -NH$_2$ content (>4 mol %) becomes insoluble in common organic solvents. In Figure 3.3(a), the combination of a complete disappearance of a sharp peak at $\delta = 0.21$ ppm (-NSi$_2$(CH$_3$)$_6$) and the co-existence of the chemical shift at $\delta = 2.77$ ppm (t, 2 H, -CH$_2$-NH$_2$)—similar peak in the starting ethylene/C$_8$N(SiMe$_3$)$_2$ copolymer—indicates a successful deprotection reaction of bis(trimethylsilyl)amino groups by HCl to form NH$_2$ groups.

Figure 3.3(b) shows a $^1$H NMR spectrum of the PE-N(iso-C$_3$H$_7$)$_2$ copolymer prepared from the ethylene/C$_8$N(SiMe$_3$)$_2$ copolymer containing 14.2 mol % of C$_8$N(SiMe$_3$)$_2$ comonomer units (run A-2). The functional group modification involves two steps: the same silane deprotection reaction to form the NH$_2$ group and the subsequent alkylation of the -NH$_2$ group to the -N(iso-C$_3$H$_7$)$_2$ group. Although both the starting ethylene/C$_8$N(SiMe$_3$)$_2$ and final PE-N(iso-C$_3$H$_7$)$_2$ copolymers are soluble in common organic solvents, the PE-NH$_2$ intermediate having 14.2 mol% NH$_2$ was insoluble. In other words, most of the reaction processes were under a heterogeneous reaction condition. In Figure 3.3(b), the absence of a chemical shift at $\delta = 0.21$ ppm [-NSi$_2$(CH$_3$)$_6$] implies effective silane deprotection in forming -NH$_2$ groups, despite the insoluble PE-NH$_2$ copolymer. There are several new chemical shifts, including $\delta = 1.41$ ppm (-CH$_2$-N(CH-(CH$_3$)$_2$)$_2$), 2.9 ppm (-CH$_2$-NH[CH-(CH$_3$)$_2$]), 3.3 ppm (-CH$_2$-N[CH-(CH$_3$)$_2$)$_2$], and 3.5 ppm (-CH$_2$-N[CH-(CH$_3$)$_2$]). Evidently, the second step of the alkylation reaction of -NH$_2$ groups was not completed. There are approximately 10 % mono-alkylation moieties (-NH[CH-(CH$_3$)$_2$]) co-existing in the PE-N(iso-C$_3$H$_7$)$_2$ copolymer. Overall, the amino functional group interconversion reactions under heterogeneous condition are quite effective, which is significant in the preparation of cross-linked x-PE-NR$_3^+Cl$ membranes.
3.3.2. Evaluation of PE-NR₃⁺Cl⁻ and x-PE-NR₃⁺Cl⁻ Membranes

Based on the polymerization results (Table 1), the \( \text{rac-CH}_2(3\text{-t-Butyl-Ind})_2\text{ZrCl}_2/\text{MAO} \) catalyst system was applied to prepare membrane precursor polymers, ethylene/C₆N(SiMe₃)₂ copolymers (III) and ethylene/C₆N(SiMe₃)₂/BSt terpolymers (III’), with a combination of high molecular weight, high C₆N(SiMe₃)₂ comonomer content, and only 0.2 mol % BSt units in the terpolymer, in order to assure good solubility. Both precursor polymers were solution-casted into films (thickness: 50-70 μm). During the film drying step under elevated temperatures, the ethylene/C₆N(SiMe₃)₂/BSt terpolymers also engaged in a cross-linking reaction by cyclo-addition between two pendant styrene units, resulting in cross-linked x-PE-N(SiMe₃)₂ films. The combination of a high molecular weight terpolymer and effective cross-linking reaction is crucial to obtain a complete 3-D network structure. The pendant -N(SiMe₃)₂ groups were then deprotected to form -NH₂ groups by treating them in an aqueous HCl solution. Under acidic conditions, they converted into PE-NH₃⁺Cl⁻ and x-PE-NH₃⁺Cl⁻ membranes with high purities. A further solid-state treatment of -NH₂ groups with alkyl iodine reagents was also carried out to obtain PE-NR₃⁺Cl⁻ (V) and x-PE-NR₃⁺Cl⁻ (V’) membranes (R: CH₃ and iso-C₃H₇), with different alkylation efficiencies (discussed later). Table 3.2 summarizes physical properties of several PE-NR₃⁺Cl⁻ and x-PE-NR₃⁺Cl⁻ membranes containing high concentrations of pendant -(CH₂)₄-NR₃⁺Cl⁻ groups. For comparison, several commercially-available Cl⁻ ion conductive membranes were also evaluated side-by-side. They include four Neosepta type AEMs produced by Tokuyama Soda and a Selemion high temperature AEM produced by Asahi Glass. They are based on cross-linked styrene/divinylbenzene copolymers with various concentrations of quaternary ammonium chloride groups and cross-linking densities, with or without supporting materials. However, their detailed structural compositions are not available.
Table 3.2. Summary of physical properties of PE-NR₂⁺Cl⁻, x-PE-NR₂⁺Cl⁻, and several commercial anion-conductive membranes

