Examining Structure-Property Relationships of Proton Exchange Membranes through the Study of Model Sulfonated Graft Copolymers

by

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B.Sc., Simon Fraser University, 2007

Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

in the
Department of Chemistry
Faculty of Science

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SIMON FRASER UNIVERSITY
Spring 2014

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Abstract

The role of polymer nanostructure on morphology, crystallinity, water sorption and proton conductivity was investigated using a model solid polymer electrolyte. Poly([vinylidene difluoride-co-chlorotrifluoroethylene]-*graft*-styrene) [P(VDF-co-CTFE)-g-PS], which consists of a hydrophobic, fluorous backbone and styrenic graft chains of varied length was synthesized with controlled chain architecture and chemical composition. The polystyrene graft chains were sulfonated to different degrees to provide three series of polymers with controlled ion exchange capacity (IEC). Due to chemical dissimilarity of the hydrophobic fluorous segments and the hydrophilic sulfonated polystyrene segments, the copolymers phase separate into ionic and non-ionic domains. The ionic domains allow transport of water and protons; the hydrophobic domains provide mechanical integrity, preventing the membranes from dissolving in water.

The design of the model graft copolymers allows systematic examination of the effects of graft length and graft density on water sorption and proton conductivity. One of the major features of this work is that the sulfonated graft copolymers with shortest graft chains exhibit highest degree of crystallinity and highest PVDF content, which restrict excessive swelling and alleviate acid dilution, leading to a wider IEC operating range for high proton conductivity. Furthermore, the short graft copolymers allow access to very high IEC membranes that are insoluble in water. These short graft polymers with high IECs exhibit exceptionally high proton conduction under reduced humidity and elevated temperatures. In addition, for a given PVDF content, the lower graft density copolymers were observed to possess higher crystallinity and more contiguous PVDF domains that allow high IEC membranes to be prepared that possess lower degrees of swelling.

Another important finding is that blending fully sulfonated graft copolymers with high molecular weight PVDF yields membranes with overall low IECs that exhibit highly localized ion content. This promotes the interconnection of ionic domains for effective proton transport while the more extended hydrophobic domains significantly reduce excessive swelling which serve to maintain the mechanical property of the membranes.

This thesis describes a systematic approach, demonstrating the design, synthesis, characterization of model polymers, followed by the analysis of structure-property relationships in proton exchange membranes.

Keywords: Proton Exchange Membranes; Structure-Property Relationships; Model Sulfonated Graft Copolymers; Membrane Morphology; Proton Conductivity; Poly(Vinylidene Fluoride) Blends
To my husband, K. C. Neyerlin,

my parents, Mei-Huei & Tsing-Tyan Yang

who inspired, supported me

and always believed in me.

And to my daughter, Ellie Neyerlin.
Acknowledgements

I would like to thank:

My senior supervisor Prof. Steven Holdcroft for allowing me to work under his supervision and for his valuable guidance and support throughout my studies.

My supervisory committee members Prof. George Agnes and Prof. Robert Young, for their supervision throughout the course of my studies and for giving constructive feedback to improve my thesis. My examining committee members, Prof. Yossef Elabed and Prof. Gary Leach for reviewing this thesis.

Dr. Rasoul Narimani and Prof. Barbara Frisken of Department of Physics, SFU, for the collaborative research project and meaningful discussions throughout my studies. Dr. Mads Nielsen for the collaborative research work presented in Chapter 5.

Drs. Tim Peckham and Emily Tsang, for their mentorship and fruitful discussions. Dr. Zhaobin Zhang, for preparing the fluororous macroinitiators and useful discussions regarding synthesis. Thomas Weissbach, Owen Thomas, and Ben Zhang, for laboratory assistance and meaningful discussions throughout my time at SFU. Past and present members of the Holdcroft group for their valuable friendship and support.

Michael Wang and Dave Edwards for TEM-related assistance. Drs. Andrew Lewis and Colin Zhang, for collecting 19F NMR data. The staff members of the electronic and machine shop at SFU, for assistance of manufacturing proton conducting cells.

Profs. Lee Hanlan, Nabyl Merbouh, Uwe Kreis, and Peggy Paduraru for fruitful discussions and teaching guidance in the organic chemistry lab.

Lynn Wood for all of the administrative assistance for this thesis and Fred Chin for computer-related assistance.

My family, extended families (the Burandts and the Neyerlins), and friends for their love, encouragement and support throughout my studies.

Simon Fraser University and the Natural Sciences and Engineering Research Council of Canada for financial support.
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<td>AC</td>
<td>alternating current</td>
</tr>
<tr>
<td>AIBN</td>
<td>azoisobutyronitrile</td>
</tr>
<tr>
<td>ATRP</td>
<td>atomic transfer radical polymerization</td>
</tr>
<tr>
<td>BAM®</td>
<td>Ballard Advanced Materials®</td>
</tr>
<tr>
<td>bpy</td>
<td>2,2-dipyridyl</td>
</tr>
<tr>
<td>CP</td>
<td>calcium Phosphate</td>
</tr>
<tr>
<td>DCE</td>
<td>1,2-dichloroethane</td>
</tr>
<tr>
<td>DMAc</td>
<td>N, N-dimethylacetamide</td>
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<td>DMFCs</td>
<td>methanol fuel cells</td>
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<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
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<tr>
<td>DP</td>
<td>degree of polymerization</td>
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<tr>
<td>DP&lt;sub&gt;PS&lt;/sub&gt;</td>
<td>degree of polymerization of polystyrene</td>
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<tr>
<td>DS</td>
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<td>differential scanning calorimetry</td>
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<td>divinylbenzene</td>
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<td>DVS</td>
<td>dynamic vapour sorption</td>
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<tr>
<td>EIS</td>
<td>electrochemical impedance spectroscopy</td>
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<tr>
<td>ETFE</td>
<td>poly(ethylene-&lt;i&gt;alt&lt;/i&gt;-tetrafluoroethylene)</td>
</tr>
<tr>
<td>ETFE-&lt;i&gt;g&lt;/i&gt;-PSSA</td>
<td>poly([ethylene-&lt;i&gt;alt&lt;/i&gt;-tetrafluoroethylene]-&lt;i&gt;g&lt;/i&gt;-styrene sulfonic acid)</td>
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<tr>
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<td>hexafluoropropylene</td>
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<td>nuclear magnetic resonance</td>
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<td>P(VDF-co-CTFE)</td>
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<td>stable free radical polymerization</td>
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<td>sulfonated hydrogenated poly(butadiene-b-styrene)</td>
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<td>sulfonated poly(arylene ether sulfone)s</td>
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<tr>
<td>SPS</td>
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<td>sulfonated poly(styrene-\textit{b}-ethylene/propylene-\textit{b}-styrene)</td>
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<td>TBA*</td>
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<td>X-ray diffractometer</td>
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<td>$\chi$</td>
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<td>membrane capacitance</td>
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<td>Faraday’s constant</td>
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<td>$k_{ct}$</td>
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<td>$k_{deact}$</td>
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<td>$k_{p}$</td>
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<td>$k_{t}$</td>
<td>rate constant of termination</td>
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<tr>
<td>$L$</td>
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<tr>
<td>$M_n$</td>
<td>number average molecular weight</td>
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<tr>
<td>$M_w$</td>
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<td>$R_m$</td>
<td>membrane resistance</td>
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<tr>
<td>$S$</td>
<td>integrated intensity of peaks of NMR spectra</td>
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<tr>
<td>$T_g$</td>
<td>glass transition temperature</td>
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<tr>
<td>$V_{NaOH}$</td>
<td>volume of NaOH solution</td>
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<td>$V_{water}$</td>
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<td>$\sigma$</td>
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Chapter 1. Introduction

1.1. Fuel Cells

Fuel cells attract great interest for automotive, stationary and portable power applications because of their potential to become significant energy conversion technologies,\(^1\)\(^-\)\(^3\) and to fulfill an expected doubling of the energy demand of all households worldwide by 2050 as well as an anticipated worldwide oil crisis.\(^4\)\(^-\)\(^6\) Fuel cells not only produce reasonable efficiencies (a maximum theoretical efficiency of 83\% at 25\(^\circ\)C compared to 58\% at 500\(^\circ\)C for combustion engines)\(^7\) but they are also able to run quietly and emit fewer pollutants compared to hydrocarbon combustion engines.

Fuel cells utilize an electrochemical process to convert the chemical energy of a fuel and an oxidant into electrical power. Principle components of a fuel cell include: catalytically-active electrodes for oxidation of the fuel (e.g., hydrogen) and reduction of the oxidant (normally O\(_2\)) at the anode and cathode respectively; an electrolyte placed between the anode and cathode that conducts ions, is an electrical insulator and which separates the two electrodes as well as oxidant and fuel. Fuel cells require infrequent maintenance and they can operate uninterrupted as long as a continuous supply of fuel is provided.\(^8\) A combination of high fuel-to-electricity efficiency, clean exhaust carbon dioxide emission, low noise and low maintenance costs theoretically make fuel cells better energy conversion devices over conventional batteries.
1.2. Proton Exchange Membrane Fuel Cells

Hydrogen/oxygen (H\textsubscript{2}/O\textsubscript{2}) fuel cells and direct methanol fuel cells (DMFCs) are the two types of fuel cells that utilize proton exchange membranes (PEMs) as electrolytes. The typical fuel is hydrogen or methanol and the typical oxidant is pure oxygen or air. In proton exchange membrane fuel cells (PEMFCs), the fuel of choice (e.g., H\textsubscript{2}) is oxidized at the anode catalyst, generating protons and electrons. The protons are conducted across the PEM from anode to cathode whereas the electrons are forced to travel through an external circuit, thereby generating electricity. The protons and the electrons react with oxygen molecules at the cathode catalyst to form water molecules as the only waste products of the reaction.

Proton exchange membrane fuel cells (Figure 1.1) are currently under intense investigation. Using a solid polymer electrolyte instead of a liquid electrolyte is advantageous because of the elimination of electrolyte leakage issues and no need to deal with corrosive acids/bases and longer cell life. PEMFCs also allow for the use of various hydrogen-containing fuels such as H\textsubscript{2}, methanol, ethanol and propane, and thus they are very versatile for variety of applications. The three major applications for PEMCFs are: automotive, stationary and portable power. PEMFCs are particularly advantageous for automotive applications in comparison to other types of fuel cells because they can operate at high power densities at relatively low temperatures (30 - 200 °C), which permits for quick start-up under different conditions. The current preferred operating conditions for automotive applications are low RH (e.g., ≤ 50%) and an operating temperature of 120 °C to minimize system support (e.g., pressure, humidification), and a goal of 0.1 S/cm for proton conductivity of the membrane.\textsuperscript{9,10}
PEMFCs can also be applied in small portable electronics such as cell phones and laptop computers because of their quiet operation. However, due to issues such as high material production cost, durability and performance under various operating conditions, and the requirements for improvements in hydrogen production and storage, widespread commercialization of PEMFCs has yet to be realized.

**Figure 1.1.** Schematic diagram of a proton exchange membrane fuel cell

### 1.2.1. Proton Exchange Membranes

Proton exchange membranes serve as electrolytes and separators in PEMFCs and are essential to solid PEMFCs. These membranes are strategically designed to provide a continuous ionic pathway for proton transport. Incorporation of acidic groups bound to the polymer (e.g., sulfonic acid) serves both as a source of protons as well as provides a conduction pathway. Important requirements that an ideal PEM should exhibit are:

- high proton conductivity
- low electronic conductivity (electrically insulating)
- mechanical and chemical integrity
- low fuel and oxidant permeability
- limited crossover and solvent transport
- thermal, oxidative and hydrolytic stability
- limited swelling in the presence of water
- good mechanical properties in both dry and hydrated states
- low production cost

1.2.2. Nafion® and Other Polyperfluorosulfonic Acid Membranes

The current state-of-the-art PEMs for PEMFCs is DuPont’s Nafion®, a perfluorosulfonic acid (PFSA) membrane developed in the late 1960s. Nafion® is considered as a standard solid electrolyte in the PEMFC industry because of its commercial availability and its excellent properties in terms of performance and stability. Nafion® membrane exhibits several attractive properties including high ionic conductivity, mechanical and chemical stability, and reasonably low water swelling. The chemical structure of Nafion® comprises a hydrophobic, perfluorinated backbone with pendent perfluoro ether side chains terminated with hydrophilic sulfonic acid groups (Figure 1.2). The ionic content of Nafion® can be modified by changing the ratio of the components, x and y in the perfluorinated backbone.

The incompatibility of the hydrophilic side chains and the hydrophobic backbone results in a phase-separated morphology and the morphology, in the presence of water, rearranges to provide a continuous pathway for ionic conduction. Upon hydration, the hydrophilic domains swell, which allow transportation of water and protons in the membrane, while the hydrophobic domains prevent dissolution of the polymer membrane in water, thereby maintaining morphological stability.
Figure 1.2. Chemical structure of alternative perfluorosulfonic acid ionomer membranes

Nafion® membranes possess good performance at hydrated state and moderate temperatures (< 90°C), but they also have several critical disadvantages.12, 19, 20 High cost in material manufacturing restricts them from achieving widespread commercialization. Moreover, thanks to their tendency for dehydration, their operating condition is limited to > 50% relative humidity (RH) and < 90 °C. In addition, Nafion® is a poor water-barrier as a result of its high electro-osmotic drag coefficient, which allows high water permeation from anode to cathode in hydrogen fuel cell systems. This leads to dehydration of the anode side of the membrane and/or flooding of the cathode. For DMFC applications, Nafion® also exhibits high methanol permeability, resulting in reduced fuel efficiency. For the reasons stated above, it is important to develop advanced PEMs with improved properties and low cost.
Other PFSA membranes with similar structures but varied length of the perfluorinated ether side chains have been developed. The structures of these alternative membranes are also shown in Figure 1.2. The Asahi Chemical Company and Asashi Glass Company have developed Aciplex® and Flemion®, which exhibit similar performance to Nafion® membranes.21 The Dow Chemical Company also developed Dow’s Developmental Membrane, which has a shorter side chain than Nafion®.22 The shorter side chains allow Dow® Developmental Membrane to possess higher ion exchange capacity (IEC) (1.25 mmol/g) than Nafion® (0.9 – 1.0 mmol/g) and exhibit higher proton conductivity.23 Short side chain PFSA membranes have attracted great interest because they can be prepared with higher IEC, high acid concentration and increased crystallinity, and provide better proton transport at low humidity.24-27 Another short side chain PFSA membrane, Aquivion®, also known as Hyflon Ion®, has recently developed by Solvay-Solexis using a cheaper and more convenient synthetic approach than the original Dow® route.28 Furthermore, the original structure of Dow’s Developmental Membrane has been modified to include 3M®29 and Asahi-Kasei®,30 which have three and four CF₂ units in the side chain, respectively.

Although PFSA membranes have a number of desirable properties, they are expensive and difficult to synthesize. Therefore, several alternative classes of polymer are under intense investigation, including partially fluorinated ionomer membranes, non-fluorinated hydrocarbon-based membranes, and polymer blends, all of which will be discussed in the following sections.
1.2.3. Partially Fluorinated Ionomer Membranes

Partially fluorinated materials, which exhibit a good combination of lower cost and reliable electrochemical properties, are attractive candidates for alternative materials. Ballard Advanced Materials Corporation has prepared a class of novel copolymers known by the trademark name, BAM\textsuperscript{®} in the early 1990s, which incorporates α,β,β-trifluorostyrene and substituted α,β,β-trifluorostyrene comonomers (Figure 1.3).\textsuperscript{31} They are produced by emulsion copolymerization of the substituted and un-substituted trifluorostyrene monomers, followed by subsequent sulfonation. The synthetic approach of varying ratios of monomers and controlling post-sulfonation conditions allows a wide range of controlled IECs of the membranes to be produced in a systematic way. Furthermore, this class of copolymers is able to maintain mechanical properties even with very high water uptake up to 300 wt% of water.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure13.png}
\caption{Chemical structure of BAM\textsuperscript{®} copolymer}
\end{figure}

Poly(vinylidene difluoride) (PVDF) and poly(ethylene-alt-tetrafluoroethylene) (ETFE) (Figure 1.4 a and b) are commonly representative partially fluorinated polymers. They are easier to prepare than fully fluorinated materials and provide morphological stability and comparable electrochemical properties to fully fluorinated polymers. Moreover, they are commercially available; thus, are commonly used as the base polymers for radiation-grafted PEMs. Suitable monomers (i.e., styrene and trifluorostyrene) can be grafted onto the partially fluorinated backbone by direct radiation grafting or pre-irradiation grafting.\textsuperscript{32-34} The sulfonation process usually takes place after
the monomers are attached to the base polymer. While the base polymer provides the
desirable mechanical integrity and prevents the membrane from dissolving in solution,
sulfonation offers ionic conductivity to the PEM. Shen and Horsfall have developed a
class of partially fluorinated material consisting of ETFE and PVDF as base polymer
matrix and polystyrene sulfonic acids that are grafted onto the base matrix by the
radiation grafting technique.\textsuperscript{35} Examples of abovementioned radiation-grafted PEMs are
shown in Figure 1.4 (c) and (d).

The radiation-grafting approach provides flexibility to prepare desirable PEMs,
which reduces the fabricating cost and synthetic difficulties. By varying the grafting
parameters, a wide range of IECs can be controlled to yield a series of copolymers
systematically to allow more efficient structure-property studies to be carried out.
However, radiation grafting may happen non-uniformly because radiation polymerization
usually occurs on the surface of the base fluoropolymer membrane.\textsuperscript{36} The lack of
chemical structural control is considered as a major disadvantage.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structure.png}
\caption{Chemical structure of (a) PVDF, (b) ETFE, (c) poly(vinylidene difluoride-
g-styrene sulfonic acid) (PVDF-g-PSSA), and (d) poly([ethylene-\textit{alt}-tetrafluoroethylene]-
g-styrene sulfonic acid) (ETFE-g-PSSA)}
\end{figure}
1.2.4. Hydrocarbon Membranes

Another class of alternative PEMs that have been studied widely are non-fluorinated hydrocarbon-based membranes. Hydrocarbon-based PEMs are attractive because of cheaper cost, potential commercial availability of the base polymer and higher tolerance at high temperature operating conditions (> 120°C). PEMs operating under high temperature are favourable because high operating temperature are advantageous for reducing carbon oxide poisoning on catalyst surface, kinetically accelerating reaction, which can lead to higher performance, lowering cooling requirements for automotive applications, and enabling co-generation of heat and electricity for residential applications.