<table>
<thead>
<tr>
<th>Samples</th>
<th>Polymer Composition</th>
<th>IEC\textsuperscript{a} (mmol/g)</th>
<th>IEC\textsuperscript{b} (mmol/g)</th>
<th>DS\textsuperscript{c}%</th>
<th>λ\textsuperscript{d} value</th>
<th>Ionic conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ethylene/C₆NR₂/BSt (mole ratio)</td>
<td>H group</td>
<td>2N HCl</td>
<td>2N HCl-0.2N CuCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-2</td>
<td>85.9/14.1/0</td>
<td>H</td>
<td>3.3</td>
<td>3.1</td>
<td>29</td>
<td>5.2</td>
</tr>
<tr>
<td>B-3</td>
<td>77.6/22.4/0</td>
<td>H</td>
<td>4.3</td>
<td>3.6</td>
<td>82</td>
<td>12.6</td>
</tr>
<tr>
<td>B-4-a</td>
<td>74.6/25.4/0</td>
<td>H</td>
<td>4.6</td>
<td>4.0</td>
<td>126</td>
<td>17.5</td>
</tr>
<tr>
<td>B-4-b</td>
<td>74.6/25.4/0</td>
<td>CH₃</td>
<td>4.1</td>
<td>3.9</td>
<td>135</td>
<td>19.2</td>
</tr>
<tr>
<td>B-4-c</td>
<td>74.6/25.4/0</td>
<td>iso-C₃H₇</td>
<td>3.3</td>
<td>3.1</td>
<td>97</td>
<td>17.4</td>
</tr>
<tr>
<td>B-5</td>
<td>69.5/30.5/0</td>
<td>H</td>
<td>5.1</td>
<td>4.8</td>
<td>240</td>
<td>27.8</td>
</tr>
<tr>
<td>D-6-a</td>
<td>71.7/28.1/0.2</td>
<td>H</td>
<td>4.9</td>
<td>3.1</td>
<td>30</td>
<td>5.4</td>
</tr>
<tr>
<td>D-6-b</td>
<td>71.7/28.1/0.2</td>
<td>CH₃</td>
<td>4.3</td>
<td>2.9</td>
<td>57</td>
<td>10.9</td>
</tr>
<tr>
<td>D-6-c</td>
<td>71.7/28.1/0.2</td>
<td>iso-C₃H₇</td>
<td>3.4</td>
<td>2.6</td>
<td>45</td>
<td>9.6</td>
</tr>
<tr>
<td>AHA\textsuperscript{e}</td>
<td>no backing material (205 μm)</td>
<td>-</td>
<td>2.0</td>
<td>22</td>
<td>6.1</td>
<td>12.61</td>
</tr>
<tr>
<td>AMX\textsuperscript{e}</td>
<td>with backing fabric (140 μm)</td>
<td>-</td>
<td>1.5</td>
<td>28</td>
<td>10.4</td>
<td>7.65</td>
</tr>
<tr>
<td>AM-3\textsuperscript{e}</td>
<td>highly cross-linked (150 μm)</td>
<td>-</td>
<td>1.7</td>
<td>20</td>
<td>6.5</td>
<td>4.45</td>
</tr>
<tr>
<td>ACS\textsuperscript{e}</td>
<td>mono-anion permselective (110 μm)</td>
<td>-</td>
<td>1.7</td>
<td>25</td>
<td>8.2</td>
<td>5.30</td>
</tr>
<tr>
<td>ACM\textsuperscript{e}</td>
<td>cross-linked (100μm)</td>
<td>-</td>
<td>1.0</td>
<td>7.5</td>
<td>4.2</td>
<td>4.59</td>
</tr>
<tr>
<td>AHT\textsuperscript{f}</td>
<td>high temperature membrane (350 μm)</td>
<td>-</td>
<td>1.8</td>
<td>10</td>
<td>3.1</td>
<td>4.82</td>
</tr>
</tbody>
</table>

\textsuperscript{a} IEC value (ion exchange capacity; mmol Cl/g of dry polymer film) is estimated from \textsuperscript{1}H NMR spectrum.
\textsuperscript{b} IEC value is measured by titration.
\textsuperscript{c} Degree of Swelling: g H₂O/100 g dry polymer film.
\textsuperscript{d} Water content λ (molar ratio of water to ammonium chloride)
\textsuperscript{e} Membrane manufacturers: Tokuyama Soda.
\textsuperscript{f} Membrane manufacturers: Asahi Glass
As shown in Table 3.2, all Neosepta type commercial membranes have relatively low IEC values (between 1 and 2 mmol/g) and low water swelling with a DS value below 30%. The lowest one is the ACM membrane with only 1 mmol/g of Cl\(^-\) ion concentration and 7.5% DS value, which also reflects in low ionic conductivity. On the other hand, our PE-NR\(_3^+\)Cl\(^-\) and x-PE-NR\(_3^+\)Cl\(^-\) membranes show significantly higher IEC and DS values. The ion exchange capacity (IEC) of PE-NR\(_3^+\)Cl\(^-\) and x-PE-NR\(_3^+\)Cl\(^-\) membranes was not only measured by titration but also estimated from the -N(SiMe\(_3\))\(_2\) content of the polymers, measured by \(^1\)H NMR. As summarized in Table 3.2, all membranes show an IEC value well above 2.5 mmol/g. In addition to high -NR\(_3^+\)Cl\(^-\) content, the small ethylene mass also contributes to the high IEC value. Note that both IEC values in PE-NR\(_3^+\)Cl\(^-\) membrane (set B) are very close, only slightly lower in their titration values. However, there is a significant difference in the cross-linked x-PE-NR\(_3^+\)Cl\(^-\) membranes (set D)—the titration value is only about two third of the estimated value. The results indicate that the inter-conversion of -N(SiMe\(_3\))\(_2\) groups in the non cross-linked PE matrix was quite efficient. However, the same reaction in the cross-linked PE matrix was much more difficult. The limited swelling in the cross-linked matrix may have slowed down the diffusion of chemical reagents and reduced the overall inter-conversion efficiency.
Figure 3.4. Water content ($\lambda$) and degree of water swelling (DS) vs. IEC value for PE-NH$_3^+$Cl$^-$ membranes (samples B-2, B-3, B-a, and B-5 in Table 2) at room temperature.

Figure 3.4 compares degree of water swelling (DS) and water content ($\lambda$) vs. IEC for PE-NH$_3^+$Cl$^-$ membranes at room temperature. Generally, the water swelling follows with the IEC value. When comparing membranes B-2, B-3, B-4-a, and B-5, with a systematic increase of NH$_3^+$Cl$^-$ content in PE copolymers, the DS value increases from 29 to 240 %, as well as $\lambda$ value from 5.2 to 27.8. The degree of hydration per ammonium chloride ($\lambda$) increases with the ammonium chloride concentration, indicating a morphological change to become more continuous domains (channels) in PE-NH$_3^+$Cl$^-$ to ease water swelling. The PE-NH$_3^+$Cl$^-$ membrane with 30.5 mol % -NH$_3^+$Cl$^-$ groups (sample B-5) absorbs too much water (DS value: 240 %) and almost loses its structure integrity. High water uptake also dilutes the ion concentration and results in low ionic conductivity (discussed later). On the other hand, by introducing a very small amount (~0.2 mol %) of BSt cross-linker units in the similar PE copolymer (set D-6) the water swelling dramatically reduces. As shown in Figure
they are scaled back to 30% for x-PE-NH$_3^+$Cl$^-$ (sample D-6-a), 57% for x-PE-N(CH$_3$)$_3^+$Cl$^-$ (sample D-6-b), and 45% for x-PE-N(iso-C$_3$H$_7$)$_3^+$Cl$^-$ (sample D-6-c). It is also interesting to note that the -N(CH$_3$)$_3^+$Cl$^-$ group shows a higher hydration number than both the -NH$_3^+$Cl$^-$ and -N(iso-C$_3$H$_7$)$_3^+$Cl$^-$ groups in both cross-linked (set D-6) and non cross-linked (set B-4) membranes.