One of the basic hydrocarbon-based polymers is sulfonated polystyrene (SPS), shown in Figure 1.5a. This type of polymer membrane is inexpensive and easy to prepare, but possesses poor chemical and thermal stability. The first generation of PEMs were SPS-based which were cross-linked by divinylbenzene (DVB) to increase mechanical stability (Figure 1.5b). Their durability is low due to excessive swelling in water. Furthermore, they also have low proton conductivity, which is not suitable for fuel cell operations. However, sulfonated polystyrene-based membranes are intensively investigated because they are excellent model polymers due to styrene monomers being commercially available and easy to modify. Living polymerization routes such as atom transfer radical polymerization (ATRP) and stable free radical polymerization (SFRP) are commonly used to prepare this type of polymers, followed by subsequent sulfonation. Their flexibility to be prepared with controlled microstructure and morphology makes them extremely beneficial for studying structure-property relationships in PEMs. Examples of representative sulfonated polystyrene-bearing copolymers are shown in
Figure 1.5: (c) partially sulfonated poly(styrene-\text{-}b\text{-}[ethylene-co-butylene]\text{-}b\text{-}styrene) (S-SEBS),\textsuperscript{41-52} (d) partially sulfonated poly(styrene-b-isobutylene-b-styrene) (S-SIBS),\textsuperscript{43, 44} (e) partially sulfonated hydrogenated poly(butadiene-b-styrene) (S-HPBS),\textsuperscript{57} (f) partially sulfonated poly(styrene-b-ethylene-alt-propylene) (S-SEP),\textsuperscript{58} and (g) partially sulfonated poly(styrene-b-ethylene/propylene-b-styrene) (S-SEPS).\textsuperscript{58}

Several studies have shown that hydrocarbon backbone of polystyrene sulfonic acid (PSSA), when used as a PEM, degrades during fuel cell operation because C-H bond is weaker than C-F and less resistant to oxidative attack.\textsuperscript{59-63} The benzylic C-H bond is particularly sensitive to radical attack. In chemical degradation mechanism, cross-over oxygen from the cathode side or air bleed on the anode side, can react with hydrogen from the anode side and produce peroxides.\textsuperscript{64} The peroxides can decompose to peroxyl (HOO\textsuperscript{•}) and hydroxyl (HO\textsuperscript{•}) radicals by reacting with trace metal ions in the membranes. Peroxide radical attack causes decomposition of the membrane by attacking any reactive H-containing end groups present in the polymer. The reactive end groups can be formed during the polymer manufacturing process and may be present in the polymer in small quantities. The tertiary hydrogen at the α-carbon of the PSSA can also be attacked by actively oxidative radical species formed during fuel cell operation, which can cause chain scission (Figure 1.6a).\textsuperscript{65} Another cause for degradation of polymer chains is radical addition attacking the aromatic rings, resulting in forming benzylic radicals for subsequent attack (Figure 1.6b). These highly reactive radicals cause both mechanical and chemical instability in the membranes.
Figure 1.5. Chemical structures of (a) SPS, (b) sulfonated polystyrene-divinylbenzene (cross-linked PSSA), (c) S-SEBS, (d) S-SIBS, (e) S-HPBS, (f) S-SEP, and (g) S-SEPS
The other class of hydrocarbon membranes are sulfonated polyaromatic polymers. These membranes share similar advantages as polystyrene-based membranes: low cost, easy accessibility, easy processability. In addition, they have good thermal and chemical stability over sulfonated polystyrene membranes for fuel cell operation. This is associated to the higher bond energy in the C-H bonds of the aromatic rings than aliphatic C-H bonds. Furthermore, the backbone consisting of bulky and rigid aromatic rings allows the polymers to have high glass transition temperatures ($T_g > 200^\circ C$) and makes them potentially suitable for high temperature fuel cells.

Incorporation of sulfonic acid groups onto the polymer can be done by post-sulfonation to existing polymers or direct polymerization of sulfonated monomers. Post-sulfonation is commonly used to introduce ionicity to these polymers using strong acids such as sulphuric acid and chlorosulfonic acid. However, post-sulfonation does not provide precise control over the degree and location of functionalization and possible side reactions may occur. Direct copolymerization of sulfonated monomers would

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**Figure 1.6.** Chemical degradation mechanisms of PSSA membranes by (a) radical attacking at $\alpha$-carbon of PSSA, and (b) radical addition to the benzylic ring.
serve as a better approach to control structure and ion content for the sulfonated polyaromatic polymers.\textsuperscript{67-72}

The structures of representative sulfonated polyaromatic polymers are shown in Figure 1.7. These include sulfonated poly(phenylene oxide) (SPPO),\textsuperscript{73} sulfonated poly(ether ether ketone) (SPEEK),\textsuperscript{74, 75} and sulfonated polybenzimidazole (SPBI).\textsuperscript{76} The proton conductivity of SPEEK is observed to be similar to Nafion\textsuperscript{®} but SPEEEK has weaker phase separation and narrower channels for proton transport than Nafion\textsuperscript{®}.\textsuperscript{75} Due to the high water uptake, the long-term durability of SPEEK reduces at 80°C and 100% RH.\textsuperscript{74} Similar to SPEEK, SPPO and SPBI also possess less phase separation than Nafion\textsuperscript{®} and poorer mechanical stability because of excessive water swelling at high IECs.\textsuperscript{73, 76}

![Chemical structures of (a) SPPO, (b) SPEEK, (c) SPBI](image)

**Figure 1.7.** Chemical structures of (a) SPPO, (b) SPEEK, (c) SPBI

### 1.2.5. Polymer Blends

Blending different copolymers which contain distinct functionalities is commonly used to prepare materials with overall tailored properties in a more cost-effective way compared to designing one copolymer with all the desirable properties. Many early research efforts have been devoted to examining the phase separation and resulting morphology after blending Nafion\textsuperscript{®} with PVDF or its copolymer, PVDF-co-HFP.\textsuperscript{77-79} PVDF is frequently used for blending due to its chemical and thermal stability, and commercial availability. Its crystalline nature can provide enhanced strength into the
blend copolymers. Blending of various perfluorinated or partially fluorinated conducting polymers with non-ionic perfluorinated materials was patented by Hedhli and Billon. This type of blended membranes promotes clear phase-separated morphology and improves mechanical integrity of the membranes. Kyu et al. blended PVDF with Nafion® and observed partial miscibility below the crystalline melting point of PVDF, and that the spherulitic morphology, attributed to PVDF, is affected greatly by the solvent-casting technique and the blend composition, and they observed that the blends of PVDF with larger counterion tetrabutyl ammonium (TBA+) form Nafion® have weaker electrostatic cross-link interactions, resulting in a free-flowing melt and thus allowing for a more favorable mixing with PVDF. It is also interesting to notice that in both blend systems, the ionomer component in the blends still shows ionic aggregation of similar dimensions of hydrophilic domains to that of the pure ionomers. Lin et al. report that Nafion®/ VDF-HFP blends exhibit a two orders of magnitude decrease in proton conductivity, likely due to Nafion®/ PVDF blend membranes being poorly hydrated. However, methanol cross-over is significantly reduced on these tested blends. Song et al. prepared chemically-modified Nafion®/ PVDF blend membranes by dehydrofluorination and treated with sulfuric acid to compensate for the decreased conductivity. These blend membranes exhibit comparable conductivity and low hydrogen cross-over. The hydrophobic nature of PVDF resulting in a large decrease in water uptake appears to be one of the major limitations for blend membranes becoming commercially available.

In order to improve component compatibility, blend systems consisting of sulfonated poly(ether ketone ketone) (SPEKK) with different ion contents were studied. It has been found that the casting conditions such as temperature and solvent and composition of components have significant impact on the morphology. For instance,
membranes cast from NMP exhibit dispersed particles morphology whereas membranes cast from DMAc exhibit a co-continued morphology for SPEKK blends. SPEKK with higher IEC provides percolative pathways for proton transport and the lower IEC SPEKK restrains the overall swelling but is still possible providing a certain degree of ionicity.  

1.3. Morphological Studies of Nafion® Membrane

Previous research has observed that perfluorosulfonated polymers are promising materials with regard to having reasonably high proton conductivity for fuel cell applications. Nafion® has been used as the standard material for PEMFC research because of its excellent properties in terms of stability and reliability, performance and commercial availability. A great amount of literature has been done to investigate Nafion®'s nanostructure and morphology and the fundamental knowledge is potentially very useful for the development of new PEMs with improved properties over existing systems. Nafion® possesses crystalline and hydrophobic tetrafluoroethylene backbone sequence with perfluorinated vinyl ether side chains terminated with sulfonic acid groups as shown in Figure 1.2. Small angel x-ray and neutron scattering techniques (SAXS and SANS, respectively) have greatly used for morphological and structural study and indicated that Nafion® possesses a nanometer-sized, phase-separated morphology. Several structural models have been proposed to understand the transport properties of Nafion® membranes. A brief overview of the well-known models is described below.

Hsu and Gierke proposed a “cluster network model”, suggesting that the ionic sulfonic acid groups aggregate to form spherical ionic clusters. These inverted micelles with diameters of approximately 4-5 nm are interconnected by narrow channels with
widths of approximately 1 nm and embedded in the hydrophobic fluorocarbon matrix (Figure 1.8).\textsuperscript{15, 16} Gierke and co-workers estimated that each ionic cluster contains around 70 sulfonic acid groups for a fully hydrated acidified Nafion\textsuperscript{®} membrane.

![Cluster network model for the morphology of hydrated Nafion\textsuperscript{®}](image)

\textbf{Figure 1.8.} Cluster network model for the morphology of hydrated Nafion\textsuperscript{®}


Subsequently, Gebel proposed a conceptual model illustrating the morphological reorganization and continuity of the ionic domains in Nafion\textsuperscript{®} over a wide range of water contents according to the results of scattering analysis (Figure 1.9).\textsuperscript{17} This model starts with dry Nafion\textsuperscript{®} membranes (where IEC = 0.91 meq/g), which are proposed to contain isolated spherical ionic clusters with diameters of \(~ 1.5\) nm and an inter-cluster spacing (center-to-center separation distance) of \(~ 2.7\) nm. Due to poor connectivity between the isolated ionic clusters, proton conductivity in dry Nafion\textsuperscript{®} membranes is strictly limited. This result is consistent with Gierke's model at low water content. After the membrane absorbs water, the clusters swell to \(~ 2\) nm in diameter and form ionic domains, where water molecules are surrounded by sulfonic acid groups at the polymer-water interface. The inter-cluster spacing increases to 3 nm, but the ionic spheres are still isolated, thus, proton conductivity is still low. As the water content increases, the ionic clusters swell more to diameters of 4 nm with slight increase in inter-cluster spacing. With further
increase in water content at $X_v > 0.2$, a percolation threshold is reached, at which point
the previously isolated ionic domains are now connected by water channels, leading to a
significant increase in proton conductivity. As water content increases between $X_v = 0.3$
and 0.5, the morphology of the membrane resembles to comprise spherical ionic
domains with diameters from 4 nm to 5 nm, which are interconnected by cylinders of
water distributed in the polymer matrix. Proton conductivity increases steadily within this
range of water content. At $X_v > 0.5$, structural inversion occurs and the morphology
reorganizes to consist of a connected network of polymer rods surrounded by water. As
water content increases to a very high level ($X_v > 0.75$), the membrane dissolves into
solution and the structure transforms to a colloidal dispersion of isolated rods.

Later, Kreuer et al. revealed the phase-separated morphology of sulfonated
poly(ether ether ketone ketone) (S-PEEKK) and Nafion® for comparison according to
SAXS measurements (Figure 1.10) and examined the impact of distinct microstructure
on transport properties and swelling behaviour. While S-PEEKK possesses narrower,
highly branched, more dead-ends as well as less connected water-filled channels due to
less pronounced difference between hydrophilic and hydrophobic domains; Nafion®
exhibits wide, less branched, and more connected hydrophilic channels, which results in a more connected ionic pathway for proton transport. Moreover, larger separations between the tethered \(-\text{SO}_3^-\) groups in S-PEEKK cause lower proton conductivity and mobility with respect to Nafion®.

**Figure 1.10.** Schematic representation of phase-separated morphology of hydrated Nafion® and S-PEEKK


Later, a “water-channel network model” was proposed by Kim et al. based on SANS data, which describes that the hydrated clusters form locally cylindrical micelles (ionic domains) that merge randomly and form a water channel network as shown in Figure 1.11. They examined the relationship between the sorption behavior and the changes in membrane structure and realized a strong correlation between the inter-ionic
domain distance and water uptake. As water content increases, the water molecules are primarily accumulated in the phase-separated hydrophilic ionic domains without penetrating the hydrophobic fluorocarbon matrix. With increasing sorption time, the more water in the ionic domains, the longer inter-ionic domain distance, causing the mobility of polymer chains. Consequently, the matrix structure changes.

More recently, Schmidt-Rohr and Chen proposed a “parallel water-channel model”, which was obtained by quantitatively simulating the previously reported SAXS measurements of hydrated Nafion®. This model describes that water channels are aligned in parallel with the ionic side groups, forming cylindrical inverted micelles as shown in Figure 1.12a. At a hydration level of 20 vol% water, the densely packed cylindrical water channels have diameters of between 1.8 nm and 3.5 nm, with an

![Figure 1.11. Schematic representation of amorphous domain structure of perfluorinated sulfonic acid membranes (Nafion®), illustrating a water channel network consisting of interconnected cylindrical ionic domains.](image-url)
average diameter of 2.4 nm, stabilized by a shell of hydrophobic polymer backbones (Figure 1.12a and b) and have a persistence length of tens of nanometers. The polymer backbones parallel to the water channels grow elongated and cylindrical crystallites with cross-sections of \( \sim (5 \text{ nm})^2 \) (black area in Figure 1.12c), which form physical crosslinks and provide mechanical integrity of Nafion® membranes. The relatively wider parallel water channels identified in this model account for the excellent transport properties of hydrated Nafion®.

![Parallel water-channel model of Nafion®](image)

**Figure 1.12.** Parallel water-channel model of Nafion®: (a) Cross-sectional and side views of a cylindrical inverted micelle (water channel) aligned with the hydrophilic side chains and shelled by hydrophobic polymer backbone, (b) approximately hexagonal packing of several cylindrical inverted micelles, (c) cross-sectional view of cylindrical water channels (white) and the Nafion® crystallites (black) in the amorphous Nafion® matrix (gray)


According to several morphological models of Nafion® being proposed, it is generally agreed that phase separation occurs due to incompatibility of hydrophilic and
hydrophobic segments when the membrane is hydrated. The ionic groups aggregate to form ionic clusters which can form contiguous nanometer-sized hydrophilic channels/domains, responsible for the transport of protons that assist proton conduction in PEMs, whereas, the hydrophobic segments contribute to mechanical integrity and prevent from dissolving in the water. Besides, the water channels are controlled by the equilibrium driven between the internal osmotic pressure of the ionic clusters and chain elasticity of the polymer matrix.  

1.4. Mechanism of Proton Transport in PEMs

The study of proton conduction in PEMs is essential as it is very important to understand how high proton conductivity can be achieved in order to maximize fuel cell current densities. One of the factors affecting proton conductivity of PEMs is chemical structure such as composition, polymer architecture, sequence distribution, nature of acid group, and ion content. The nanostructure and morphology of the resulting membranes also have significant impact on proton conductivity. Furthermore, the water content in the membranes and operating conditions (i.e., operating temperature and relative humidity) have great influence on proton conductivity. Fundamental study on correlation of proton conductivity and these variables and mechanism of proton transport in PEMs is crucial and can be extremely useful for the design of advanced membranes.

As mentioned in the previous section, at a given level of hydration, phase separation occurs in PFSA membranes (e.g., Nafion® membranes). While the hydrophobic segments provide mechanical integrity to the membrane, the hydrophilic acid groups form interconnected, nanometer-sized ionic domains, allowing protons to transport within. Generally, proton conduction happens when protons dissociate from
the -SO$_3$H groups and are transported within the continuous water channels or bulk water. The degree of proton dissociation is greatly affected by water content of the membrane. Paddison et al. reported that three water molecules are required to dissociate the acid in PFSA ionomers and up to six water molecules are required for complete dissociation.\textsuperscript{95} Eikerling et al.\textsuperscript{96} stated that proton transport can occur with a minimal hydration level of 1-2 water molecules per sulfonic acid group via a proton “hopping” mechanism (also known as surface mechanism), where protons migrate between the sulfonic acid groups along the pore surface. Thus, closer proximity of the tethered sulfonic acid groups requires lower activation enthalpy using the surface mechanism, which would ease the transport of the protons and require lower water content.\textsuperscript{96, 97} The rate of proton transport via the surface mechanism can also be affected by the conformation of the polymer backbone, flexibility of the side chains, and the degree of sulfonation.

Proton transport is believed to occur via three competing mechanisms: the surface mechanism, the Grotthus mechanism, and the vehicular mechanism. A schematic illustration of these mechanisms is shown in Figure 1.13. As mentioned above, via the surface mechanism, protons “hop” between the sulfonic acid groups along the surface of the pore wall and are mediated by intermediate water molecules.\textsuperscript{96} The vehicle mechanism is a molecular diffusion process taking place in the aqueous channels, where water molecules act as vehicles to transport the protons as a single entity from one side of the membrane to the other.
Figure 1.13. Schematic representation of proton transport in fully hydrated Nafion® PEMs, illustrating the surface mechanism, the Grotthuss mechanism, and vehicle mechanism


Protons in bulk water are strongly associated with water molecules to form dynamic aggregates such as the hydronium ion (H₃O⁺), the Zundel ion (H₅O₂⁺), and the Eigen ion (H₉O₄⁺). The Grotthuss mechanism is a structural diffusion process taking place in bulk water ("water pool"), where protons are transferred across a chain of hydrogen bonds of water molecules followed by reorientation of the water dipoles (i.e., H₅O₂⁺, and H₉O₄⁺) as shown in Figure 1.13 and Figure 1.14. The Grotthuss mechanism depends on the formation and cleavage of hydrogen bonds of water molecules, which provide a transporting path for protons. The transformation process of hydrogen bonds between the H₅O₂⁺ and the H₉O₄⁺ is rapid as fast proton transfer is favoured in short and strong hydrogen bonds (Figure 1.14). Therefore, it has been believed that the rate of Grotthuss mechanism is faster than the vehicular mechanism in fully hydrated state. Since the rate of the transformation process of hydrogen bonds has great impact
on the mechanisms, any constraints to the dynamics of water molecules can reduce the mobility of the protons. Elliot and Paddison reported that at the minimally hydrated state ($\lambda \sim 2.5$), the dissociation of the protons and the formation of protonated aggregates (e.g., $H_5O_2^+$ and $H_9O_4^+$) can be controlled by the conformation of the fluorocarbon backbone conformation, side chain flexibility, degree of aggregation and association of acid groups, influencing the rate of proton transport.$^{25,100}$

Figure 1.14. Schematic representation of proton transport involving formation and cleavage of hydrogen bonds by the Grotthuss mechanism


It is possible for the abovementioned transport mechanisms all involve in the proton conduction in PEMs. Nevertheless, it has been realized that one mechanism may dominate over another according to the condition of the membrane (i.e., temperature and water content). It has been suggested that vehicle mechanisms are more dominate than the Grotthuss mechanisms with increasing temperature.$^{101}$ Furthermore, the water content of the membrane is a key factor. As described previously, the surface mechanism only requires a minimal of 1-2 water molecules per sulfonic acid group to occur. The vehicle and the Grotthuss mechanism, however,
require higher level of hydration. Zawodzinski et al. reported that the vehicular and the Grotthuss mechanisms both contribute to proton conduction at high water content, having the Grotthuss mechanism more dominant. However, as water content decreases, the number of hydrogen bonding interactions also decreases, causing a lower rate of formation and cleavage of hydrogen bonds of water molecules required for structural diffusion process in the Grotthuss mechanism. As a result, the vehicle mechanism becomes more dominant.

1.5. Structure-Property Relationships in PEMs

In the previous sections (1.3 and 1.4), the morphologies and proton conduction of PEMs using modeling and simulation techniques, which provide profound insights in the field of PEMFC, were reviewed. Examining possible correlations among chemical structure, morphology and proton conductivity using experimental studies is relatively less developed. Over the past decades, a tremendous amount of effort has been focused on the study of structure-property relationships in PEMs to understand the relationships amongst molecular structure, crystallinity, morphology, water content, and ionic conductivity. Several review articles summarize and highlight the recent studies, and emphasize the importance of structure-property relationships on the development for PEMFCs. PEM properties such as water sorption and proton conductivity are determined by their polymer architecture, microstructure and morphology. With the advent of robust synthetic strategies and methodologies, the development of model polymers with controlled microstructures, which phase separate into nanometer ionic and hydrophobic domains, can provide more effective fundamental understanding about
the influence of morphology upon proton conduction and other PEM properties compared to the random “hit or miss” approach.

1.5.1. **Correlation Between Morphology and Proton Transport**

Well-defined, sulfonated, acid-bearing block copolymers are excellent model systems to examine the effect of morphology and nanostructure on proton conductivity in PEMs. Micro-phase separation, which is driven by the enthalpy associated with the de-mixing of incompatible components in block copolymers, can result in numerous distinct morphologies.\textsuperscript{110} Further separation into macro-phase separation, though, is prevented by chemical bonds between segments. The variety of different morphologies that result from phase separation can be controlled by the extent of dissimilarity between copolymer blocks, block copolymer architecture, degree of polymerization (chain length of each block), volume ratio of the blocks and crystallizability. Different morphologies as a function of the interactions between the two blocks ($\chi N$, where $\chi$ and $N$ represent Flory-Huggins segmental interaction parameter of two blocks and overall degree of polymerization, respectively) and the volume fraction of the two blocks ($f_{PI}$) are displayed in the morphological phase diagrams for a series of polyisoprene-polystyrene (PI-PS) diblock copolymers shown in Figure 1.15.\textsuperscript{111} $\chi N$ is the thermodynamic mismatch between the two kinds of monomers and controls the degree of segregation between two block components. The diagram shows that when $\chi N$ is larger than 20, the volume fraction of the polyisoprene block can lead to different morphologies (i.e., spheres, cylinders, and lamellae) for the PI-PS diblock copolymers.
Figure 1.15. Morphological phase diagram for linear PI-PS diblock copolymers as a function of $\chi N$ and volume fraction of the block component ($f$).