Figure 3.5. Comparison of water content ($\lambda$) and degree of water swelling (DS) between PE-NR$_3^+$Cl$^-$ and x-PE-NR$_3^+$Cl$^-$ (R: H, CH$_3$, iso-C$_3$H$_7$) membranes at room temperature.

In addition, these cross-linked membranes exhibit very good (tough) mechanical strength. Table 3.3 shows tensile properties of two x-PE-NH$_3^+$Cl$^-$ membranes (x-D-5 and x-D-6), derived from D-5 and D-6 ethylene/C$_6$N(SiMe$_3$)$_2$/BSt terpolymers (Table 3.1), respectively. As discussed before, during the membrane preparation, both D-5 and D-6 membranes experienced temperature of up to 150$^\circ$C for a short period of time, which may have resulted in a partially cross-linked structure. On the other hand, x-D-5 and x-D-6 membranes were further treated at 220 $^\circ$C for 2 h to complete the cross-linking reaction. The tensile strength at yield of the x-D-6 membrane reaches about 20
MPa with an elongation at break of 181%, which is more than sufficient to function as an ion conductive membrane in most electrochemical assemblies.

Table 3.3. Tensile properties of two PE-NH$_3^+$Cl$^-$ membranes before and after thermal treatment.

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength at yield(MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-5</td>
<td>233±52</td>
<td>10±2</td>
<td>210±42</td>
</tr>
<tr>
<td>x-D-5</td>
<td>311±50</td>
<td>19±2</td>
<td>141±30</td>
</tr>
<tr>
<td>D-6</td>
<td>273±50</td>
<td>12±2</td>
<td>255±44</td>
</tr>
<tr>
<td>x-D-6</td>
<td>358±53</td>
<td>20±2</td>
<td>158±30</td>
</tr>
</tbody>
</table>

Conductivity of the membrane was measured in 2 N HCl aqueous solution and 2 N HCl-0.2 N CuCl aqueous solution to model the catholyte and anolyte solutions in the CuCl-HCl electrolyzer used for hydrogen production$^{111-112}$. All membranes were equilibrated in the same solutions for 20 hours before we began measurements. The conductivity is impacted by the combination of the IEC value, water swelling, and ion mobility. All Neosepta type commercial membranes (Table 3.2) show moderate ionic conductivity (4-13 mS/cm) in 2 mol/L HCl solution and significantly lower conductivity (0.11-2.06 mS/cm) in 2N HCl-0.2N CuCl solution. The AHA membrane shows the highest conductivity (12.61 mS/cm) in 2 mol/L HCl solution among the tested commercial AEMs. The AMX membrane has a similar composition with AHA but with additional reinforcement to provide higher mechanical strength and reduced thickness. It demonstrated a small reduction of the ionic conductivity (7.65 mS/cm) in 2 mol/L HCl solution, but exhibited the highest conductivity (2.06 mS/cm) in 2 M HCl+0.2 M CuCl solution among the tested membranes. The AM-3 membrane is highly cross-linked. In spite of moderate conductivity, a positive effect of high cross-linking on the membrane performance is to decrease the Cu permeability. The ACS membrane is designed as a mono-anion permselective AEM, which allows for the selective transport of chloride in preference to multivalent anions. The AHT, a Selemion membrane designed for high temperature
applications, was also tested. It shows relatively low Cl\(^-\) ion conductivity, especially in 2N HCl-0.2N CuCl solution. Note that the Cl\(^-\) ion conductivity in 2N HCl-0.2N CuCl solution is always lower than that in 2 mol/L HCl solution, which may be due to the association between Cu\(^+\) species and some amino groups in the polymer, therefore reducing the quaternary ammonium chloride (Cl\(^-\) carrier) concentration. In fact, during the measurement in 2N HCl-0.2N CuCl solution the starting clear solution in the cathode gradually changes to a blue hue in all cases, indicating some type of Cu\(^{+2}\) species diffusion throughout the commercial membranes.

![Figure 3.6. Comparison of Cl\(^-\) ion conductivity vs. IEC of PE-NH\(_3\)\(^+\)Cl\(^-\) membranes (samples B-2, B-3, B-4-a, and B-5 in Table 3.2) with various concentrations of -NH\(_3\)\(^+\)Cl\(^-\) groups in (a) 2N HCl and (b) 2N HCl-0.2N CuCl solutions at room temperature. (Data was obtained by Dr. E. Chalkova.)](image)

Most of our PE-NR\(_3\)\(^+\)Cl\(^-\) and x-PE-NR\(_3\)\(^+\)Cl\(^-\) membranes, containing >25 mol % of NR\(_3\)\(^+\)Cl\(^-\) content (Table 3.2), show significantly higher ionic conductivity in both 2N HCl and 2N HCl-0.2N CuCl solutions. Figure 3.6 compares several PE-NH\(_3\)\(^+\)Cl\(^-\) membranes (B-2, B-3, B-4-a, and B-5)
with various IEC values. Generally, the higher -NH₃⁺Cl⁻ concentration will have the higher conductivity, with the conductivity increasing more than one order to 30.1 mS/cm in 2N HCl solution and 3.6 mS/cm in 2N HCl-0.2N CuCl solution when the IEC value increases from 3.1 (B-2) to 4.0 mmol/g (B-4-a). The combination of DS, λ, and conductivity data implies a morphology change to form more continuous ion conductive domains embedded in the hydrophobic PE matrix. In fact, the further increase of the IEC value (sample B-5) results in lower conductivity, due to the higher IEC leads to higher water swelling that dilutes the concentration of the Cl⁻ ion. In addition, high water swelling significantly weakens the mechanical properties of the B-5 membrane. Overall, it seems that the PE-NH₃⁺Cl⁻ with about 25 mol % (sample B-4-a) is a suitable composition for the anion membrane. In the subsequent study, we decided to further investigate this specific composition range with some structure alternations, including the NR₃⁺Cl⁻ group (with R: H, CH₃, and iso-C₃H₇) and cross-linking feature in the PE matrix.

Figure 3.7 compares the ionic conductivity for two sets of PE-NR₃⁺Cl⁻ (B-4-a, B-4-b, and B-4-c) and x-PE-NR₃⁺Cl⁻ (D-6-a, D-6-b, and D-6-c) membranes in 2N HCl and 2N HCl-0.2N CuCl solutions, respectively. In each set, they have the same -NR₃⁺Cl⁻ concentration, but a changing R group from H, CH₃, to iso-C₃H₇. It is clear that the conductivity shows strong dependence on R groups, especially in 2N HCl-0.2N CuCl solution. Evidently, the bulkier R groups significantly reduce the ionic association between the Cl⁻ ion and stationery -NR₃⁺ group, therefore increasing Cl⁻ ion mobility and the ionic conductivity. In the B-4 set, the PE-N(CH₃)₃⁺Cl⁻ membrane (B-4-b) exhibits impressive conductivities of 106.1 mS/cm in 2N HCl solution and 62.9 mS/cm in 2N HCl-0.2N CuCl solution; both are 1 order of magnitude higher than that shown in commercial membranes. However, when further increasing the size of the R group to the bulkier iso-C₃H₇ group, the IEC value decreases along with its conductivity, due to the dilution effect. A similar trend was also observed in x-PE-NR₃⁺Cl⁻ membranes (set D-6). As discussed, cross-linking dramatically
reduces water swelling and increases ion concentration, which is helpful in ion conductivity. However, cross-linking may also reduce the ion mobility. The commercial cross-linked AM-3 membrane shows a slight reduction in conductivity from the corresponding non cross-linked AHA membrane. When comparing two parallel D-6 and B-4 sets with similar -NR₃⁺Cl⁻ (R: H, CH₃, and iso-C₃H₇) concentration, but with or without cross-linking, the conductivity difference is relatively small. In fact, the x-PE-N(CH₃)₃⁺Cl⁻ membrane (D-6-b) shows slightly higher conductivities of 119.6 mS/cm in 2N HCl solution and 78.8 mS/cm in 2N HCl-0.2N CuCl solution. High mobility of the Cl⁻ ion in the flexible side chains may minimize the negative ion mobility effect induced by cross-linking. Evidently, the x-PE-N(CH₃)₃⁺Cl⁻ membrane (D-6-b), containing 28.1 mol % of C₆N(CH₃)₃⁺Cl⁻ units, possesses the structure that results in the best combination of high Cl⁻ ion concentration and mobility.