The morphology and properties of PEMs are strongly associated. Elabd et al. examined the transport properties of a triblock copolymer, partially sulfonated poly(styrene-b-isobutylene-b-styrene) (S-SIBS). It has been reported that as ion content increases, the morphologies change from a periodic lamellae morphology to a non-periodic co-continuous morphology as shown in Figure 1.16. The lamellae (LAM) morphology possesses ionic channels oriented perpendicular to the direction of transport, which is detrimental to proton transport; while the co-continuous morphology provides an array of ionic channels that are in the same direction of transport, thus, increasing the mobility of protons. The authors also examined the effect of casting
solvent on the morphology and proton conductivity and realized that membranes cast
from tetrahydrofuran (THF) have the highest proton mobility and membranes cast from
chloroform have the lowest proton mobility.

Figure 1.16. Schematic diagram illustrating morphological change with increasing ion
content for S-SIBS copolymers

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Winey, K. I. 39, (1), 399. © 2006, American Chemical Society.]

The orientation or the alignment of domains and their degree of ordering is vital
to proton transport. Soboleva et al. conducted a study by examining the effect of
anisotropy of ion channels upon proton conductivity. This was done by measuring the
ratio of in-plane conductivity to through plane conductivity of various morphological
structures for a series of diblock copolymers of sulfonated poly([vinylidene difluoride-co-
hexafluoropropylene]-b-styrene (P[VDF-co-HFP]-b-SPS). The TEM micrographs of
examined samples are shown in Figure 1.17. It has been found that for lamellae and
perforated lamellae (HPL) morphologies, higher in-plane proton conductivities were obtained, revealing ionic conducting pathways are oriented along the plane of the membrane. The disordered morphology was found to exhibit slightly higher through-plane proton conductivity than lamellae morphology, which is beneficial for the design of the MEA in PEMFCs.

![Figure 1.17. TEM micrographs of (a) Nafion® and P[VDF-co-HFP]-b-SPS with (b) disordered morphology, (c) perforated lamellae morphology, and (d) lamellae morphology

More recently, Balsara and co-workers studied morphologies for a series of symmetric diblock copolymers containing sulfonated polystyrene and poly(methylbutylene) (sPS-b-PMB) of various ion content and molecular weight (mol. wt.) under different relative humidity and temperatures.\(^{113-116}\) It has been found that for copolymers possessing low mol. wt. (< 6200 g/mol) with volume fractions ~ 0.5 for each block, disordered morphologies were obtained because of low segregation strength. The degree of sulfonation is shown to have great impact on resulting morphologies for low mol. wt. copolymers. With degree of sulfonation (DS) between 0 and 44.7%, disordered morphologies change to gyroid, then lamellae (LAM), followed by
hexagonally perforated lamellae (HPL) morphologies.\textsuperscript{114} For copolymers possessing higher mol. wt. (\textgreater 7700 g/mol), morphologies change from lamellae to hexagonally perforated lamellae and hexagonally packed cylinders (HEX). For high mol. wt. copolymers, the gyroid morphologies disappear and a new morphology of HEX occurs. Furthermore, coexistence of two morphologies – LAM and HPL were found for high mol. wt. copolymers, which the authors associated to the distribution of sulfonation in term of DS and their positions on the polymer chains. The authors also examined the correlation between proton conductivity and morphology in the series of copolymers.\textsuperscript{117} In particular, Parker and Balsara \textit{et al.} applied various processing techniques such as solvent casting, pressing, shearing and electric field alignment to prepare membranes with different domain orientation as shown in Figure 1.18. It was reported that the pressed sample exhibited highest anisotropic proton conduction, revealing large differences between in-plane and through plan proton conductivity.

\textbf{Figure 1.18.} 2D SAXS patterns and schematic representation of domain orientation of membranes prepared by indicated methods

[Reprinted with permission from \textit{Macromolecules}, Park, M. J.; Balsara, N. P. 43, (1), 292 © 2010, American Chemical Society.]\textsuperscript{117}
1.5.2. Structure-Property Relationships in PEMs

Copolymer Architecture

As mentioned in the last section, major factors such as copolymer architecture, components’ dissimilarity and crystallizability can have significant impacts on microphase separation, resulting in different morphologies. Investigating the effect of copolymer architectures on morphology and properties of the membranes such as proton conductivity and water content allows further understanding in the design of novel membranes. A wide range of copolymer architectures, which are commonly used to fabricate PEMs, are illustrated in Figure 1.19. These copolymer architectures are identified by the arrangement of repeating units in the polymer chain.

Random copolymers possess repeating units distributed in a statistical fashion. Alternating copolymers comprise alternating repeat units along the main chain. Block copolymers are linear polymers possessing one or more uninterrupted sequences of each repeat unit and can be further sub-categorized as diblock, triblock, multiblock, and

![Illustration of various copolymer architectures](image-url)
star block. Graft copolymers may be considered as a special type of block copolymers and they are identified as having a graft chain of a different repeat unit to the main chain. The sequential runs of random copolymers and alternating copolymers are usually too short to cause phase separation and thus, they usually exhibit a single-phase morphology. Nevertheless, block and graft copolymers are able to produce a variety of morphologies because their segments are mutually incompatible due to differences in chemical composition.

Model polymers with controlled polymer architectures, chemical structures, and polymer composition are commonly used to ensure more efficient and systematic research on a fundamental understanding of structure-property relationships in PEMs. Diblock and graft copolymers are ideal candidates for structure-property relationship studies. A proton conducting material of a diblock would possess a length of ionic and non-ionic polymer. Controlling the length of the blocks would allow structure-property relationships to be studied. Since the ionic block structures easily dissolve in water, phase separation could be reduced. The use of a highly hydrophobic non-ionic block such as fluoropolymers improves phase separation. Several groups examined the effects of fluoro-blocks upon copolymers.\textsuperscript{119-123} Ghassemi \textit{et al.}\textsuperscript{119} prepared sulfonated-fluorinated poly(arylene ether) multi-blocks and discovered that these copolymers showed a well-defined phase separation and exhibited high conductivity (Figure 1.20a). Shi \textit{et al.} have also studied flouro-containing blocks such as poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-co-HFP))\textsuperscript{120, 121}, which exhibit an interconnected network of ionic channels of 8 -15 nm in diameter for the membranes possessing IEC \textasciitilde 0.6 – 1.2 mmol/g. and similar proton conductivity to Nafion\textsuperscript{®} 117 was observed (Figure 1.20b).
Yang et al. examined sulfonated poly(sulfone-\textit{b}-vinylidene fluoride)\footnote{122, 123}, which show enhanced phase separation and resulted in improved proton conductivity (Figure 1.20c).

\begin{align*}
\text{(a)} \quad & \quad \begin{array}{c}
\text{O} - \text{SO}_3\text{H} \\
\text{HO}_3\text{S} \\
\end{array} \\
\text{O} - \text{Ar}_x - \text{O} - \text{Ar}'_y - \text{O} - \text{CF}_3 \\
\text{CF}_3 \\
\end{array} \\
\text{(b)} \quad & \quad \begin{array}{c}
\{\text{CF}_2\text{CF}_2\}_x \{\text{CF}_2\text{CF}_2\}_y \{\text{CH}_2\text{CH} \} \{\text{CH}_2\text{CH} \}_m \\
\end{array} \\
\text{(c)} \quad & \quad \begin{array}{c}
\{\text{CF}_2\text{CF}_2\}_m \text{CH}_2\text{CF}_2 \text{CF}_3 \\
\end{array}
\end{align*}

\textbf{Figure 1.20.} Chemical structure of (a) sulfonated-fluorinated poly(arylene ether) block copolymers, (b) P(VDF-co-HFP) and sulfonated poly(sulfone-\textit{b}-PVDF)

Graft copolymers possess a different moiety in the side chain versus in the main chain. The length of the graft chain can affect the size of ionic domains and the number density of graft chains can determine the number of ionic domains per unit volume.\footnote{12} Both the size and number density of ionic clusters control the degree of connectivity between ionic domains. Therefore, if the length and the number density of graft chains can be controlled, systematic studies of the effect of molecular structure on morphology and PEM properties can be developed.

The most extensively studied graft copolymers in the form of PEMs are those having ionic sulfonated polystyrene graft chains onto fluorinated matrices such as hexafluoropropylene (FEP),\footnote{124-127} PVDF,\footnote{128-133} and ETFE.\footnote{126, 134} Ionic conductivity can be
introduced to the graft chains through post-sulfonation reactions while maintaining the desirable mechanical integrity associated with the base polymer. A novel class of well-defined graft copolymers containing styrenic main chain and styrenesulfonic acid graft chains (PS-g-PSSA) was prepared by Ding et al.\textsuperscript{135-137} The authors compared the graft copolymers of PS-g-PSSA with random copolymers of styrene and styrenesulfonic acid (PS-r-PSSA) and realized that the more structurally ordered graft copolymers exhibit higher proton conductivity.\textsuperscript{135} Figure 1.21 displays two copolymers' structures and their TEM micrographs, where no clear phase separation is visible for PS-r-PSSA, while, sharp and well-defined microphase separation and a network of ionic channels are observed for PS-g-PSSA. It has been learned that polymer architectures can affect morphology significantly, consequently influencing PEMs' properties. Furthermore, graft copolymers with more ordered structures promote higher levels of phase separation, resulting in higher proton conduction.

![Figure 1.21. Chemical structures, TEM micrographs and proton conductivity of PS-r-PSSA and PS-g-PSSA](image)

[Reprinted with permission from Chemistry of Materials, Ding, J.; Chuy, C.; Holdcroft, S. 13, (7), 2231, © 2001, American Chemical Society.]\textsuperscript{135}
Furthermore, Tsang and Holdcroft et al.\textsuperscript{138} examined structure-property relationships of graft and diblock ionic copolymers containing fluorous and sulfonated polystyrene segments. The two copolymers are designed to possess similar chemical compositions but different architectures as shown in Figure 1.22. Two types of copolymers resulted in distinct nanoarchitectured morphologies, which greatly influence their PEM properties. Diblock copolymers exhibit a higher degree of long-range ionic order; however, this appears to cause the membranes to swell excessively, leading to dilution of proton concentration and thus reduced proton conductivity. On the other hand, graft copolymers exhibit disordered cluster morphology and are observed to tolerate higher ion contents without excessive swelling and thereby possess better mechanical properties. Furthermore, with IEC around 2 mmol/g, graft membranes are able to reach proton conductivity values similar to that of Naion\textsuperscript{®} 117. Based on these intriguing results, further investigation on the graft copolymers would be worthwhile.

![Chemical structures](image)

**Figure 1.22.** Chemical structures, TEM micrographs and proton conductivity of graft P(VDF-co-CTFE)-g-SPS and diblock P(VDF-co-HFP)-b-SPS copolymer

Polymer Components’ Dissimilarity

In addition to copolymer architectures, which can greatly influence PEM’s morphology and property, dissimilarity between polymer’s segments has significant impact on the morphology and consequently affects their properties. Miyatake, Watanabe and coworkers examined the impact of the size of the hydrophobic components on the properties of sulfonated poly(arylene ether sulfone)s (SPAES) (Figure 1.23). The authors realized that as the volume dimensions of the hydrophobic components decrease from SPE1 to SPE4, the size of ionic domains increase accordingly. For instance, SPE4 has the largest size of ionic domains and more defined ionic clusters, which possess higher proton conductivity.

Figure 1.23. Chemical structures and TEM micrographs of sulfonated poly(arylene ether sulfone)s with different volume size of hydrophobic segments
[Reprinted with permission from *Macromolecules*, Bae, B.; Miyatake, K.; Watanabe, M. 42, (6), 1873, © 2009, American Chemical Society.]

Moreover, Miyatake, Watanabe and coworkers investigated poly(arylene ether)s with superacidic perfluorosulfonic acid groups. It was discovered that the strong acidity of perfluorosulfonic acid group (pKa < -6) facilitates proton dissociation and
enhances phase separation between hydrophilic and hydrophobic domains. As a result, the superacid-bearing membranes exhibit much higher proton conductivity relative to typical sulfonated poly(arylene ether)s, which have sulfonic acid groups directly attached to aromatic rings (pKa ~ -1 for aromatic sulfonic acid group).

Recently, Hickner and coworkers have examined the effect of the location of sulfonated block, the composition, and the properties of the unsulfonated blocks on PEM's properties.\textsuperscript{142} The ABA triblock copolymers consist of a hydrophilic block containing SPS located in the center and hydrophobic outer blocks containing either a hydrocarbon (poly(hexyl methacrylate), PHMA) or a partially fluorinated (poly(perfluorooctyl methacrylate), PFMA) block. Intuitively, the fluorinated components would increase the degree of phase separation between hydrophilic and hydrophobic domains and result in higher proton conductivity compared to the hydrocarbon component. Both copolymers were observed to show phase separation. However, SAXS results reveal that the partially fluorinated PFMA-based membranes exhibit a lesser degree of order and lower proton conductivity. This is attributed to a combination of the higher glass transition temperature ($T_g$) and lower solubility of PFMA during the solvent casting process, causing decrease in microphase separation.

\textit{Effect of Crystallinity on PEMs}

Crystallinity is another important factor, which can affect morphology and property of PEM materials. The structure of a polymer greatly affects its crystallinity. If the structure is regular and orderly, it will pack into crystals easily. Normally, the degree of crystallinity of polymer molecules is semi-crystalline, consisting of a few of randomly oriented crystalline domains in amorphous phase. Some highly crystalline polymers include polypropylene, syndiotactic polystyrene and Nylon. Highly amorphous polymers
include poly(methyl methacrylate), atactic polystyrene and polycarbonate. Crystallinity is an important area to study because it can influence phase separation,\textsuperscript{12} consequently having an impact on mechanical property and morphological related properties such as water uptake and proton conductivity of PEMs.\textsuperscript{143, 144} A high degree of crystallinity remaining in a membrane not only can enhance its mechanical property but can also suppress excessive water swelling in PEMs.

Many groups have utilized SAXS and WAXS to investigate the structure and crystallinity, respectively. Nafion\textsuperscript{®} is a crystalline polymer and its degree of crystallinity has been reported between 0 to 40\%, calculated from the relative intensity of the amorphous halo and crystalline peak.\textsuperscript{15} It has been reported that the crystallinity of Nafion\textsuperscript{®} decreases with increasing IEC values.\textsuperscript{15, 94, 145} According to WAXS data, the crystallinity of Nafion\textsuperscript{®} 117 (IEC ~ 0.91 mmol/g) has been estimated to range between 5 to 20\%.\textsuperscript{15} Kim,\textsuperscript{87} Schmidt-Rohr,\textsuperscript{93} and van der Heijiden et al.\textsuperscript{94} suggested that the stiff polymer backbone contains 10 vol\% crystallites, which form parallel, elongated and cylindrical crystalline domains to help align the water channels.

Kim \textit{et al.} investigated the effect of structure on the crystallinity, subsequently affecting phase separation and yielding different morphologies. It was revealed that the nanostructure is greatly dependent on the distribution of side chains along the backbone and the sample thickness. For polymer chains with a longer linear chain sequence, chain segments form semi-crystalline lamellae as shown in Figure 1.24a; whereas, chains with a shorter chain sequence may crystallize in a fringed micelle shape (Figure 1.24b and c). No crystallization occurs, however, when the cooling process is fast enough (Figure 1.24d).
Several studies have investigated the effect of crystallinity in Nafion® upon water sorption and conductivity in the PEMs and methanol permeability. Park and Yamazaki have prepared Nafion®/Hydroxyapatite (HA) composite membranes with higher crystallinity compared to cast Nafion®. They have found that the crystallinity of composite membranes increases with increase of HA content. With an increase in crystallinity from 28% in cast Nafion® up to 38% in the composite membranes, water uptake decreases from 31% down to 18%. The composite membranes incorporating HA into Nafion® with higher crystallinity and lower water uptake were found to suppress methanol permeability and methanol crossover. Park and Yamazaki also prepared
another type of composite membranes incorporating calcium phosphate (CP) into Nafion® which exhibit lower methanol crossover and higher proton conductivity compared to the cast Nafion®. The Nafion®/CP composite membranes were evaluated to have higher degree of crystallinity, which enhance their mechanical and thermal properties and moderate water uptake to decrease methanol crossover. Sacca used a well-defined doctor-blade casting method to recast Nafion® membranes with higher crystallinity and also discovered that increasing the crystallinity leads to an increase in the elastic energy of the polymer matrix, thereby lowering the swelling behavior of the re-cast membranes.

Moore and Martin studied Dow's perfluorosulfonic acid ionomers (PFSA), which were structurally and morphologically similar to that of Nafion®, having both crystalline and ionic domain structures. These ionomers were prepared to have shorter side chains than Nafion®. SAXS was used to show that PFSAs contain ionic clusters, and their sizes altered with ion content and water content. WAXS and differential scanning calorimetry (DSC) were used to show that the PFSIs with lower ion content possess higher crystallinity than PFSIs with higher ion content and the crystalline domains can serve as barriers to solvent swelling to a lower water uptake.

Gebel et al. revealed that by annealing Nafion® membranes at temperature higher than 80°C, the size of the crystalline domains can be increased and long-range order in the membranes can be obtained. Later, Moore and Martin examined Nafion® membranes solution-cast at high temperature (> 125 °C) and low temperature (< 70 °C) and realized that the high-temperature, solution-cast membranes are partially crystalline and possess better mechanical properties. Low-temperature solution-cast membranes possess poor mechanical properties and higher water uptake. The authors
suggested that the crystalline domains act as crosslinks, providing a rigid matrix to oppose excessive swelling.

According to the previous studies, it was learned that several factors affect crystallinity (i.e., temperature\textsuperscript{143, 150}, ion content\textsuperscript{15, 94, 145} and chain sequence between side chains and thickness\textsuperscript{87}), subsequently leading to different phase separation, and having great impact on mechanical properties and water uptake\textsuperscript{143-150}. However, how does each of these factors affect crystallinity and membrane’s properties is still poorly understood. Thus, examining the relationship between crystallinity, phase separation, and the morphological-related properties such as water uptake and proton conductivity using model polymers in a systematic approach is beneficial to gain fundamental insights in PEMFCs research.

1.6. Research Overview

Up to now, Nafion\textsuperscript{®} and other PFSA membranes are still the preferred class of PEMs for PEMFC operating under ambient conditions. However, due to its drawbacks such as limited operating temperature (usually below 80 °C), expensive cost and challenging synthesis, widespread commercialization of PEMFCs is still difficult. Thus, development of novel advanced materials with lower cost and improved properties is highly desirable. An iterative or random “hit or miss” method is generally not efficient for developing desirable membranes. A more effective strategy to design ideal PEMs would be to gain fundamental insight into the structure-property relationships in PEMs before attempting to design a new PEM material.
From the overview provided in Chapter 1, it was revealed that polymer architecture, chemical composition, ion content, crystallinity, polymer dissimilarity between segments can greatly influence phase separation – affecting aggregation and connectivity of ionic domains and consequently have significant impact on water sorption and proton transport. It has been reported that graft copolymers possess more defined phase separation over random copolymers, enhancing proton conductivity and they exhibit disorder cluster morphology, which has less swelling compared to diblock copolymers having lamellae morphology with excessive swelling. Graft copolymers demonstrate excellent properties and their unique architecture allows further in-depth studies – e.g., the effect of graft side chain length and graft density on morphology and PEM properties. The objective of this research is to expand fundamental knowledge of structure-morphology-property relationship on model graft copolymers and gain understanding into preferred structures for design of next generation membranes.