Figure 3.7. Comparison of Cl⁻ ion conductivity between PE-NR₃⁺Cl⁻ (samples B-4-a, B-4-b, and B-4-c), x-PE-NR₃⁺Cl⁻ (D-6-a, D-6-b, and D-6-c) membranes and several commercial membranes in 2N HCl and 2N HCl-0.2N CuCl solutions at room temperature. (Data was obtained by Dr. E. Chalkova.)
All four PE-N(CH$_3$)$_3^+$Cl$^-$ (B-4-b), PE-N(iso-C$_3$H$_7$)$_3^+$Cl$^-$ (B-4-c), x-PE-N(CH$_3$)$_3^+$Cl$^-$ (D-6-b), x-PE-N(iso-C$_3$H$_7$)$_3^+$Cl$^-$ (D-6-c) membranes display close ionic conductivities in 2N HCl and 2N HCl-0.2N CuCl solutions. In addition, the solution in the cathode side remains colorless during the measurement in 2N HCl-0.2N CuCl solution, indicating no Cu$^{+2}$ species diffusion through the membrane. The bulky R groups may significantly reduce the association between Cu species and amino groups, therefore providing selective Cl$^-$ ion diffusion throughout the membranes. This explanation is also in agreement with a phenomenon observed in PE-NH$_3^+$Cl$^-$ (B-4-a) and x-PE-NH$_3^+$Cl$^-$ (D-6-a) membranes, with the ionic conductivity in 2N HCl-0.2N CuCl solution gradually decreasing with the measurement time; this is because the Cu species slowly consumes the ammonium salt.

3.4. Conclusion

A new class of high performance polyethylene-based anion exchange membranes has been developed, which contains flexible ammonium chloride (-NR$_3^+$Cl$^-$) groups and a cross-linking PE network structure. The combination of direct metallocene-mediated copolymerization and effective functional group interconversions in film form allows us to prepare a wide range of well-defined x-PE-NR$_3^+$Cl$^-$ membranes with good mechanical strength and relatively low thickness (50-70 μm; without backing material). A systematic structure-property study on both PE-NR$_3^+$Cl$^-$ and x-PE-NR$_3^+$Cl$^-$ membranes was performed in order for us to understand the PE structure’s effect (concentration of -NR$_3^+$Cl$^-$ groups, R in the quaternary ammonium group, cross-linking density, etc.) on the water uptake and ionic conductivity. The most desirable x-PE-NR$_3^+$Cl$^-$ membrane contains 28.1 mol % -N(CH$_3$)$_3^+$Cl$^-$ groups in the flexible side chains and possesses a fully cross-linked hydrophobic PE matrix (formed by 0.2 mol % BSt units). This membrane offers an excellent combination of desirable properties, including adequate water swelling, high thermal stability, and
exceptionally high ionic conductivities of 119.6 mS/cm in 2N HCl solution and 78.8 mS/cm in 2N HCl-0.2N CuCl solution (one order higher than all commercially-available AEM membranes).
Chapter 4.

Conclusion

4.1. Conclusion

Polyolefin based proton exchange membrane (PE-PEM) and anion exchange membrane (PE-AEM) were developed and studied in this research. Both membranes show unique properties and promising results for applications in fuel and electrolytic cells. Chapter 2 discusses PE-PEMs with focusing on the combination of high proton conductivity, low water swelling, low methanol permeability, and good mechanical properties. The new synthesis method developed in this study offers a flexible route to prepare PE-PEMs with a good control of morphology. Some PE-PEMs with high PE molecular weight and high IEC values (>3 mmol/g) in sulfonated PAES domains show well micro-phase separated morphology containing a highly hydrophobic and crystalline PE matrix and the imbedded continuous proton conductive channels. In addition to high proton conductivity, the control of water swelling, and maintaining good mechanical properties, the PE-PEMs possess a thin PE hydrophobic surface layer that is reflected in the water contact angle and the anisotropic ion conductivity. By this character, PE-PEMS showed low methanol permeability and high selectivity compared to Nafion 117. Overall, this new class of PE-g-s-PAES PEMs offer a desirable set of properties, including conductivity, water uptake, mechanical strength, and cost-effectiveness for fuel cell applications. This unique combination of bulk and surface morphology may also affect fuel selectivity and humidity effects to the conductivity; they will be addressed as a future work.