In Chapter 2, an overview of synthetic methods utilized to produce the model polymer system studied in this thesis is provided. This includes ATRP, a greatly developed approach to synthesize polymers with well-defined structure with low polydispersity distribution and post-sulfonation. Descriptions of the instruments and techniques used to characterize the resulting polymers and membranes are included. These include gel permeation chromatography (GPC), water sorption measurements, acid-base titration, AC impedance spectroscopy for measurements of proton conductivity, TEM and WAXS.

In Chapter 3, structure-property relationships based on a completely new series of fluorous ionic graft copolymers, sulfonated poly([vinylidene difluoride-co-chlorotrifluoroethylene]-g-styrene) (P[VDF-co-CTFE]-g-SPS) are described. This section
is based on published work, which reports the nanostructure, morphology, and properties of fluorous-graft-ionic model copolymer, which are purposely synthesized to possess nearly constant graft density but various graft lengths to examine the effect of ionic graft chain lengths on membrane morphology and properties. The number density of the polymers is reduced so as to enhance the crystallinity of the membranes. Graft density effect is also discussed by comparing with a previously reported series of graft copolymers, which has higher graft density, hence lower crystallinity. A thorough description of correlations between polymer structure (ion content, graft chain length, number density of graft), degree of crystallinity, the size and nature of the ionic domains, water sorption, and the proton conductivity is examined. Furthermore, proton conductivity as a function of RH and temperature for membranes with high IEC is investigated.

In Chapter 4, the study of graft copolymer blends with controlled microstructure is described. One highly sulfonated graft copolymer described in Chapter 3, is used to blend with a highly hydrophobic component: a low mol. wt. PVDF and a high mol. wt. PVDF to distinguish the effect of crystallinity and chain entanglement on water sorption and proton conductivity of PEMs. The work describes how the nanostructured morphology changes or remains unchanged, as samples of PVDF of different mol. wt. are blended with the sulfonated graft copolymer. Interesting results between water uptake, proton conductivity, acid concentration, and proton mobility were observed. Moreover, a series of graft blend membranes containing different ratios of ionic graft copolymer and high m. wt. PVDF are prepared to investigate the optimal blending ratio for controlled swelling and promising proton conductivity. Results of how these membranes perform under limited RH and high temperature are also provided. The
blending approach offers to prepare membranes with overall tailored properties in a more efficient way as opposed to developing a new copolymer with all the desirable properties.

Chapter 5 is based on published work, which is a continuous study to the work described in Chapter 4, investigating a completely new sulfonated graft copolymer with even lower graft density than the ones described in previous Chapters and three fully sulfonated graft copolymer blend membranes. The low-graft-density copolymer and the three graft blends contain similar volumetric percentage (vol%) of hydrophobic and hydrophilic components to ensure meaningful comparison. Three graft copolymers of different graft length described in Chapter 3 are fully sulfonated to yield membranes with very high ion content (short, medium, and long graft copolymers possessing 3.52, 4.05, and 4.29 mmol/g, respectively). Membranes with high ion content are favoured because they tend to have more connected ionic domains and promote better proton conductivity, but suffer from excessive swelling and dissolving in water. Thus, a blending approach is applied here, in which the fully sulfonated graft copolymers are mixed with a high mol. wt. PVDF with the intention to reduce swelling and improve the mechanical integrity in the membranes. This work represents an advancement of previous studies as it shows the advantage of blending fully sulfonated graft copolymers to eliminate the uncertainty from any of the unsulfonated polystyrenes remaining in the structure of partially sulfonated graft copolymers, hence, allowing a more precise investigation on formation of ionic channels. Furthermore, completing sulfonation of polystyrenes leads to closer proximity between sulfonated groups, which is expected to enhancing connectivity between ionic domains. The three fully graft sulfonated blends are also used to compare with their pristine series of partially sulfonated graft copolymers described in
Chapter 3. Intriguing results of comparison are revealed. A detailed analysis of nanostructure, morphology and properties of these graft blends is given.

Finally, a summary of the primary examination observed from this thesis and potential future work are provided in Chapter 6.
Chapter 2. Synthetic Routes and Characterization

In order to prepare model polymers with controlled microstructures, controlled radical polymerization techniques were used. In this chapter, a general overview of synthetic polymerization techniques and post-sulfonation is introduced. Several characterization techniques used to evaluate the resulting polymers and an overview of membrane preparations and definitions of membrane properties are followed.

2.1. Atom Transfer Radical Polymerization

Radical polymerization is the most widely used synthetic method for producing polymers and material composites in industry, such as plastics, rubbers and synthetic fibers. Free radicals have extremely high chemical reactivity, allowing radical polymerizations to be powerful and versatile polymerization techniques. In addition, radical polymerizations are relatively convenient to handle experimentally with respect to other polymerization techniques. For instance, they can be carried out in the bulk, solution, suspension and emulsion phases; the reaction only requires moderate reaction temperatures (typically from room temperature to 140°C according to the monomers and initiators used in the reaction); the purity of reagents used is less demanding in comparison to other methods (e.g., anionic polymerizations); and high tolerance to several functional groups (e.g., acid, amino, hydroxyl), making the protection of functional groups generally unnecessary. Radical polymerizations are carried out
through a sequence of multiple steps: initiation, propagation, and termination. A generalized mechanism of radical polymerizations is shown in Figure 2.1.

**Figure 2.1.** Mechanisms of radical polymerizations

Initiation is the first step of a radical polymerization. During this step, an initiator forms initiating radicals (Figure 2.2a), \( R'^* \), which reacts with a monomer, M, to initiate chain growth. Examples of an initiation reaction are shown in Figure 2.2b. Typical initiators used in radical polymerization are compounds that can generate free radicals by photolysis, thermal decomposition, or redox reaction such as organic peroxides, azoisobutyronitrile (AIBN), organometallic compounds, and \( \text{K}_2\text{S}_2\text{O}_8 \). Free radicals can also be produced from monomer by heat or radiation with light or high-energy sources such as X-rays.

Propagation is the process whereby the polymer chain length increases. This step involves sequential addition of monomers to the active radical chain ends. While
the radical reacts with the $\pi$ bond of the monomer to form a stable bond with the carbon, an unpaired electron stabilizes the second carbon atom, reforming another radical site after each addition (Figure 2.2c). The radical growing species in radical polymerizations are typically organic free radicals, which can be stabilized by resonance, inductive and/or polar effects.

Termination may occur by several different mechanisms. Combination occurs when two active radical polymer chain ends couple together to form one long chain, which can result in polymers with high molecular weights (Figure 2.2d). Disproportionation involves the abstraction of a hydrogen atom from one chain to another, which generates two polymers with different chemical structures – one with a terminal saturated group and the other with a terminal unsaturated group (Figure 2.2e). Chain transfer occurs when the free radical site is transferred to a chain transfer agent, consequently, the agent that gains the radical site can initiate a new chain and the molecule that loses the radical site is terminated (Figure 2.2f). The chain transfer agent (XY in Figure 2.1) can be a solvent, initiator, monomer, or polymer. If the chain transfer agent is a solvent or a monomer, the newly formed radical is often not capable of further propagation. A chain transfer reaction usually generates polymers with low molecular weight. At elevated temperatures, an increase in the ratio of rate of propagation to rate of termination can be observed, which leads to better control of polymerization. However, chain transfer and other side reactions also become more competitive at higher temperatures. Therefore, determination of optimal temperature for the polymerization depends on the monomer, catalyst and the desired molecular weight.\textsuperscript{152}
Figure 2.2. Examples of reactions in radical polymerization: (a) formation of initiating species, (b) initiation, (c) propagation, (d) chain termination by combination of two active radical chain ends, (e) termination by disproportionation, and (f) chain transfer

Due to irreversible termination and chain transfer reactions, conventional radical polymerization exhibits poor control of molecular weight, molecular weight distribution, and composition of the polymers, thereby restricting the synthesis of polymers with well-defined architectures and functionalities. To overcome the drawbacks, “living”/controlled radical polymerization methods have been developed, in which, the irreversible termination and chain transfer processes can be effectively restrained to produce structurally well-defined polymers with low polydispersities. Generally, requirements for a livingcontrolled radical polymerization include the following features:

- Chain transfer or other termination reactions are suppressed.
- Narrow molecular weight distribution with low polydispersities.
- Polymerization continues until all of the monomers consumed and chain growth proceeds upon further addition of monomers.
- Initiation process is faster than propagation – all polymer chains start to grow at the same time.
- Degree of polymerization (DP) versus time is linear.
- Molecular weight ($M_n$) is linear function of monomer conversion – which allows $M_n$ to be controlled by the ratio of consumed monomer and initiator added.

- Graft or block copolymers can be prepared by sequential addition of different monomers.

Living/controlled radical polymerizations rely on a dynamic equilibrium between active radical species ($M_n\cdot$) and their corresponding dormant species ($M_n-X$). The equilibrium reaction is illustrated in Figure 2.3.

![Equilibrium reaction of living/controlled radical polymerizations](image)

Figure 2.3. Equilibrium reaction of living/controlled radical polymerizations

Catalyst Y activates the dormant species ($M_n-X$) to produce active radical species ($M_n\cdot$), which subsequently reacts with additional monomers to generate the active propagating radical chain ($M_{n+1}\cdot$). In living/controlled radical polymerizations, chain transfer and termination are effectively suppressed because the rate constant of deactivation ($k_{deact}$) is much larger than the rate constant of activation ($k_{act}$) ($k_{act}/k_{deact} \sim 10^{-4} - 10^{-10}$), causing the equilibrium to favour the dormant species. The active species can be reversibly deactivated by coupling with X-Y to reform the dormant species ($M_n-X$). As a result, the concentration of active radical species is very low ($\sim 10^{-9}$ M) and the propagation rate of polymerization is reduced. This is advantageous to prevent termination or chain transfer occurring, which helps to have better control in synthesizing polymers with well-defined structures, controlled composition and molecular weights.

Atom transfer radical polymerization (ATRP) is the most widely studied living/controlled radical polymerization technique, developed by Wang and
Matyjaszewski in 1995.\textsuperscript{156} ATRP inherits the merits of living/controlled radical polymerization system (e.g., facile to perform under very standard experimental conditions and able to produce well-defined polymers); additionally, it allows for the controlled polymerization of a wide variety of monomers, including styrene, (meth)acrylates, (meth)acrylamides, and acrylonitrile.\textsuperscript{157} To perform ATRP, an initiator with a transferable halogen (R-X, the dormant species, where X is the halogen atom) and a transition metal catalyst (Mt\textsuperscript{n}-Y/Ligand, where Y is a counterion) are typically used with the choice of the monomer (M). A typical mechanism of ATRP is shown in Figure 2.4, where the halogen atom is abstracted by the transition metal catalyst, producing a radical species (R•) and an oxidized species (Mt\textsuperscript{n+1}-Y/L).\textsuperscript{152, 158} Since \( k_{\text{deact}} \) is typically much larger than \( k_{\text{act}} \), the dynamic equilibrium is predominantly shifted toward the dormant species, lowering the concentration of the active radicals thus lowering the probability of chain transfer and termination. The radical species reacts with a monomer to generate a propagating radical (P•), which can be reversibly deactivated by the oxidized species (Mt\textsuperscript{n+1}-Y/Ligand) to transform into the dormant species (P-X) “capped”/protected by the halide without undergoing termination. The reversible deactivation process of propagating radical chains allows uniform growth of polymer chains without being interfered by chain transfer and termination. Thus, polymers with predetermined molecular weight, composition, and microstructure can be achieved.

![Figure 2.4](image-url)

\textbf{Figure 2.4.} General mechanisms of ATRP illustrating (a) initiation, (b) equilibrium, and (c) propagation
The transition metal catalyst plays a significant role in ATRP, which controls the equilibrium constant between the active radical and dormant species.\textsuperscript{152} If the equilibrium constant is too small, it can slow or even restrain the polymerization; on the other hand, if the equilibrium constant is too large, it can cause chain transfer and termination, losing control of polymer chain lengths. Requirements for a suitable metal catalyst include:

- Having two accessible oxidation states, separated by one electron;
- Having reasonable affinity for a halogen;
- The coordination sphere around the metal should be expandable when it is oxidized to accommodate the halogen;
- The ligand should strongly complex the metal catalyst.

The most common transition metal catalyst used in ATRP is copper due to its versatility. Nitrogen-based ligands such as bipyridine and diethylenetriamine are commonly used for copper-based catalysts.

In ATRP, the initiator determines the number of growing polymer chains.\textsuperscript{152} A faster initiation leads to lower probabilities of terminations and chain transfer, thus, yielding a consistent number of growing chains equal to the initial initiator concentration. Alkyl halides (R-X) with activating substituents on the α-carbon such as aryl, carbonyl, or allyl groups are commonly used. The halide group should be able to rapidly and selectively transfer between the propagating radical chains and the transition metal complex. Bromine and chlorine are good choices for achieving molecular weight control whereas fluorine is not suitable because the C-F bond is too strong to undergo homolytic cleavage. Macroinitiators consisting of the initiating substituents attached to the macromolecular species can be used to synthesize polymers with predetermined architectures as illustrated in Figure 2.5.\textsuperscript{159} For instance, if the initiating halides are
attached at the chain ends of the macroinitiators, diblock copolymers can be obtained; whereas, if they are attached on the side chains of the macroinitiators, graft copolymers can be prepared. Furthermore, star copolymers can be synthesized by using macroinitiators with multiple alkyl halides on a single core.

![Diagram](image)

**Figure 2.5.** Schematic diagrams of the formation of (a) diblock copolymer, (b) graft copolymer and (c) star copolymer using macroinitiators in ATRP

2.2. **Post-Sulfonation**

Introduction of acid sites into the polymer and absorption of water is necessary to initiate mobile protons for proton transport. Sulfonic acid (\(-\text{SO}_3\text{H}\)) is predominantly utilized because of its high dissociation constant. Post-sulfonation based on electrophilic aromatic sulfonation has been widely studied and is the most common route to introduce ionicity to existing polymers for application as a PEM due to its expediency. Common sulfonating reagents for aromatic polymers include concentrated sulfuric acid, acetyl sulfate, chlorosulfonic acid and sulfur trioxide.\(^3\)\(^,\)\(^{160}\) Previous studies have shown that strong sulfonating agents such as chlorosulfonic acid can cause polymer degradation
and side reactions, resulting in inhomogeneous reactions.\textsuperscript{161} Using mild sulfonating agents such as methylsilylchlorosulfonate avoids polymer degradation and side reactions but suffers from low sulfonating efficiency and long reaction time.\textsuperscript{161} Makowski \textit{et al.} prepared acetyl sulfate as the sulfonating agent for polystyrene and \textit{t}-butyl-styrene-isoprene copolymers. The sulfonation reaction can be conducted in mild reaction conditions (i.e., \(\sim50^\circ\text{C}\) for 1 - 2.5 h) and the results showed that no crosslinking was observed.\textsuperscript{162} Acetyl sulfate was prepared by mixing acetic anhydride and concentrated sulfuric acid in dichloroethane solution at temperature lower than \(10^\circ\text{C}\) (Figure 2.6). Weiss \textit{et al.} then used the method developed by Makowski, using acetyl sulfate as the sulfonating agent to sulfonate a triblock copolymer of poly(styrene-ethylene/butylene-styrene) in dichloroethane solution at \(50^\circ\text{C}\) for 2 h.\textsuperscript{42} They reported that the sulfonated groups were randomly distributed along the polystyrene chains. The approach of using acetyl sulfate as the sulfonating agent can be performed in mild reaction conditions and leads to consistent and anticipated products. The approach is utilized for the work described in this thesis due to the above-mentioned advantages (i.e., in mild reaction conditions, no polymer degradation or side reactions). The sulfonation reaction is based on electrophilic aromatic substitution, in which acetyl sulfate acts as an electrophile and reacts with the delocalized \(\pi\)-electron of the aromatic ring as shown in Figure 2.7. The degree of sulfonation can be controlled by varying the sulfonation reaction time.

\textbf{Figure 2.6.} Mechanism of synthesis of acetyl sulfate as the sulfonating agent from acetic anhydride and sulfuric acid
2.3. Gel Permeation Chromatography

Gel permeation chromatography (GPC) is a technique commonly used to obtain molecular weight distributions and molecular weights of polymers. GPC separates molecules according to the hydrodynamic volume or the size of the analytes using columns packed with porous particles. The sizes of the porous particles are controlled and varied in a range of sizes. The GPC instrument used for this study was equipped with three styragel high temperature columns with pore sizes of $10^3\text{Å}$, $10^4\text{Å}$, and $10^5\text{Å}$. Several GPC columns are connected in series to improve the resolution of the separation. Columns with different pore sizes differentiate different ranges of molecular weights that can be separated.

A schematic diagram of a GPC is shown in Figure 2.8. For a sample to be measured by GPC, the polymers need to be dissolved in a proper solvent, followed by injecting the polymer mixture into a continually flowing stream of solvent inside GPC. A solvent delivery pump system is required to deliver the sample and solvent through the columns and the whole system. The analytes and the solvent (mobile phase) flows through the highly porous particles packed in the columns. Larger analytes (blue analytes shown in Figure 2.8) do not enter the pores easily and therefore spend less
time in the pores and are eluted faster. On the other hand, the smaller analytes (green analytes shown in Figure 2.8) have higher possibilities for being trapped in the pores and thus spend more time in the pores, thereby increasing their retention time. After the mobile particles pass through the columns, detectors monitor and record the separation. An ultraviolet absorption detector and/or a differential refractive index detector are commonly used.

![A schematic diagram of a GPC system](image)

**Figure 2.8.** A schematic diagram of a GPC system

In order to determine the molecular weight of the polymer, the GPC is initially calibrated with a set of polymer standards of known molecular weight. The retention time of the polymer sample is fitted to the standards to estimate its molecular weight. Thus, GPC is merely a relative tool obtaining molecular weight of polymers. The molecular weights of the polymers are typically characterized by the number average molecular weight ($M_n$) and weight average molecular weight ($M_w$), which are calculated by Equation 2.1 and 2.2, respectively:

\[
M_n = \frac{\sum n_i M_i}{\sum n_i},
\]

\[
M_w = \frac{\sum n_i M_i^2}{\sum n_i M_i},
\]
where \( n_i \) is the number of molecules of mass \( M_i \). The width of the peak resulted from GPC measurement reveals the distribution of the molecular weight for a tested polymer sample. The narrower the molecular weight distribution, the sharper the peak is and vice versa. The molecular weight distribution is quantified by the polydispersity index (PDI), which is defined as the ratio of \( M_w \) to \( M_n \), denoted in Equation 2.3,

\[
PDI = \frac{M_w}{M_n}.
\]  

PDI is equal to, or greater than, 1. If the tested polymers all possess uniform chain lengths with a very narrow molecular weight distribution, its PDI approaches unity, which usually only occurs for some natural polymers. For commercial polymers, it is typically greater than 2.

### 2.4. Membrane Characterization

#### 2.4.1. Membrane Casting

Membranes were prepared by dissolving the graft copolymers in N, N-dimethylacetamide (DMAc) and drop casting on a Teflon® sheet. The films were dried at room temperature and then dried in the vacuum oven at 60°C overnight. The membranes were pretreated to convert to their protonic form by soaking them in 2 M aqueous hydrochloric acid solution (HCl) overnight. Finally the protonated membranes were rinsed with Milli-Q water (18 MΩ, Millipore Systems) repeatedly and placed in Milli-Q deionized water overnight to wash out any excess acid from the membranes.
2.4.2. Water Uptake

The following properties of the membranes, such as water uptake, water content and proton conductivity were measured in their protonic form. The membranes were equilibrated in Milli-Q deionized water at room temperature overnight and pat-dried with a Kimwipe tissue to remove surface water before their wet weights were measured. Membranes of Nafion® 117 were measured as a baseline for all of the experiments during all the measurements.

The water uptake was calculated as the percentage increase in mass over the dry weight of the membrane as given by Equation 2.4,

\[
\text{water uptake (wt\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% ,
\]

where \( W_{\text{wet}} \) and \( W_{\text{dry}} \) represent the wet and dry weight of the membrane, respectively.

The water content was calculated as a mass percentage of water in the wet membrane according to Equation 2.5,

\[
\text{water content (wt\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}} \times 100\% .
\]

Lambda (\( \lambda \)) ([H\(_2\)O]/[SO\(_3\)H]), is also commonly used for analysis of water content in PEMs. It represents the average number of water molecules per sulfonic acid group and is calculated according to Equation 2.6,

\[
\lambda = \frac{\text{moles } H_2O}{\text{moles } SO_3H} = \frac{\text{water uptake} \times 10}{18 \times \text{IEC}} ,
\]

where IEC is ion exchange capacity (mmol/g), which will be discussed next.
2.4.3. Acid-Base Titration and Ion Exchange Capacity

Ion exchange capacity (IEC) is one of the key factors affecting water sorption in the membranes. The total hydrophilicity of the membranes increases as the acid content increases, which can lead to higher water uptake. In the case of the majority of PEMs, IEC, also known as ion content, is the amount of exchangeable SO$_3$H present in the membrane. It is expressed as a ratio of acid content determined by acid-base titration normalized to the mass of a dry membrane in units of mmol per gram. Membranes were first equilibrated in 2 M NaCl for at least 4 h to release the protons, which were then titrated with 0.001 M NaOH to a phenolphthalein end point. After titration, the membranes were immersed in 2 M HCl to reprotonate the sulfonic sites. The membranes were dried under vacuum at 80 °C overnight. Finally, the membranes were cooled in a desiccator before their dry weights were measured to prevent from absorbing humidity in the air. IEC (mmol/g) of the membrane was calculated by Equation 2.7,

\[
\text{IEC} = \frac{V_{\text{NaOH}} \times M_{\text{NaOH}}}{W_{\text{dry}}},
\]

where $V_{\text{NaOH}}$ and $M_{\text{NaOH}}$ are the volume (mL) and molar concentration (mol/L) of NaOH solution, respectively. $W_{\text{dry}}$ is the dry weight of the membrane.
2.4.4. **Electrochemical Impedance Spectroscopy and Proton Conductivity**

Proton conductivity of the membranes was measured using electrochemical impedance spectroscopy (EIS) with a Solartron 1260 frequency response analyzer (FRA), employing an in-plane, two-probe electrode configuration. Data analysis and fitting were calculated using Z plot/Z view® software (Scribner Associates, Inc.). The membranes were placed in a probe that possesses two platinum electrodes across to each other. A plane strip of water-saturated membrane, generally having dimension of approximate 10 mm in length and 5 mm in width, was placed between the Pt-foiled electrodes and stabilized in place by placing another Teflon® block on top as shown in Figure 2.10. Two Teflon® blocks were clipped tightly by plastic clothepins to ensure the membrane was in tight contact with the electrodes.

![Figure 2.10. Pt/Teflon® conductivity probe](image)

The electrochemical probe was connected to the FRA by employing two wires that were attached with alligator clips (Figure 2.10). An alternating current with an
amplitude of 100 mV was passed along the plane membrane over a frequency ranged from 10 MHz to 100 Hz to generate a Nyquist plot (Figure 2.11). Membrane resistance ($R_m$) was the diameter of the plot (difference of x-intercepts between high frequency and low frequency), which was determined by fitting the data to the standard Randles equivalent circuit model consisting of a membrane bulk capacitor ($C_m$) and a membrane bulk resistor ($R_m$) in parallel shown in Figure 2.11. The diameter of the plot varies with both IEC and membrane dimensions.

![Randles equivalent circuit](image)

**Figure 2.11.** Nyquist plot for Impedance measurement

Proton conductivity ($\sigma$) (S/cm) was calculated according to Equation 2.8,

$$\sigma = \frac{L}{R_m A},$$  \hspace{1cm} (2.8)

where $L$ (cm) is the length of the conductor, distance between two electrodes; $A$ (cm$^2$) is the cross-sectional area of the membrane (width x thickness); and $R_m$ ($\Omega$) is the ionic resistance of the membrane. The width of the membrane and distance between the two electrodes were measured with a Mitutoyo Digimatic caliper and the thickness was
measured with Series 293 Mitutoyo Quickmike caliper. All measurements were performed on fully hydrated membranes under ambient atmosphere and at room temperature. Membranes were re-cast for reproducibility and their proton conductivity were measured several times to ensure consistent results.

2.4.5. Proton Conductivity as a Function of RH and Temperature and Dynamic Water Vapour Sorption

Proton conductivity under various RHs and temperatures was performed using both electrochemical impedance instrument and an ESPEC SH-241 environmental chamber. Membranes were initially equilibrated at a predetermined RH from 95% to 55% RH and a predetermined temperature (i.e., 25, 50 and 80 ºC) in the environmental chamber depending on the targets of the measurement. After the membranes were equilibrated in the environmental chamber overnight, they were taken out to measure their dimensions, followed by setting them up onto the Pt/Teflon® conductivity probe. Measurements of conductivity were taken inside the environmental chamber at the predetermined RH and temperature until 3 or more conductivity values were consistent over a 2 h period, and this equilibrating process usually took ~ 5 h. These membranes were recast and their proton conductivities were measured several times to obtain reproducible data.

The gravimetric water dynamic vapour sorption technique (DVS-1000, Surface Measurement Systems, U.K) was used to study water vapour sorption by membranes under different relative humidity (RH). A schematic diagram of the DVS instrument is shown in Figure 2.12. The targeted RH was reached using a mixture of water vapour-saturated flow of nitrogen gas with a dry flow of gas. RH was maintained and controlled
by a dew-point sensor. Water uptake of the membranes was calculated according to Equation 2.9,

\[
\text{water uptake}_{DVS} = \frac{W_{RH} - W_{dry}}{W_{dry}} \times 100\% ,
\]

where \( W_{RH} \) is the equilibrated weight of the sample at the targeted RH, and \( W_{dry} \) is the equilibrated weight of the sample at 0% RH.

**Figure 2.12.** Schematic diagram of a DVS environmental chamber for determination of water vapour sorption of examined PEMs at various RHs and temperatures
2.4.6. Analytical Acid Concentration and Proton Mobility

The analytical acid concentration \([-\text{SO}_3\text{H}]\) (M) represents the overall concentration of protons in the membrane and was calculated according to Equation 2.10,

\[
[-\text{SO}_3\text{H}] = \frac{\text{moles of } -\text{SO}_3\text{H}}{V_{\text{wet}}} = \frac{W_{\text{dry}}}{V_{\text{wet}}} \times \text{IEC},
\]

2.10

where \(-\text{SO}_3\text{H}\) refers to bound sulfonic acid groups in a membrane, \(V_{\text{wet}}\) is the volume of the wet membrane (cm\(^3\)), and moles of \(-\text{SO}_3\text{H}\) can be obtained by multiplying IEC with dry weight of the membrane.

The effective proton mobility (\(\mu_{\text{eff}}, \text{cm}^2/\text{sV}\)) was estimated by Equation 2.11,

\[
\mu_{\text{eff}} = \frac{\sigma}{F \times [-\text{SO}_3\text{H}]},
\]

2.11

where \(\sigma\) is proton conductivity (S/cm), \(F\) is the Faraday’s constant, and \([-\text{SO}_3\text{H}]\) is analytical acid concentration (M). \(\mu_{\text{eff}}\) represents a “normalized” proton conductivity, i.e., acid concentration effects can be removed. The use of effective proton mobility advantageously allows examining the relative contributions of proton mobility and acid concentration to the experimentally measured proton conductivity.

In addition to acid dissociation (pKa), tethered anionic groups and water content, tortuosity and spatial proximity of neighbouring acid groups are also greatly influencing proton mobility.\(^{18, 75, 96, 97, 164, 165}\) An illustration demonstrating how tortuosity affects proton mobility is shown in Figure 2.13, where (a) illustrates a more tortuous conduction pathway with several dead-ends; whereas, (b) demonstrates a smoother and linear
conduction pathway for proton transport. Therefore, a more connected conduction pathway leads to more effective proton mobility in (b).

**Figure 2.13.** Connectivity of ionic domains within PEMs. Red pathways represent the ionic domains. The degree of tortuosity of proton conduction of (a) is greater than that of (b), causing lower proton mobility in (a).


Spatial proximity of neighbouring acid groups, meaning the distance between acid groups, is also vital in proton mobility. Figure 2.14 illustrates different proximities between neighbouring acid groups in ionic channels. The positively charged proton-bearing species such as H$_3$O$^+$, H$_5$O$_2^+$ or H$_9$O$_4^{4+}$ are transported through the negatively charged tethered -SO$_3^-$ groups. Given that all of other factors are fixed, if the distance between tethered -SO$_3^-$ groups is large as shown in Figure 2.14 (a), it is more difficult for proton-bearing species to be transported within the PEMs and would require higher activation energy for proton transport. Thus, there is a smaller value of proton mobility in (a) because the distance between acid groups is larger compared to (b). Proton mobility is widely mentioned in the following chapters because it serves a useful parameter for gaining insights into tortuosity in ionic channels, acid association and spatial proximity of neighbouring acid groups.$^{164}$
Figure 2.14. Spatial proximity of neighbouring acid groups in ionic channels. The distance between acid groups is greater in (a) than (b), thus lower proton mobility in (a).


2.4.7. Transmission Electron microscopy

Transmission electron microscopy (TEM) provides images at greatly higher resolution than conventional optical microscopes, and can be used to study structures at atomic levels, which allows for direct visualization of the morphology and phase separation in PEMs. TEM uses a beam of electrons as its “light source”, which is transmitted through an ultra thin sample and interacts with the sample to generate TEM images at nanometer-scale resolution. The common electron source is a tungsten filament, which is heated at the top of the microscope to generate electrons that travel through a vacuum in the column of the TEM. Instead of using glass lenses to focus the light in the light microscope, TEM uses electromagnetic lenses to focus the electrons into a very fine beam. The beam of electrons travels down the column and interacts with the sample as it passes through the sample. Depending on the intrinsic and physical properties of the studied sample (i.e., the density, crystallinity, atomic number/weight of the scattering atom and the thickness of the specimen), a different amount of the electrons is scattered when it interacts with the sample. Non-scattered electrons hit a fluorescent screen at the bottom of the microscope, where electron intensity is converted to light intensity, forming a “shadow image” of the sample with different shades of darkness. The image is magnified and focused onto an imaging device. The bright field
imaging mode is the most commonly used mode of operation for a TEM. In this mode, contrast formation is generated directly by absorption (unscattered) and scattering of electrons. The regions of the sample with heavier atom, higher density and crystallinity or larger thickness, where more electron are scattered out of the sample, appear dark in the image. Conversely, the regions of the sample with lower atomic number for instance, where more electrons are transmitted through, appear bright in the image. It is important with this technique to prepare ultra-thin specimens so that electrons could transmit the samples and afford sufficient intensity to produce an explicable image. For polymeric materials, sectioning the samples with an ultramicrotome or spin-casting from diluted polymer solutions are common approaches to prepare ultra-thin samples. The membranes are commonly stained with reagents such as Pb\(^{2+}\), Cs\(^{+}\), RuO\(_4\) to enhance image contrast.

2.4.8. **Wide Angle X-ray Scattering**

Scattering techniques, such as X-ray and neutron scattering are useful tools for structural studies at sub-micron scales. Scattering techniques utilize a beam of photons or particles to project the sample and detect the scattered beam to study its structure as shown in Figure 2.15. The incident beam source passes through the sample and the scattered beam are detected at different scattering angles \(2\theta\).

![Figure 2.15](image.png)

**Figure 2.15.** A schematic diagram representing the basic measuring set up for scattering techniques.
Scattering techniques are used to investigate polymeric materials at two different length scales. Small-angle X-ray scattering (SAXS) and small-angel neutron scattering (SANS) are commonly used on the order of nanometers (i.e., the order of the distance between different segments of the polymeric materials), which is particularly useful to study phase separation that is resulted from the incompatible segments in the polymer (e.g., hydrophilic segments vs hydrophobic segments). On the other hand, wide-angle X-ray scattering (WAXS) is mainly used on the order of angstroms (i.e., the order of the distance between atoms), and is especially useful to examine the crystallographic structure of the polymeric materials. WAXS was employed to determine if the polymers are crystalline and their degree of crystallinity for the studies described in this thesis. A general concept of the technique is summarized below. WAXS is based on the elastic scattering of X-rays which interact with the electron clouds of atoms to form various diffraction patterns according to the electron density. Bragg’s law (Equation 2.12) applies to the occurrence of the diffractions:

\[ 2d \sin \theta = n \lambda, \]  

where \( d \) is the inter-planar lattice spacing (i.e., the distance between identical planes), \( \theta \) is the angle of the incident X-ray, \( n \) is an integer, and \( \lambda \) is the wavelength of the X-rays. When the atoms form a crystal lattice with inter-planar \( d \)-spacing which is comparable to the wavelength of the incident X-rays, diffraction effects are created (Figure 2.16). When the X-ray beams scattered from atoms in parallel planes which differ by an integer multiple number of wavelengths, these beams interfere constructively and result in a peak in the diffraction pattern at a scattering angle \( \theta \). With known wavelength, and the measurement of the angles at which peaks in the scattered beams take place, the inter-planar \( d \)-spacing can be determined. A typical X-ray diffractometer (XRD) possesses a
copper X-ray source (i.e., Cu Kα source, \( \lambda = 1.5418 \text{ Å} \)), a sample holder, and an X-ray detector (Figure 2.15). The detailed parameters that were used for the measurements are described under experimental section in Chapter 3.

![Diagram of X-ray scattering](image.png)

**Figure 2.16.** Refracted X-ray beams from atoms in different planes of a crystal lattice with inter-planar d spacing

As mentioned previously, WAXS is useful to study the crystallinity of polymeric materials, which is typically performed with a common angular range of \( 5^\circ < 2\theta < 50^\circ \). The degree of crystallinity in a polymer was determined using Equation 2.13, \(^{170}\)

\[
x_{cr} = \frac{\int_0^\infty I_{cr}(q)q^2dq}{\int_0^\infty I_{total}(q)q^2dq} = \frac{I_{cr}}{I_{cr} + I_{am}} \tag{2.13}
\]

where \( x_{cr} \) is the ratio of the scattering due to the crystalline domains to the total scattering, and \( I_{cr} \) and \( I_{am} \) are the integrated signals of the crystalline peak and amorphous peak for WAXS diffractogram, respectively. \( I_{total} \) is the integrated signal of the overall peak, and \( q \) is the magnitude of the scattering vector \( (q = \frac{4\pi}{\lambda} \sin\theta) \).
The average crystalline domain sizes can be calculated according to the Scherrer equation (Equation 2.14),

$$t = \frac{0.9 \times \lambda}{B \times \cos \theta_B},$$  \hspace{1cm} \text{(2.14)}$$

where $t$ represents the grain size in Å, $\lambda$ is the wavelength of radiation ($\lambda = K\alpha = 1.5418$ Å), $B$ is the full width at half max (FWHM, the line broadening at half of the maximum intensity) in radians, and $\theta_B$ is the position of the maximum of diffraction.

[Reprinted in parts with permission from Chemistry of Materials, Yang, A. C. C.; Narimani, R.; Zhang, Z.; Frisken, B. J.; Holdcroft, S. 25, (9), 1935. © 2013, American Chemical Society.]\(^{171}\)

3.1. Introduction

Proton conducting polymers are central to the future of proton exchange membrane fuel cell (PEMFC) commercial viability. Not only are they responsible for the conduction of protons from the anode to the cathode, they also act as separators to prevent fuel from the anode and oxidant from the cathode from mixing together. An ideal PEM for fuel cells should exhibit mechanical and chemical integrity, low permeability to gases, limited swelling in the presence of water and high proton conductivity.\(^2,3,172\) These properties are significantly controlled by the polymer that constitutes the membrane. State-of-the-art PEMs are based on perfluorosulfonic acid (PFSA) ionomers, but these have drawbacks including a limited range of operating conditions and high cost. Therefore, less expensive materials with improved properties are highly desired. One approach is to prepare membranes with high ion exchange capacity (IEC) that do not dissolve in water and can conduct protons under low relative humidity (RH). Several classes of polymer have been investigated for this purpose, including copolymers of PFSA,\(^{13,14,21,173}\) partially fluorinated ionomers,\(^{120-123,127,174-179}\) poly(arylene ether)s,\(^{70,180-186}\) polyimides,\(^{67,187-190}\) and polyphosphazenes.\(^{191-194}\)
A rational design of PEMs requires a fundamental understanding of the role that polymer microstructure plays in determining morphology. The study of model polymers is particularly useful. Over the past decade, several morphological ionic polymer systems have been investigated. Specifically, polymer systems in the form of block copolymers, graft copolymers, and copolymers of short, multi-sulfonated side chains have been gaining much interest and examining widely. It is generally accepted that incompatibility of hydrophilic sulfonic acid groups and the hydrophobic polymer backbone results in phase separation. Upon sorption of water, ionic domains interconnect to form ionic “channels” that facilitate proton transport – thus the ionic morphology plays a significant role in transport properties. Einsla et al. examined the effect of microstructure and morphology on proton conductivity at low RH by utilizing three sulfonated aromatic copolymers with distinct sequence lengths (i.e., an alternating, a random and a multiblock PEM). It was revealed that three copolymers display different morphology: the alternating copolymer having sulfonic acid groups located evenly along the polymer main chain has larger but isolated ionic domains (65 ± 18 nm); the random copolymer with statistical distribution of sulfonic acid groups has smallest ionic domain (18 ± 6 nm); and the multiblock copolymer possesses interconnected ionic domains (23 ± 10 nm). Although the alternating copolymer has the largest ionic domain, there is a lack of connectivity between ionic domains, causing lowest water diffusion and proton conductivity among three copolymers. The random copolymer represents a disordered morphology with partial connectivity between the ionic domains, whereas the multiblock copolymer displays high level of phase separation between hydrophobic and hydrophilic domains, leading to well-defined long-range hydrophobic and hydrophilic pathways for fast water transport and proton transport even at low RH. The authors
demonstrated the significance of membrane morphology and microstructure in water sorption and proton conductivity and that a good phase connectivity in multiblock copolymer resulted in higher proton conductivity and less dependency on RH.

Unravelling the origin of structure-property relationships in proton conductive polymers has been a major focus of our research group.\textsuperscript{12, 105, 108} We reinforced the point that architecture greatly influences morphology and transport properties through a comparison of \textit{diblock} and \textit{graft} copolymer membranes. It was shown that diblock polymer membranes exhibit high degrees of long-range ionic order, but also swell excessively, leading to a dilution of protons and reduced proton conductivity.\textsuperscript{138} In contrast, graft copolymers exhibiting an interconnected network of small disordered ionic clusters can be designed to tolerate higher ion contents without excessive swelling. Graft membranes with IECs in excess of 2 mmol/g have been shown to possess proton conductivities similar to that of Nafion\textsuperscript{®} 117,\textsuperscript{138} with the advantage that the synthetic route is versatile to prepare much higher IEC membranes.