In chapter 3, PE-AEMs having superior chloride ion conductivity were studied. Different chemistry from PE-PEMs was developed and utilized to synthesize PE-AEMs. Likewise, a wide
variety of compositions of hydrophobic and hydrophilic components were investigated to find the best conditions for anion exchange membrane. With the aid of cross-linker in copolymer sequence, the membranes didn’t swell so much that the membrane maintained its mechanical integrity even with a large volume of hydrophilic component. Studied AEMs possessed 10 times high conductivity than commercial membranes with good mechanical properties.

Overall, in this thesis it is concluded that polyethylene (PE) graft or random copolymers provided substantial advantages as ion conductive membranes for applications in fuel and electrolytic cells.

4.2. Suggestions

Regarding materials that are studied in this thesis, it will be an interesting try to use polypropylene instead of polyethylene. Polypropylene has a high melting point thus a better thermal property than polyethylene. Since catalyst poison by carbon dioxide is less likely to happen at high temperature, polypropylene may have a more wide temperature window for fuel cell operations than polyethylene. Although chemistry is more complicated and it is more difficult to functionalize polypropylene, the method developed in this thesis may be applied with some adjustments. Related to morphology of the PE-PEMs, transmission electron microscopy (TEM) should be applied. Although we argue that morphology of the PE-PEMs is expected to be co-continuous channel imbedded in polyethylene matrix, TEM will make it very clear and more supportive. Energy dispersive x-ray spectroscopy (EDAX) will also be applied to monitor and trace the sulfur compounds, which allows us to know the components of the films through the thickness. By using EDAX, cross-sectional area of the films can be investigated. As we argued, it may be seen that the surface of the film is covered by polyethylene mostly. It will be very interesting to see how much sulfur is on the surface. Membrane fabrication, including hot pressing, annealing, and crystallization,
shall be systematically investigated to find the optimized procedure for making the membranes with defect-free and highly crystalline matrix.

Appendix

A1. DSC curves

Figure A1. DSC curve of PE-g-PAES graft copolymer and PAES homopolymer
A2. Description of the conductivity cell for in-plane conductivity

Figure A2. Top view of two probe conductivity cell for in-plane conductivity

In-plane conductivity was measured by Solartron 1260 gain/phase analyzer in Dr. Hickner’s group. The two probe cell with polymer film is immersed under deionized water to hydrate the cell and the film. At room temperature, the cell was left in the deionized water for at least 10 mins before conductivity measurement to make sure the cell is completely wet under water. As a software for the measurement, Z view and Z plot were utilized. AC impedance was applied with the

\[ \sigma = \frac{I}{(R \times \delta \times w)} \]
frequency range from 10 to 106 Hz and imaginary impedance (y axis) is plotted against real impedance (x axis). By having an intercept on x axis, resistance of polymer film was determined.

To make sure the validity of experiments, well known material, Nafion was measured for each experiment. When conductivity of Nafion is ranged from 70 to 85 mS/cm, the data was accepted to be in valid. Measurements were conducted at least three times to get an average value of proton conductivity of samples.

A3. Description of the conductivity cell for through-plane conductivity

![Side view of two probe conductivity cell for through-plane conductivity](image)

\[ \sigma = \frac{b}{(\Delta R \times As)} \]

Figure A3. Side view of two probe conductivity cell for through-plane conductivity
Through-plane conductivity cell is shown above. Through-plane conductivity is measured by the two probe cell in Dr. Lvov’s group. Polymer film was cut out a round piece and sandwiched between two chambers with two platinum electrodes at each side in 1 mol/L HCl aqueous solution. Resistance was measured by Gamry electrochemical system. ΔR was obtained by difference of resistance with and without film. Resistance measurement was conducted at least five times until lowest value of resistance was obtained by Gamry electrochemical system. Like in-plane conductivity, Nafion was measured before all the other measurements for validity test. Acceptable conductivity value of Nafion was between 65 to 85 mS/cm.

A4. Description of the conductivity cell for in-plane conductivity at various humidity and temperature conditions
Figure A4. Top view of four probe conductivity cell for in-plane conductivity at various relative humidity conditions

Four probe conductivity cell for in-plane conductivity at various humidity and temperature conditions was utilized (cell from Dr. Lvov’s group). Inner two platinum electrodes were attributed to the potential drop and outer two platinum electrodes were attributed to the current. The unit cell was sandwiched by two gas diffusion layers and compacted tightly by bolts and nuts. Tightly assembled membrane electrode assembly (MEA) was connected into Gamry electrochemical system by wires. Humidifier, humidity controller, and temperature controller were equipped and arranged for the measurement. Relative humidity was controlled by having different temperatures between humidifier and conductivity cell. The calibration curve is shown below,
From this curve, it is possible to know relative humidity at a fixed temperature. Relative humidity was set to 30, 50, 70, and 95 %. The polymer film was placed in the unit cell and sandwiched with gas diffusion layers as described above. First, relative humidity was set up to 70 % at a fixed temperature and the cell was equilibrated with environment for at least two hours. Resistance was then measured and recorded. In all the measurements, deionized water was utilized. Temperature was first low and elevated aftermath to see the difference in proton conductivity depending on temperature.