One strategy to decrease excessive swelling of ionic polymers is to induce crystallization within the polymer. This method has been demonstrated by: Park and Yamazaki \textit{et al.} through Nafion\textsuperscript{®} composite membranes,\textsuperscript{146, 147} by Sacca \textit{et al.} through recast Nafion\textsuperscript{®} membranes,\textsuperscript{148} and by Moore and Martin \textit{et al.} through shorter-side-chain Dow Corp’s experimental PFSA ionomer membrane.\textsuperscript{149} Despite these studies, which focus exclusively on PFSA ionomers, there are few systematic studies that seek to alter the polymer microstructure itself and examine the synergistic effects of such alterations on membrane structure, crystallinity, and fuel cell relevant properties (e.g., membrane swelling and proton conductivity).
Graft copolymers having ionic graft side chains attached to the hydrophobic backbone are useful model systems to study structure-property relationships because the number density and length of the graft chains can be varied systematically. Zhang and Russell report a synthetic method that utilizes $g$-ATRP to prepare partially fluorinated graft copolymers of poly([vinylidene difluoride-co-chlorotrifluoroethylene]-graft-styrene) [P(VDF-co-CTFE)-$g$-PS]. The advantage of this approach is that the copolymers are synthesized in one batch, resulting in identical experimental conditions for each of the resulting products. According to the $g$-ATRP synthetic approach, Chung et al. investigated two families of graft copolymers, which were prepared based on a low molecular weight and a high molecular weight polymer backbone with different graft density, graft length, and degree of sulfonation. Chung et al. discovered that P(VDF-co-CTFE)-$g$-PS prepared from a high molecular weight PVDF (> 312,000g/mol), low polystyrene graft density (~0.3 mol%) and large graft length (~ 120 styrene units) yielded membranes that exhibited long-range lamella/cylinder ionic channels imbedded in the hydrophobic PVDF matrix. These materials offer improved resistance to water swelling at high IEC, with comparable proton conductivity to Nafion® up to 120 °C and high RH. Graft copolymers based on high molecular weight PVDF, higher polystyrene graft density (1.4-2.4 mol%) and shorter graft length (14-21 styrene units) resulted in a disordered cluster-network morphology which exhibited lower water swelling and less sensitivity to RH.

In complementary work, Tsang et al. investigated graft copolymers of P(VDF-co-CTFE)-$g$-PS using a higher graft density, resulting in higher polystyrene (PS) to vinylidene difluoride (VDF) molar ratios. Copolymers possessing shorter graft side chains yielded larger and purer ionic domain clusters because of the higher degree of
sulfonation (DS) compared to other analogues with similar IEC. For higher IEC membranes, short graft copolymers were found to possess larger ionic aggregates due to the high DS but a lower number density of clusters; the ionic domains are therefore more isolated, which strengthened the cohesivity of the surrounding hydrophobic matrix, resulting in lower water uptake.

Despite all of the above findings, the impact of the ionomer’s nanostructure on membrane crystallinity, and the effect of crystallinity on water uptake and proton conductivity are not yet completely understood. In this chapter, we focus on these concerns through the design of model ionic fluorous graft copolymers P(VDF-co-CTFE)-g-PS, synthesized according to Scheme 3.1. The series of graft copolymers examined here were designed to possess a lower CTFE content compared to analogous materials studied by Tsang et al.\textsuperscript{211} A lower CTFE content results in a lower number density of graft side chains (i.e., a larger sequence length between graft side chains) and promotes higher crystallinity of the fluorous backbone. The macroinitiator P(VDF-co-CTFE) (Scheme 3.1a) was used to prepare three series of copolymers possessing different lengths of graft side chains (Scheme 3.1b). Graft copolymers were then sulfonated to different degrees and solution cast to yield membranes with varying IECs (Scheme 3.1c).

In the first section of this Chapter, the effect of graft length is described. The effect of graft density is then examined in the second section. Four factors associated with this model polymer system are discussed in both sections: (1) the effect of the polymer architecture (ion content, graft chain length, and graft density) on the degree of crystallinity; (2) the effect of the polymer architecture (ion content, graft chain length, and graft density) on the size and nature of the ionic and hydrophobic domains; (3) the
effects of crystallinity and nature of the ionic and hydrophobic domains on water sorption, and their combined effects on proton conductivity; (4) the properties of high IEC membranes on proton conductivity under conditions of low RH.

Scheme 3.1. Synthetic scheme for P(VDF-co-CTFE)-g-SPS

3.2. Experimental Section

3.2.1. Materials.

Vinylidenedifluoride (VDF, Aldrich, 99+%), chlorotrifluoroethylene (CTFE, Aldrich, 98%), potassium persulfate (K₂S₂O₈, Allied Chemical, reagent grade), sodium
metabisulfite (Anachemia, anhydrous, reagent grade), pentadecafluorooctanoic acid (Aldrich, 96%), 2,2-dipyridyl (bpy, Aldrich, 99+%), 1,2-dichloroethane (DCE, Caledon, reagent grade), N-methyl-2-pyrrolidone (NMP, Aldrich, anhydrous, 99.5%), sulfuric acid (Anachemia, 95-98%, ACS reagent), cuprous chloride (CuCl, Aldrich, 99%), and acetic anhydride (Aldrich, 99.5%) were used as received. Copper(II) chloride (CuCl$_2$, Aldrich, 99.999%) was purified according to the literature.$^{216}$ Styrene (Aldrich, 99+%) was washed with aqueous 5 wt% NaOH and water, dried overnight with MgSO$_4$, distilled over CaH$_2$ under reduced pressure, and stored under N$_2$ at -20 °C.

Nafion® membranes were used as standard membranes and tested along with all of the experiments. By varying the ratio of two components (x and y in Figure 1.2), the ion content of Nafion® can be altered. Nafion® 117 possessing an IEC of 0.91 mmol/g is widely used as a standard material because of its high proton conductivity and reasonable swelling in water, which is very suitable for most of the current applications. Due to its versatility and commercial availability, Nafion® 117 membranes were used as the standard membranes throughout the work described in this thesis.

Nafion® 117 membranes were pretreated by boiling in 3 vol% hydrogen peroxide for 30 minutes to wash out the organic materials, followed by boiling in Milli-Q water (18 MΩ, Millipore Systems) for another 30 minutes. Then the membranes were boiled in 0.5 M sulfonic acid for 30 minutes to convert them into protonic form, followed by rinsing with Milli-Q water and storing in Milli-Q water until use.
3.2.2. Synthesis of Fluorous Macroinitiators.

Emulsion copolymerization of VDF and CTFE was performed to synthesize the macroinitiator P(VDF-co-CTFE) by Dr. Zhaobin Zhang. A mixture of 100 mL of water, 0.40g of KPS, 0.29g of Na$_2$S$_2$O$_5$, 0.04g of pentadecafluorooctanoic acid was added to a 160 mL pressure vessel (Parr Instruments) equipped with a 600 psi pressure relief valve and a magnetic stir bar. Predetermined composition of a VDF and CTFE monomer mixture was introduced into the reactor to give a constant pressure of 300 psi at 60 °C. The polymerization was carried out for 1.0 - 1.5 h. The resulting polymer latex was coagulated by freezing, followed by washing with water and ethanol repeatedly. Crude polymer was purified by repeated dissolution in THF and precipitation in ethanol. The sample was dried at 80 °C under vacuum for 24 h. The composition of VDF and CTFE in the fluorous macroinitiator was determined by $^{19}$F NMR spectroscopy using a 400 MHz Varian MercuryPlus spectrometer. Chemical shifts were measured with respect to trichlorofluoromethane (CFCl$_3$). The monomer ratio of VDF to CTFE was determined according to the previously published method by integrating the areas of the peaks in the $^{19}$F NMR spectra based on Equation 3.1 and Equation 3.2,

$$\frac{P(\text{VDF})}{P(\text{CTFE})} = \frac{S_1 + S_2 + 3S_3 - S_4}{S_5 + S_6 + 2(S_4 - S_3)} \times \frac{3}{2},$$ \hspace{1cm} (3.1)$$

$$\text{% CTFE} = \frac{1}{1 + \frac{P(\text{VDF})}{P(\text{CTFE})}},$$ \hspace{1cm} (3.2)

where $S_a$ is the integrated intensity of the assigned peak. Peaks’ # and their corresponding fluorine atoms are presented in the $^{19}$F NMR spectra, which are discussed in the results and discussion section.
3.2.3. **Graft-ATRP of Styrene.**

Graft-ATRP was performed to synthesize P(VDF-co-CTFE)-g-PS. The Cl sites of the macroinitiator P(VDF-co-CTFE) were used to initiate ATRP of styrene. The synthetic procedures are as followed: P(CTFE-co-VDF) ([macroinitiator]=8.63×10^{-3} M, 1.1071 g) was first dissolved in N-methylpyrrolidone (40 mL) in a dry round bottom flask. Bipyridine ([pby] = 0.16 M, 3.0029 g), styrene ([M]₀ = 1.44 M, 20 mL), catalyst CuCl ([CuCl]=5.25×10^{-2} M, 0.6430 g), and CuCl₂ ([CuCl₂]=5.87×10^{-3} M, 0.0892 g) were added to the flask, and sealed with a septum and degassed by three freeze-pump-thaw cycles to remove oxygen and water. The reaction mixtures were heated in an oil bath under nitrogen at 110 °C for a total reaction time of 24 h. Polymer mixtures were collected after 8, 16, and 24 h reaction and precipitated in methanol to yield polymers with different graft lengths. Polystyrene homopolymers were removed by rinsing repeatedly with cyclohexane. The polymer precipitates were filtered and dried under vacuum at 60 °C. GPC, ¹⁹F and ¹H NMR spectra were used to determine the degree of polymerization (DP) of styrene and the molecular weights of the graft copolymers. ¹H NMR spectra were recorded in d₆-acetone using a 600 MHz Varian Inova spectrometer. By comparing the ratio of protons attributed to VDF and to PS units, the average DP of the PS chain was calculated according to Equation 3.3,

\[
DP = \frac{(2 \times n_{VDF}) \times (integral_{PS})}{(5 \times n_{CTFE} \times % Cl_{reacted}) \times (integral_{VDF})}
\]

where \( n_{VDF} \) and \( n_{CTFE} \) refer to the units of VDF and CTFE in P(VDF-co-CTFE). The integral signals of PS and VDF in the ¹H NMR spectra are to be discussed later in the results and discussion section.
3.2.4. Sulfonation of Polystyrene Graft Side Chains.

Sulfonation was carried out in 1,2-dichloroethane at 40 °C. To a 50 mL three-neck flask equipped with a condenser, 15 mL of 1,2-dichloroethane and 0.6 g of P(VDF-co-CTFE)-g-PS were added, and the mixture heated to 50 °C under N\textsubscript{2} and stirred. Acetyl sulphate was prepared by injecting 1 mL of acetic anhydride and 3 mL of dichloroethane into a N\textsubscript{2}-purged vial. The solution was cooled in a 10 wt% CaCl\textsubscript{2} ice bath and 95% - 97% sulphuric acid was injected into the mixture. The resultant acetyl sulphate was immediately transferred to the polymer solution kept at 40 °C. Samples with different degrees of sulfonation were periodically extracted and precipitated in a mixture of ethanol/hexanes (50:50 by vol.). The precipitate was washed with Millipore deionized water until the pH of the residual water was 7. The sulfonated polymers were dried under vacuum at 60 °C overnight. The DS was determined from $^1$H NMR spectra and calculated from the areas under the peaks according to Equation 3.4,

$$DS (\%) = \frac{c/2}{c/2 + b/3} \times 100\%,$$

where b and c represent integrals of peak “b” and “c”, respectively shown in the $^1$H NMR spectra in Figure 3.3, which are to be discussed later. Titration was also performed to measure the ion content and to confirm successful sulfonation.

3.2.5. Membrane Preparation and Properties

Gel permeation chromatography (GPC) was used to estimate the molecular weights of the macroinitiator and graft copolymers in DMF, 0.01 M LiBr at 80 °C. GPC instrument was equipped with three styrargel high temperature (HT) columns with pore sizes of $10^3$ Å, $10^4$ Å, $10^5$ Å (HT3, HT4, HT5, respectively) manufactured by American
Polymer Standards Corporation, a Waters 1515 isocratic HPLC pump, a Waters 2414 differential refractometer, and a Waters 2487 dual UV absorbance detector ($\lambda = 254$ nm). Polystyrene standards were used for calibration.

Membranes were produced using drop casting method by dissolving the sulfonated graft copolymers in N, N-dimethylacetamide, followed by casting the solution mixture on a Teflon® sheet. The membranes were initially dried at room temperature overnight and further dried under vacuum at 60 °C overnight. The membranes were soaked in 2 M HCl overnight, converting to their protonic form and then were rinsed with Millipore deionized water several times to wash out excess acid from the membranes, and finally were stored in Millipore deionized water for future use. The thickness of the membranes was ~ 100 µm.

Water uptake was calculated as the percentage increase in mass over the dry weight of the membrane. Water content was calculated as a mass percentage of water in the wet membrane. Lambda ($\lambda$), was determined as the ratio of the moles of water to the moles of exchangeable $\text{SO}_3\text{H}$ site according to Equation 2.6, representing the number of water molecules per sulfonic acid group. Detailed descriptions regarding the above-mentioned parameters are presented in Section 2.4.2.

IEC was determined by acid-base titration, in which the protons released from the membranes in 2 M NaCl were titrated with standardized NaOH solution to a phenolphthalein end point. The IEC is expressed as a ratio of the amount of exchangeable $\text{SO}_3\text{H}$ determined by titration normalized to the mass of a dry membrane in units of mmol per gram. The dry weight of the membrane was obtained after titration. The membranes were reprotonated in HCl and dried under vacuum at 80°C overnight.
before their dry weight were measured. A detailed description regarding IEC is presented in Section 2.4.3. For every measurement, multiple membranes of similar dimension were prepared for each sample (~3 to 5 films) and measured at the same time under identical conditions. Water uptake, water content, \( \lambda \), and IEC values are calculated from the average of five membrane samples. Errors were calculated based on the standard deviation of experiments.

The in-plane conductivity was measured by AC impedance spectroscopy using a Solartron 1260 frequency analyzer. Detailed description for conductivity measurement is described in Section 2.4.4. Briefly, by applying a frequency from 10 MHz to 100 Hz at an AC voltage of 100mV, Nyquist plots can be obtained. The resulting Nyquist plots are fitted to the standard Randles equivalent circuit to determine the membrane resistance. Measuring results were collected until a constant ionic resistance was achieved. The proton conductivity \( \sigma \) (S/cm) was calculated using the membrane resistance and the sample geometry according to Equation 2.8. Membranes were re-cast and their proton conductivities were measured several times. Proton conductivity was calculated as the average of several measurements.

For measurements under controlled RH, membranes were equilibrated at a predetermined RH between 95 to 55% RH in an ESPEC SH-241 environmental chamber at 25 °C. The membranes were also equilibrated at a predetermined temperature between 25 °C to 80 °C at 95% RH. Measurements of proton conductivity were taken inside the environmental chamber until consistent conductivity values were obtained over a 2 h period, and this usually took ~5 h for each RH or temperature stage. Gravimetric water vapour sorption techniques were used to obtain water vapour sorption
at different RH (DVS-1000, Surface Measurement Systems, U.K). More details regarding these measurements are described in Section 2.4.5.

The analytical acid concentration [-SO₃H] (mol/L, M) in wet membranes was calculated as the moles of ionic exchange sites per unit volume of a hydrated membrane based on Equation 2.10. The effective proton mobility \( \mu_{\text{eff}} \) (cm²/s V) in wet membranes was calculated according to Equation 2.11, serving as a normalized proton conductivity, at which the effect of acid concentration can be excluded, thus, a more reasonable comparison of proton mobility can be evaluated. A thorough description of acid concentration and effective proton mobility is described in Section 2.4.6.

### 3.2.6. Instruments and Techniques Used for Morphological Study

Transmission electron microscopy (TEM) was used to study membrane morphology. Detailed information about the instrument and its operation principle is presented in Section 2.4.7. A short procedure of membrane preparation is as followed: the membranes were stained by immersing overnight in a saturated lead acetate solution, then rinsed with water and dried completely under vacuum at room temperature for at least 5 h, followed by embedding in Spurr’s epoxy resin, and sectioning to produce 60-100 nm thick slices using a Leica UC6 microtome. The thin slices were collected on a copper grid, which was then measured under a Hitachi H7600 TEM with an accelerating voltage of 100 kV to generate electron micrographs. Based on the TEM micrographs, the domain sizes (e.g., ionic domain shown in dark) were measured according to the scales given on each TEM image using software Image J®. Approximately 150 measurements were performed in order to obtain an average value of ionic domain size for each copolymer. The number density in 2-dimensions was
obtained by using a 1 x 1 cm grid overlaid on a TEM micrograph so that the number of ionic clusters present in the predetermined area can be counted. Thirty areas were randomly chosen and the number densities of ionic clusters were calculated as the average over the 30 areas.

Wide angle X-ray scattering (WAXS) measurements were performed on a Rigaku Rapid Access XRD with an image plate detector and analyzed by Rasoul Narimani of Department of Physics, Simon Fraser University. The X-ray instrument was operated at 46 kV and 42 mA using a nickel filter and a copper source (X-ray wavelength is 0.154 nm). Data was acquired in transmission mode under ambient conditions. Data acquisition time was set as 2 min, which was typically sufficient to achieve an adequate signal to noise ratio. A detailed description of WAXS is present in Section 2.4.8. The degree of crystallinity in the sample was determined by calculating the ratio of scattering due to the crystalline domains to the total scattering intensity according to Equation 2.13.\textsuperscript{170} The average crystalline domain size was calculated by Equation 2.14 based on the Scherrer equation.\textsuperscript{218, 219}

### 3.3. Results and Discussion

#### 3.3.1. Synthesis and Characterization

The perfluoroalkane macroinitiator P(VDF-co-CTFE) was synthesized using the method of emulsion copolymerization of VDF and CTFE, which contains chlorine sites suitable for graft-ATRP. According to the previously published method by Isbester \textit{et al.}\textsuperscript{217} the macroinitiator P(VDF-co-CTFE) was determined to contain 97.4 ± 0.3 mol%
VDF and 2.6 ± 0.3 mol% CTFE by estimating the integral of peaks in the $^{19}$F NMR spectra (Figure 3.1) based on Equation 3.1 and Equation 3.2.

Grafting of styrene onto the macroinitiator was achieved by ATRP. $^{19}$F NMR spectra and $^1$H NMR spectra both provide evidence for the growth of polystyrene from the fluorous backbone. $^{19}$F NMR spectra of the graft copolymers exhibit similar signature peaks corresponding to that of the macroinitiator and an additional peak at -164 ppm corresponding to tertiary fluorine atoms (-CF$_2$-CF*CH$_2$(C$_6$H$_5$)-CF$_2$-) juxtapositioned to styrenic groups (Figure 3.1) is observed. A considerable reduction in intensity of the peaks at ~ -120 to -122 ppm (due to -CF$_2$-CF$_2$-CF*Cl-CH$_2$-CF$_2$) is also observed in the $^{19}$F NMR spectra of the graft copolymers with respect to the macroinitiator due to CFCl units being consumed during ATRP. By measuring the percentage reduction in the peaks at -120 to -122 ppm using peaks at -89.0 to -94.0 ppm (-CF$_2$-CH$_2$-CF$_2$*-CH$_2$-CF$_2$-) as a reference, the % Cl sites initiated was estimated to be 65, 65 and 67 for the three graft copolymers subjected to 8, 16, and 24 h ATRP reaction time, respectively. The graft number density of the three copolymers was estimated ranging from 1.68 ± 0.02 – 1.72 ± 0.03 mol % by multiplying the mol % of CTFE in the macroinitiator (2.6 mol%) and the percentage of CTFE initiated. $^1$H NMR spectra of the macroinitiator and a typical graft copolymer are shown in Figure 3.2 (a) and (b), respectively. The integral signals of PS and VDF are labeled peak “d”, “e” and “a”, respectively. In Figure 3.2 (b), additional peaks at 6.40-7.40 ppm corresponding to the grafted PS were revealed for the graft copolymer.

Molecular weight ($M_n$) of the linear fluorous macroinitiator was ~ $1.23 \times 10^5$ g/mol, and the PDI was 1.59 as estimated by GPC using polystyrene standards. GPC results demonstrate growth of the polystyrene graft chains with increasing ATRP
reaction time. The graft copolymers exhibit a significantly different hydrodynamic volume than the linear polystyrene standards, thus a more accurate determination of molecular weight was obtained by NMR analysis. According to the $^1$H NMR spectra, by comparing the ratio of protons attributed to VDF and to polystyrenic units, the average degree of polymerization of PS (DP$_{PS}$) was calculated to be 39 ± 3, 62 ± 2, and 79 ± 4 per graft chain for ATRP reaction times of 8, 16, and 24 h, respectively. These three parent graft copolymers have similar graft density (1.68 - 1.72 mol%) but different PS graft length (DP$_{PS}$ = 39 – 79). They are termed P(VDF-co-CTFE$_{2.6}$mol%)-g-PS$_{39}$, P(VDF-co-CTFE$_{2.6}$mol%)-g-PS$_{62}$, and P(VDF-co-CTFE$_{2.6}$mol%)-g-PS$_{79}$, respectively. The styrene (St)/VDF (mol%) ratio was calculated using the total moles of styrene divided by total moles of VDF. $M_n$ of P(VDF-co-CTFE$_{2.6}$mol%)-g-PS$_{39}$, P(VDF-co-CTFE$_{2.6}$mol%)-g-PS$_{62}$, and P(VDF-co-CTFE$_{2.6}$mol%)-g-PS$_{79}$ were calculated to be 2.53×10$^5$, 3.30×10$^5$, and 3.90×10$^5$ g/mol, respectively. Chemical compositions are summarized in Table 3.1.

**Figure 3.1.** 400 MHz $^{19}$F NMR spectra of (a) the macroinitiator P(VDF-co-CTFE$_{2.6}$mol%) and (b) P(VDF-co-CTFE$_{2.6}$mol%)-g-PS$_{62}$ after 16 h ATRP reaction time.
Figure 3.2. 600 MHz $^1$H NMR spectra of (a) P(VDF-co-CTFE$_{2.6mol\%}$) (b) P(VDF-co-CTFE$_{2.6mol\%}$)-g-PS$_{39}$ after 8 h ATRP reaction time. (d$_6$-Acetone)

Table 3.1. Composition of graft copolymers: P(VDF-co-CTFE$_{2.6mol\%}$)-g-PS

<table>
<thead>
<tr>
<th>ATRP reaction time (h)</th>
<th>% CTFE initiated$^a$</th>
<th>Graft number density (mol%)$^b$</th>
<th>DP$_{PS}$$^c$</th>
<th>St/VDF$^d$ (mole ratio)</th>
<th>$M_n$, PS$^e \times 10^5$ (g/mol)</th>
<th>$M_n$, P(VDF-co-CTFE)-g-PS $\times 10^5$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>65 ± 1</td>
<td>1.68 ± 0.02</td>
<td>39 ± 3</td>
<td>67/100</td>
<td>1.29</td>
<td>2.52</td>
</tr>
<tr>
<td>16</td>
<td>65 ± 1</td>
<td>1.68 ± 0.02</td>
<td>62 ± 2</td>
<td>104/100</td>
<td>2.06</td>
<td>3.29</td>
</tr>
<tr>
<td>24</td>
<td>67 ± 1</td>
<td>1.72 ± 0.03</td>
<td>79 ± 4</td>
<td>136/100</td>
<td>2.66</td>
<td>3.89</td>
</tr>
</tbody>
</table>

Note. P(VDF-co-CTFE$_{2.6mol\%}$) macroinitiator consists of 2.6 mol% CTFE, estimated from $^{19}$F NMR. $M_n$ of P(VDF-co-CTFE$_{2.6mol\%}$) is $1.23 \times 10^5$ g/mol, measured by GPC and calibrated with linear PS standards. $^a$Based on $^{19}$F NMR. $^b$Number of graft side chains per 100 units in P(VDF-co-CTFE) backbone. $^c$Styrenes per graft chain, determined by the ratio of protons in VDF units and styrenic units using $^1$H NMR. $^d$Moles of styrene divided by moles of VDF, obtained from both $^1$H and $^{19}$F NMR. $^e$Calculated from DP$_{PS}$.

Sulfonation of PS side chains and the DS were verified by $^1$H NMR spectroscopy, as illustrated in Figure 3.3, where the $^1$H NMR spectra of the pristine graft copolymer P(VDF-co-CTFE$_{2.6mol\%}$)-g-PS$_{79}$ and its partially sulfonated graft copolymers are present.
The pristine copolymer exhibits peaks at 6.5 - 6.8 ppm (peak “a”) and 6.9 - 7.4 ppm (peak “b”) corresponding to ortho- and meta/para- protons of the phenyl ring, respectively. The partially sulfonated copolymers exhibit an additional peak at 7.6 ppm, which corresponds to protons adjacent to the sulfonated group (peak “c”). A greater intensity of peak “c” represents a higher DS in the copolymer. IEC measured by acid-base titration was compared to that derived from NMR data shown in Figure 3.4. A slight deviation with the titration-IEC data being up to 10% less was observed. However, this is not deemed sufficient significant to affect any of the conclusions and can be construed as being within experimental error. It also demonstrated that the acid groups in the membrane are accessible to water.

![NMR spectra](image)

**Figure 3.3.** 600 MHz $^1$H NMR spectra corresponding to graft PS of (a) P(VDF-co-CTFE$_{2.6mol\%}$)-$g$-SPS$_{79}$ after 24 h ATRP reaction time and its partially sulfonated graft copolymers: (b)P(VDF-co-CTFE$_{2.6mol\%}$)-$g$-SPS$_{79}$, DS= 12%; (c) P(VDF-co-CTFE$_{2.6mol\%}$)-$g$-SPS$_{79}$, DS= 48% (d$_6$-Acetone)
3.3.2. Effects of Ion Content and Graft Chain Length

Degree of Crystallinity

The degree of crystallinity in the graft membranes was determined by WAXS. WAXS experiments were performed and analyzed by Dr. Rasoul Narimani of Department of Physics, Simon Fraser University. WAXS patterns for the macroinitiator, the three unsulfonated graft copolymers and their selected sulfonated copolymers are shown in Figure 3.5. The scattered intensity is shown as a function of the scattering angle 2θ (top axis) and the scattering wave vector \( q = \frac{4\pi}{\lambda} \sin(\theta) \) (bottom axis), where \( \lambda =0.154 \text{ nm} \). Four peaks are observed for each copolymer. The peak positioned at \( 2\theta = 10^\circ \) is associated with PS chain-to-chain order,\(^{220}\) and decreases as DS increases. This behaviour is consistent with our previous work.\(^{211}\) The peaks observed at \( 2\theta = 19^\circ \) and \( 2\theta = 20^\circ \) are due to amorphous and crystalline domains, respectively.\(^{221,222}\) A very broad fourth peak positioned around \( 2\theta = 27^\circ \) is due to the presence of water. An example of WAXS spectrum showing three Gaussians peaks fitting to the data in the \( q \)-range of 0.45
Å⁻¹ to 1.6 Å⁻¹ is shown in Figure 3.6 for determination of degree of crystallinity of samples.

According to Equation 2.13, the degree of crystallinity of the fluorous macroinitiator (VDF-co-CTFE)₂.₆mol%·g-PS and representative graft copolymers can be calculated, and tabulated in Table 3.2 and displayed in Figure 3.7. A much lower degree of crystallinity ~ 6.7%, 6.4%, and 5.6% is observed for the three unsulfonated graft copolymers: P(VDF-co-CTFE₂.₆mol%)-g-PS₃₉, P(VDF-co-CTFE₂.₆mol%)-g-PS₆₂, and P(VDF-co-CTFE₂.₆mol%)-g-PS₇₉, respectively compared to the fluorous macroinitiator P(VDF-co-CTFE₂.₆mol%) (24%). The introduction of graft side chains leads to lower degrees of crystallinity because PS chains are inherently amorphous, moreover, they seem to hinder the crystallization of the fluorous backbone. Figure 3.7 also shows the degree of crystallinity of the graft copolymers containing various ion contents. For the P(VDF-co-CTFE₂.₆mol%)-g-PS₆₂ and P(VDF-co-CTFE₂.₆mol%)-g-PS₇₉ series, the degree of crystallinity of the sulfonated copolymers is similar to that of the unsulfonated copolymers, but the degree of crystallinity in the sulfonated versions of P(VDF-co-CTFE₂.₆mol%)-g-PS₃₉ (~12%) is nearly double that of the unsulfonated copolymer (~6.7%), leading to the conjecture that short sulfonated graft side chains enhance ordering of the PVDF backbone. A more precise explanation on the increase in crystallinity of sulfonated version of short side-chain polymers is not yet understood. Techniques such as SAXS and SANS can be used in the future for further details. The average crystalline domain sizes were calculated to be ~ 6 nm for all of the graft copolymers according to the Scherrer equation, Equation 2.14.²¹⁸,²¹⁹
Figure 3.5. WAXS patterns of (a) $\text{P(VDF-co-CTFE}_{2.6\text{mol\%}})-g-\text{PS}_{39}$ (blue), (b) $\text{P(VDF-co-CTFE}_{2.6\text{mol\%}})-g-\text{PS}_{62}$ (red), and (c) $\text{P(VDF-co-CTFE}_{2.6\text{mol\%}})-g-\text{PS}_{79}$ (green) series and the macroinitiator $\text{P(VDF-co-CTFE}_{2.6\text{mol\%}})$ (black).
Figure 3.6. WAXS spectrum of the graft polymer P(VDF-co-CTFE<sub>2.6mol%</sub>)-<i>g</i>-SPS<sub>39</sub>. Three Gaussian curves were fit to the data in order to estimate the degree of crystallinity.

Table 3.2. Degree crystallinity of P(VDF-co-CTFE<sub>2.6mol%</sub>)-<i>g</i>-PS copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>DS (%)</th>
<th>IEC (mmol/g)</th>
<th>Degree of Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(VDF-co-CTFE&lt;sub&gt;2.6mol%&lt;/sub&gt;)-&lt;i&gt;g&lt;/i&gt;-PS&lt;sub&gt;39&lt;/sub&gt;</td>
<td>0</td>
<td>-</td>
<td>6.7 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>1.12</td>
<td>12.6 ± 1.5</td>
</tr>
<tr>
<td></td>
<td>53</td>
<td>2.27</td>
<td>11.5 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>3.02</td>
<td>12.5 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>-</td>
<td>6.4 ± 0.3</td>
</tr>
<tr>
<td>P(VDF-co-CTFE&lt;sub&gt;2.6mol%&lt;/sub&gt;)-&lt;i&gt;g&lt;/i&gt;-PS&lt;sub&gt;62&lt;/sub&gt;</td>
<td>19</td>
<td>1.23</td>
<td>6.8 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>2.00</td>
<td>6.5 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>58</td>
<td>3.07</td>
<td>5.8 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>-</td>
<td>5.6 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>0.74</td>
<td>6.6 ± 0.6</td>
</tr>
<tr>
<td>P(VDF-co-CTFE&lt;sub&gt;2.6mol%&lt;/sub&gt;)-&lt;i&gt;g&lt;/i&gt;-PS&lt;sub&gt;79&lt;/sub&gt;</td>
<td>30</td>
<td>1.81</td>
<td>5.7 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>33</td>
<td>2.05</td>
<td>5.6 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>56</td>
<td>2.91</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 3.7. Degree of crystallinity for P(VDF-co-CTFE$_{2.6\text{mol\%}}$) and P(VDF-co-CTFE$_{2.6\text{mol\%}}$)-g-PS copolymers as a function of IEC

**Size and Nature of Ionic and Hydrophobic Domains**

TEM micrographs of representative dry graft membranes are displayed in Figure 3.8. The samples were stained with lead acetate prior to imaging to improve image contrast. The brighter regions represent hydrophobic domains and the darker regions represent ion-rich domains. In the dry state, a phase-separated morphology consisting of ion-rich domains 2 to 5 (± 1) nm in size is determined. These TEM images are similar to Nafion® membranes which have been reported to possess 4 – 10 nm diameter ionic clusters, but dissimilar to ionic fluorous diblock copolymers of similar ionic to fluorous ratio, which exhibit lamella-like morphologies.

The average diameter and number density of the ion-rich domains are summarized in Table 3.3. The domain size and number density of the ion-rich domains vs DS are plotted in Figure 3.9 (a) and (b), respectively to demonstrate the trend. For a
given series, the ion-rich domain size increases as DS increases. For example, in the P(VDF-co-CTFE$_{2.6\text{mol}\%}$)-g-SPS$_{39}$ series, the membrane having DS 18% possesses 2.5 ± 0.4 nm diameter ion-rich domains; whereas the completely sulfonated membrane possesses 3.8 ± 0.6 nm ion-rich domains. As DS is decreased, the sulfonic acid groups are separated to greater and greater extents by hydrophobic unsulfonated PS. Thus ionic aggregation, stabilized by the proximity of ion pairs and electrostatic forces, and influenced by the chain elasticity of the host polymer, is hindered by the need to expel hydrophobic PS. The result is that a lower DS confers smaller ionic aggregates. Moreover, DS also affects the number density of the ion-rich domains in these graft samples. For a given series, the number density of the ion-rich domains decreases as DS increases. We postulate that as DS is increased, the closer proximity of sulfonic acid groups along the PS side chain promotes ionic aggregation by stronger electrostatic interactions between ion pairs, leading to slightly larger, but fewer ion-rich domains.

Table 3.3. Average diameter and 2-D number density of ion-rich domains for representative P(VDF-co-CTFE$_{2.6\text{mol}\%}$)-g-SPS membranes

<table>
<thead>
<tr>
<th>Image label</th>
<th>IEC (mmol/g)</th>
<th>DS (%)</th>
<th>Ionic domain diameter (nm)</th>
<th>2-D cluster number density (per $10^4$ nm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(VDF-co-CTFE$<em>{2.6\text{mol}%}$)-g-SPS$</em>{39}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>1.12</td>
<td>18</td>
<td>2.5 ± 0.4</td>
<td>86 ± 5</td>
</tr>
<tr>
<td>B</td>
<td>3.52</td>
<td>100</td>
<td>3.8 ± 0.6</td>
<td>56 ± 3</td>
</tr>
<tr>
<td>P(VDF-co-CTFE$<em>{2.6\text{mol}%}$)-g-SPS$</em>{62}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1.23</td>
<td>19</td>
<td>2.3 ± 0.3</td>
<td>104 ± 7</td>
</tr>
<tr>
<td>D</td>
<td>4.05</td>
<td>100</td>
<td>4.1 ± 0.7</td>
<td>55 ± 2</td>
</tr>
<tr>
<td>P(VDF-co-CTFE$<em>{2.6\text{mol}%}$)-g-SPS$</em>{79}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>1.35</td>
<td>23</td>
<td>2.5 ± 0.4</td>
<td>126 ± 6</td>
</tr>
<tr>
<td>F</td>
<td>4.29</td>
<td>100</td>
<td>4.7 ± 0.6</td>
<td>53 ± 1</td>
</tr>
</tbody>
</table>
Figure 3.8. TEM images of P(VDF-co-CTFE_{2.6mol%})-g-SPS membranes. P(VDF-co-CTFE_{2.6mol%})-g-SPS\textsubscript{39} (A) IEC = 1.12 mmol/g, DS = 18%; (B) IEC = 3.52 mmol/g, DS = 100%. P(VDF-co-CTFE_{2.6mol%})-g-SPS\textsubscript{62} (C) IEC = 1.23 mmol/g, DS = 19%; (D) IEC = 4.05 mmol/g, DS = 100%. P(VDF-co-CTFE_{2.6mol%})-g-SPS\textsubscript{79} (E) IEC = 1.35 mmol/g, DS = 23%; (F) IEC = 4.29 mmol/g, DS = 100%.

For a more meaningful comparison, the membranes chosen for illustration in Figure 3.8 were prepared from copolymers of different graft length but comparable DS, thus aiding the examination of the effect of graft length on morphology. At lower DS \(\sim\) 20%, hydrophobic regions are more defined and there is enhanced contrast between hydrophobic and ion-rich regions (Figure 3.8 (A), (C), and (E)). The size of ionic domain diameters was measured to be \(\sim\) 2.3-2.5 nm for the three series having DS \(\sim\) 20%. Not much difference in ionic domain size is found for copolymers with different graft lengths. However, the number density of the ion-rich domains is 86, 104, and 126 per \(10^4\) \(\text{nm}^2\) for
P(VDF-co-CTFE$_{2.6\text{mol\%}}$)-g-PS$_{39}$, P(VDF-co-CTFE$_{2.6\text{mol\%}}$)-g-PS$_{62}$, and P(VDF-co-CTFE$_{2.6\text{mol\%}}$)-g-PS$_{79}$, respectively. At lower DS (~20%), copolymers having longer side chains possess ions that are dispersed along the chain, which restricts the formation of large ionic aggregates. As DS increases, the size of the ion-rich domains increases, while the number density decreases for all of the three series. At DS ~100%, the number density of ion-rich domains is similar for the three series of copolymers ~ 53 - 56 per $10^4$ nm$^2$. For samples in which DS is ~ 100%, (Figure 3.8 (B), (D), and (F)), the ions are closer together and there is less hydrophobic styrenic material in between. Since the PS chains are completely sulfonated, strong electrostatic attractions between sulfonic acid groups facilitate formation of ionic aggregates and as the graft length increases, larger ion-rich domains are observed. Here, TEM analyses are used to gain insight into relative size of ionic-rich domains. Examination of phase separation on these membranes were performed by SAXS and SANS by Narimani et al.$^{228}$

**Figure 3.9.** The diameter and number density of the ion-rich domains vs DS
Water Sorption

The water sorption properties of the membranes are expressed as water uptake, water content, and $\lambda$, as tabulated in Table 3.4. Water uptake as a function of IEC for P(VDF-co-CTFE$_{2.6\text{mol\%}}$)-g-SPS membranes is plotted in Figure 3.10 (a), corresponding values of $\lambda$ are reported in parentheses. P(VDF-co-CTFE$_{2.6\text{mol\%}}$)-g-SPS membranes possessing a similar IEC to Nafion® 117 (IEC = 0.91 mmol/g) were observed to possess water uptakes between 11 and 18 wt%, which are significantly lower than Nafion® 117 (30 wt%); which translates to lower values of $\lambda$ (7 – 9) compared to Nafion® 117 ($\lambda = 24$) even when the graft copolymers possessed much higher IEC values ~ 1.8 mmol/g. This is consistent with the idea that the graft copolymers possess strong interconnected hydrophobic domains which oppose the osmotic pressure-driven swelling and dissolution.

Figure 3.10 (a) shows that the water uptake of the membranes increases gradually for IEC values below 1.8 mmol/g. Above an IEC of 1.81 mmol/g, a percolation threshold occurs, at which the water uptake of the P(VDF-co-CTFE$_{2.6\text{mol\%}}$)-g-SPS$_{79}$ series increases dramatically with IEC to values up to 815 wt%. Relative to the long length SPS side chain series (DP$_{PS}$ = 79), the medium length SPS side chain series (DP$_{PS}$ = 62) is more tolerant to excessive swelling, and the short length SPS side chain series (DP$_{PS}$ = 39) can tolerate even higher IECs, up to 3 mmol/g, before excessive swelling occurs. Similarly, $\lambda$ values increase steadily up to IECs ~1.8 mmol/g, but increase significantly above a given threshold of IEC. Upon complete sulfonation, the short grafts remain insoluble while the medium and long grafts partially dissolve in water. We conjecture that the relatively high tolerance against excessive swelling in the short grafts is due to either the higher PVDF content or the higher crystallinity of this series. The
PVDF content of the short grafts is 49 wt% compared to 37 and 32 wt% in the medium and long grafts, respectively. In addition, the short side chain analogue, DP$_{PS} = 39$, has the highest crystallinity with the tendency of the polymers to form crystalline domains, which serve a cross-linking function, can reduce the swelling. Furthermore, as observed from TEM analyses, the hydrophobic matrix in the SPS$_{39}$ series is more defined and connected; whereas in the SPS$_{62}$ and SPS$_{79}$ series, ion-rich domains are more clearly observed and the hydrophobic matrix less connected. It appears that, for the latter scenario, the internal elastic forces that oppose osmotic pressure-driven swelling are not as strong. This observation is reinforced later in the discussion of the role of graft density.