A5. Description of the conductivity cell for through-plane conductivity at various humidity and temperature conditions
Two probe conductivity cell was utilized to measure through-plane conductivity at various humidity and temperature conditions (cell from Dr. Lvov’s group). The schematic is shown above. In this experiment, resistance is directly measured from the film. Polymer film is sandwiched between two round shape platinum electrodes and compacted by Teflon mold. Like in-plane conductivity measurement, the unit cell is sandwiched and sealed by two gas diffusion layers to maintain relative humidity and temperature inside. The MEA was equilibrated with humidifier for at least three hours before measurements. First, relative humidity was set up to 70 % at room temperature. After measuring resistance of the film, humidity was decreased 50 and 30 %. Finally,
relative humidity was increased up to 95 % at same temperature. Experiments were continued to change temperature to 50 °C and 80 °C. Resistance of Nafion 117 was measured before all the other measurements to validate the accurate test.

Figure A7. Schematic of two probe conductivity cell for through-plane conductivity

A6. Description of methanol permeability measurement system
As shown above, homemade permeability cells equipped with refractive index detector and Waters 1515 pump were utilized to measure methanol permeability (cell from Dr. Hickner’s group). Like through-plane conductivity measurement, a polymer film is placed in between two chambers, one is filled with 2 mol/L methanol aqueous solution and the other is filled with deionized water. Pump sucks in deionized water along with time. By permeation of methanol from the right chamber to left chamber, concentration of methanol in the left chamber is altered and recorded by the change of refractive index, followed by conversion to concentration of solution in the left chamber with respect to time. By using the equation \[ \ln \frac{M_{R,t} - M_{L,t}}{M_{R,0} - M_{L,0}} = -DH \chi t \] and substituting known values, it is possible to obtain DH, that is, methanol permeability. The regression curve for the conversion of refractive index to concentration is shown below,
Figure A9. Regression curve of methanol concentration against difference in refractive index

Due to difference in concentration of methanol solution with respect to time, refractive index is accordingly changed and linear relationship of methanol concentration and del RI is obtained by the regression curve. From this curve, it is possible to trace methanol concentration with respect to del RI and by using the equation, methanol permeability (DH in equation) can be calculated. Film geometry including thickness, length and width is also considered as parameter $\chi$ as well as the elapsed time as $t$.

A7. Summary of types of polymers and their definition
(1) Homopolymer: composed of one type of repeat unit (e.g. polyethylene, polystyrene, polypropylene) (e.g. AAAAAAA)

(2) Copolymer: composed of two types or more of repeat units (e.g. polyethylene-polypropylene copolymer)

  * Random copolymer: copolymer which two types or more of repeat units are randomly distributed along the polymer chain (e.g. AAABBBABABBA).

  * Block copolymer: copolymer which is composed of two blocks polymer, each polymer is connected by chemical bond between two polymers (e.g. AAAAAABBBBBBBBBB).

  * Graft copolymer: copolymer which one block polymer is grafted (attached) onto the other polymer chain (e.g. AAAAAAAAABBBB)

(3) Polyethylene (PE): homopolymer, composed of ethylene repeat unit

(4) Polyethylene-co-para-methylstyrene (PE-co-p-MS): random copolymer having ethylene and p-MS repeat units which are randomly distributed along the polymer backbone chain.

(5) Brominated Polyethylene-co-para-methylstyrene (Br-PE-co-p-MS): random copolymer having ethylene and p-MS repeat units which are randomly distributed along the polymer backbone chain and benzylic position of some p-MS units is brominated.

(6) Poly(arylene ether sulfone) (PAES): random copolymer, composed of bisphenol A and phenyl sulfone repeat unit

(7) Polyethylene-graft-poly(arylene ether sulfone) (PE-g-PAES): graft random copolymer, PAES is grafted onto Br-PE-co-p-MS in this particular polymer.
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