**Figure 3.10.** (a) Water uptake ($\lambda$ is reported in parentheses), (b) proton conductivity, (c) analytical acid concentration, and (d) effective proton mobility as a function of IEC for: P(VDF-co-CTFE$_{2.6\text{mol\%}}$)-g-PS$_{39}$, P(VDF-co-CTFE$_{2.6\text{mol\%}}$)-g-PS$_{62}$, P(VDF-co-CTFE$_{2.6\text{mol\%}}$)-g-PS$_{79}$, and Nafion® 117
<table>
<thead>
<tr>
<th>Membrane</th>
<th>IEC(^a) (mmol/g)</th>
<th>DS (%)</th>
<th>Water uptake(^b) (%)</th>
<th>Water content(^b) (%)</th>
<th>(\lambda)</th>
<th>Conductivity (mS/cm)(^c)</th>
<th><a href="M">(-\mathrm{SO}_3\mathrm{H})</a></th>
<th>(\mu_{\text{eff}} \times 10^3) (cm(^2)/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCV-g-SPS(_{30})</td>
<td>1.12 ± 0.01</td>
<td>18</td>
<td>18 ± 1</td>
<td>15 ± 1</td>
<td>9 ± 1</td>
<td>8 ± 1</td>
<td>1.07 ± 0.04</td>
<td>0.07 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>1.72 ± 0.04</td>
<td>31</td>
<td>47 ± 6</td>
<td>32 ± 1</td>
<td>15 ± 1</td>
<td>47 ± 2</td>
<td>1.34 ± 0.04</td>
<td>0.37 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>2.27 ± 0.07</td>
<td>53</td>
<td>155 ± 8</td>
<td>61 ± 1</td>
<td>38 ± 2</td>
<td>72 ± 2</td>
<td>1.04 ± 0.07</td>
<td>0.77 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>2.66 ± 0.06</td>
<td>60</td>
<td>211 ± 6</td>
<td>67 ± 1</td>
<td>45 ± 2</td>
<td>84 ± 11</td>
<td>0.89 ± 0.02</td>
<td>0.96 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>3.02 ± 0.05</td>
<td>70</td>
<td>278 ± 25</td>
<td>73 ± 1</td>
<td>53 ± 4</td>
<td>77 ± 9</td>
<td>0.77 ± 0.02</td>
<td>1.03 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>3.33 ± 0.08</td>
<td>85</td>
<td>788 ± 33</td>
<td>89 ± 1</td>
<td>136 ± 7</td>
<td>44 ± 2</td>
<td>0.39 ± 0.02</td>
<td>1.12 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>3.52 theoretical</td>
<td>100</td>
<td>1790 ± 55</td>
<td>96 ± 1</td>
<td>283</td>
<td>41 ± 3</td>
<td>0.30 ± 0.08</td>
<td>1.42 ± 0.03</td>
</tr>
<tr>
<td>PCV-g-SPS(_{52})</td>
<td>1.23 ± 0.04</td>
<td>19</td>
<td>15 ± 1</td>
<td>13 ± 1</td>
<td>7 ± 1</td>
<td>1 ± 0.1</td>
<td>0.82 ± 0.01</td>
<td>0.01 ± 0.00</td>
</tr>
<tr>
<td></td>
<td>1.79 ± 0.04</td>
<td>23</td>
<td>36 ± 1</td>
<td>26 ± 1</td>
<td>11 ± 1</td>
<td>21 ± 1</td>
<td>1.21 ± 0.07</td>
<td>0.18 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>2.00 ± 0.05</td>
<td>28</td>
<td>48 ± 2</td>
<td>32 ± 1</td>
<td>13 ± 1</td>
<td>34 ± 2</td>
<td>1.38 ± 0.05</td>
<td>0.26 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>2.74 ± 0.04</td>
<td>49</td>
<td>298 ± 11</td>
<td>75 ± 1</td>
<td>62 ± 3</td>
<td>68 ± 4</td>
<td>0.66 ± 0.02</td>
<td>1.01 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>3.07 ± 0.05</td>
<td>58</td>
<td>835 ± 66</td>
<td>89 ± 1</td>
<td>158 ± 8</td>
<td>33 ± 1</td>
<td>0.33 ± 0.01</td>
<td>1.04 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>4.05 theoretical</td>
<td>100</td>
<td>Partially dissolve in water</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PCV-g-SPS(_{70})</td>
<td>0.74 ± 0.03</td>
<td>12</td>
<td>11 ± 1</td>
<td>10 ± 1</td>
<td>9 ± 2</td>
<td>3 ± 2</td>
<td>0.45 ± 0.07</td>
<td>0.06 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>1.35 ± 0.02</td>
<td>23</td>
<td>29 ± 3</td>
<td>22 ± 2</td>
<td>12 ± 1</td>
<td>15 ± 2</td>
<td>1.07 ± 0.05</td>
<td>0.14 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>1.48 ± 0.04</td>
<td>27</td>
<td>38 ± 2</td>
<td>27 ± 1</td>
<td>14 ± 1</td>
<td>23 ± 1</td>
<td>1.11 ± 0.03</td>
<td>0.24 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>1.81 ± 0.04</td>
<td>30</td>
<td>65 ± 4</td>
<td>39 ± 2</td>
<td>20 ± 1</td>
<td>45 ± 1</td>
<td>1.19 ± 0.03</td>
<td>0.37 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>2.05 ± 0.09</td>
<td>33</td>
<td>128 ± 12</td>
<td>56 ± 2</td>
<td>33 ± 2</td>
<td>69 ± 4</td>
<td>0.91 ± 0.08</td>
<td>0.80 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>2.35 ± 0.02</td>
<td>48</td>
<td>815 ± 63</td>
<td>89 ± 1</td>
<td>199 ± 14</td>
<td>33 ± 9</td>
<td>0.34 ± 0.03</td>
<td>1.02 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>2.91 ± 0.04</td>
<td>56</td>
<td>1060± 94</td>
<td>92±1</td>
<td>211±10</td>
<td>36±7</td>
<td>0.28±0.06</td>
<td>1.23±0.08</td>
</tr>
<tr>
<td></td>
<td>4.29 theoretical</td>
<td>100</td>
<td>Partially dissolve in water</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Note. \(^a\)By titration. \(^b\)Room temperature. \(^c\)Soaked in H\(_2\)O overnight and pat-dried with a Kimwipe paper before measurements at room temperature. *Errors were calculated based on standard deviation of several experiments.
**Proton Conductivity and Proton Mobility**

Proton conductivity ($\sigma$) as a function of IEC is plotted in Figure 3.10 (b). The trends are non-linear, which are in a good accord with other PEM systems.\textsuperscript{138, 164, 211, 229} Proton conductivity initially increases with increasing IEC, but decreases above IEC $\sim$ 2.7 mmol/g for the P(VDF-co-CTFE\textsubscript{2.6mol\%})-$g$-SPS\textsubscript{39} and P(VDF-co-CTFE\textsubscript{2.6mol\%})-$g$-SPS\textsubscript{62} series and above IEC $\sim$ 2.05 mmol/g for the P(VDF-co-CTFE\textsubscript{2.6mol\%})-$g$-SPS\textsubscript{79} series. Taking into account of both Figure 3.10 (a) and (b), we note that $\sigma$ decreases when the water uptake exceeds $\sim$ 300%. The maximum proton conductivities are 84 ± 11, 68 ± 4, and 69 ± 4 mS/cm for the SPS\textsubscript{39}, SPS\textsubscript{62}, and SPS\textsubscript{79} series, respectively, which are similar to values for Nafion\textsuperscript{®} 117 (75± 4 mS/cm). The short side chain SPS\textsubscript{39} series shows steady increases in $\sigma$ as a function of IEC and $\sigma$ remains relatively high ( $\sim$ 72 ± 2, 84 ± 11, and 77 ± 9 mS/cm for high IEC values $\sim$ 2.27, 2.66, and 3.02 mmol/g, respectively), demonstrating a wider operating range for high $\sigma$. In contrast, the medium and long side chain membranes exhibit a sharper increase in $\sigma$ with increasing IEC and a sharper decline in $\sigma$ after reaching their maximum conductivity of $\sim$ 70 mS/cm, due to the large drop in acid concentration caused by excessive swelling. Analytical acid concentration [-SO$_3$H] as a function of IEC is shown in Figure 3.10 (c). With increasing IEC, [-SO$_3$H] initially increases, but drops significantly above IEC $\sim$ 1.7 - 2.0 mmol/g for all series. This trend has been previously observed for other PEM systems,\textsuperscript{138, 164, 211, 229} and is due to dilution of acidic sites with increasingly high water uptake. Effective proton mobility ($\mu$\textsubscript{eff}) in hydrated membranes is plotted versus IEC in Figure 3.10 (d) and increases as a function of IEC and thus water content. This is consistent with the fact that water aids dissociation and provides a contiguous path for the transport of
For all graft membranes, the proton mobility increases asymptotically with increasing IECs and levels off.

Proton conductivity is plotted as a function of $\lambda$ in Figure 3.11 to understand how efficiently the series with different graft length utilize water to transport protons. From the inset of Figure 3.11, we can observe that the number of water molecules commensurate with a significant increase in $\sigma$ is 9 for SPS$_{39}$, 7-11 for SPS$_{62}$, and 9-12 for SPS$_{79}$. Proton conductivity increases with increasing $\lambda$ up to values of 40-50 after which $\sigma$ drops with further increases, which is similar to that observed for other polymer systems (e.g., SPEEK, ETFE-g-PSSA, sPI, BAM and Nafion® membranes), and confirms that at $\lambda \sim 40-50$, $\sigma$ values are maximized, and additional water is often superfluous, even detrimental to $\sigma$ because the proton concentration is further diluted.

**Figure 3.11.** Proton conductivity as a function of $\lambda$ for: P(VDF-co-CTFE$_{2.6\text{mol\%}}$)-g-PS$_{39}$, P(VDF-co-CTFE$_{2.6\text{mol\%}}$)-g-PS$_{62}$, P(VDF-co-CTFE$_{2.6\text{mol\%}}$)-g-PS$_{79}$, and Nafion® 117.
**Conductivity as a Function of Temperature and RH**

Water sorption and proton conductivities of $P(VDF-co-CTFE_{2.6\text{mol}\%})$-$g$-SPS$_{39}$ and $P(VDF-co-CTFE_{2.6\text{mol}\%})$-$g$-SPS$_{79}$ membranes possessing IEC $> 2.0$ mmol/g were measured as a function of RH and temperature. These two groups of polymers were chosen because they represent two extremes of the series: short side chains versus longer side chains; higher PVDF wt% versus lower PVDF wt%. As shown in Figure 3.12, both $\sigma$ and water content increase with increasing RH. The conductivity of the membranes remains low, $\sim 13$ mS/cm for RH $< 65\%$, but is similar to benchmark Nafion® 117 ($\sim 22$ mS/cm). For RH above 65\%, the conductivity of graft membranes possessing higher IECs increases more quickly with RH. For instance, for the $P(VDF-co-CTFE_{2.6\text{mol}\%})$-$g$-SPS$_{79}$ membranes possessing IEC $\sim 2.35$ mmol/g, $\sigma$ increases from 13 to 54 mS/cm as RH is increased from 65\% to 85\%, whereas $\sigma$ of Nafion® 117 increases from 22 to 45 mS/cm. An even larger increase in $\sigma$ between RH 85\% and 95\% is observed. For example, $\sigma$ for SPS$_{79}$ membranes having IEC $\sim 2.35$ mmol/g increases from 54 to 127 mS/cm and SPS$_{39}$ membranes possessing IEC of 3.02 mmol/g increases from 40 to 139 mS/cm, whereas $\sigma$ of Nafion® 117 increases from 45 to 66 mS/cm. While this is simply the result of the greater water uptake, the striking feature of the conductivity vs RH plot is that the graft membranes exhibit similar conductivity to Nafion® 117 in the lower RH regions (below 80% RH) even though the $\lambda$ values are lower than Nafion® 117. This is attributed to the higher concentration of protons in the graft membranes. The relative slopes of the log ($\sigma$) as a function of RH shown in Figure 3.12 reveal the impact of relative humidity on membranes’ conductivity. The smaller the value of slope, the lesser the effect of RH on proton conductivity. In both series, it appears that the highly sulfonated graft membranes possess higher slope than the ones.
with lower ion content, suggesting that the conductivity is more dependent on RH for graft membranes having higher ion content.

Figure 3.13 shows the relationship between conductivity and temperature for selected membranes at 95% RH. For a given series, membranes possessing higher ion content exhibit higher $\sigma$ between 25°C to 80°C. At 80°C, the highly sulfonated membranes in both series exhibit proton conductivities up to $\sim 340$ mS/cm at 95% RH. These values are exceptionally high compared to Nafion® 117 (165 mS/cm). This may be attributed to high ionic purity in the graft copolymers, promoting well connected hydrophilic conducting channels.

The activation energy for proton transport can be extracted through an Arrhenius plot of the data. According to Arrhenius plots, the activation energy decreases from 20.0 to 15.9 KJ/mol as IEC is increased from 2.05 to 2.35 mmol/g for P(VDF-co-CTFE$_{2.6\text{mol}\%}$)-g-PS$_{79}$ membranes and is lowered further to 13.4 KJ/mol for the completely sulfonated long graft membrane. The result suggests that the higher sulfonated membranes possess more water content to form well-connected ionic pathways, thus require lower activation energy for proton transport. A similar trend is also observed in short series, except that there is only slight difference between the activation energy for membranes having IEC $\sim 2.66$ and 3.02 mmol/g. The values for highly sulfonated graft membranes are similar to Nafion® 117 (13.4 KJ/mol, which is consistent with previously reported value 13.5 kJ/mol).
Figure 3.12. (a) Hydration number ($\lambda$) and (b) proton conductivity as a function of RH at 25°C. Samples were equilibrated under water vapour.

Figure 3.13. Proton conductivity versus temperature at 95% RH

3.3.3. Effect of Graft Number Density

In order to differentiate the effects of crystallinity and PVDF content on the properties of these materials, two series of graft polymers possessing different graft number densities were selected for comparison. These two series were chosen...
because they possess similar weight fractions of PS to fluorous polymer and similar graft lengths, but different CTFE content in the P(VDF-co-CTFE) backbone so that upon grafting of PS, the average VDF sequence length between PS side chains is different, thereby resulting in different degree of crystallinity, as represented in Scheme 3.2. The polymers studied here are: (i) P(VDF-co-CTFE$_{2.6\text{mol\%}}$)-g-SPS$_{39}$ series, described previously in this chapter, based on an initial CTFE content of 2.6 mol% and containing a PS weight fraction of 51 wt% after grafting; (b) P(VDF-co-CTFE$_{5.8\text{mol\%}}$)-g-SPS$_{35}$, described in a previous study from our group,\textsuperscript{211} based on 5.8 mol% CTFE content, and containing a PS weight fraction of 54 wt% after grafting. The pristine graft copolymers are labeled P(VDF-co-CTFE$_{2.6\text{mol\%}}$)-g-PS$_{39}$ and P(VDF-co-CTFE$_{5.8\text{mol\%}}$)-g-PS$_{35}$, respectively and their chemical properties are compared in Table 3.5. The data for P(VDF-co-CTFE$_{5.8\text{mol\%}}$)-g-PS$_{35}$ are taken from Tsang et al.\textsuperscript{211}

**Scheme 3.2.** Schematic representation of graft copolymers possessing similar weight fraction of polystyrene but different graft number density
Table 3.5. Chemical composition of P(VDF-co-CTFE$_{2.6\text{mol}}$%-g-PS$_{39}$ and P(VDF-co-CTFE$_{5.8\text{mol}}$%-g-PS$_{35}$)

<table>
<thead>
<tr>
<th>CTFE content$^a$ (mol%)</th>
<th>Graft density$^b$ (mol%)</th>
<th>DP$_{PS}$$^c$</th>
<th>Mn, PS$^d$ × 10$^5$ [g/mol]</th>
<th>Weight fraction of PS$^e$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6</td>
<td>1.7</td>
<td>39</td>
<td>1.29</td>
<td>51</td>
</tr>
<tr>
<td>5.8</td>
<td>2.3</td>
<td>35</td>
<td>3.64</td>
<td>54</td>
</tr>
</tbody>
</table>

Note. $^a$Calculated based on $^{19}$F NMR. $^b$Number of PS graft side chains per 100 units of fluorous backbone, calculated from the mol% of CTFE content in fluorous backbone multiplied by the % of CTFE reacted during ATRP. $^c$Number of styrenes per graft chain. $^d$Calculated from DP$_{PS}$. $^e$M$_n$,PS/M$_n$,total.

**Nature of Ionic and Hydrophobic Domains and Degree of Crystallinity**

TEM micrographs are shown in Figure 3.14 for membranes having low DS (~18% and 13%) and intermediate DS (53% and 59%) in the P(VDF-co-CTFE$_{2.6\text{mol}}$%-g-PS$_{39}$ (Figure 3.14 A and B) and P(VDF-co-CTFE$_{5.8\text{mol}}$%-g-PS$_{35}$ (Figure 3.14 C and D, provided by Dr. Emily Tsang). The IEC, DS, domain diameter and number density, and degree of crystallinity are compared in Table 3.6. Both series yield 2 to 4 nm ionic clusters. However, the 2.6 mol% CTFE polymers yield fewer ionic clusters and the hydrophobic matrix is more contiguous. This can be realized that the 2.6 mol% CTFE polymers have longer sequence length in the fluorous backbone associated to their lower graft density of side chains. Therefore, the hydrophobic domains are more pronounced. Furthermore, due to their lower graft density of side chains, the overall number of sulfonic acid groups is much less; therefore, the series was observed to possess fewer ionic clusters. According to WAXS data, it was revealed that P(VDF-co-CTFE$_{2.6\text{mol}}$%-g-PS$_{39}$ possesses a higher degree of crystallinity (~12.5%) than P(VDF-co-CTFE$_{5.8\text{mol}}$%-g-PS$_{35}$ (<5%).
Figure 3.14. TEM images of selected P(VDF-co-CTFE)-g-SPS graft membranes. P(VDF-co-CTFE$_{2.6\text{mol\%}}$)-g-SPS$_{39}$ (A) IEC = 1.12 mmol/g, DS = 18%. (B) IEC = 3.02 mmol/g, DS = 70%. P(VDF-co-CTFE$_{5.8\text{mol\%}}$)-g-SPS$_{35}$ (C) IEC = 0.64 mmol/g, DS = 13%. (D) IEC = 2.48 mmol/g, DS = 59%.

Table 3.6. Quantitative data from TEM analysis and the degree of crystallinity for P(VDF-co-CTFE$_{2.6\text{mol\%}}$)-g-SPS$_{39}$ and P(VDF-co-CTFE$_{5.8\text{mol\%}}$)-g-SPS$_{35}$

<table>
<thead>
<tr>
<th>Image label</th>
<th>IEC (mmol/g)</th>
<th>DS (%)</th>
<th>Ionic domain diameter (nm)</th>
<th>2-D cluster number density (per $10^4$ nm$^2$)</th>
<th>Degree of Crystallinity (%)</th>
</tr>
</thead>
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<tr>
<td>P(VDF-co-CTFE$<em>{2.6\text{mol%}}$)-g-SPS$</em>{39}$</td>
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</tr>
<tr>
<td>A</td>
<td>1.12</td>
<td>18</td>
<td>2.5 ± 0.4</td>
<td>86 ± 5</td>
<td>12.6 ± 1.5</td>
</tr>
<tr>
<td>B</td>
<td>2.27</td>
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<td>3.5 ± 0.6</td>
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<td>12.5 ± 0.6</td>
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<tr>
<td>C*</td>
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<tr>
<td>D*</td>
<td>2.48</td>
<td>59</td>
<td>3.3 ± 0.4</td>
<td>190 ± 20</td>
<td>&lt; 5%</td>
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</tbody>
</table>

Note. *Data of (C) and (D) was extracted from Tsang et. al.$^{211}$

Water Sorption and Proton Conductivity.

Selected properties for the two series are plotted as a function of IEC in Figure 3.15 and the data is listed in Table 3.7. A lower water uptake is observed for the P(VDF-co-CTFE$_{2.6\text{mol\%}}$)-g-SPS$_{39}$ series as show in Figure 3.15 (a). This is possibly due to its considerably higher degree of crystallinity. In the series having 5.8 mol% CTFE,
membranes with IEC > 2.5 mmol/g dissolve in water. Based on TEM data, this series of polymers possess a higher number density of ionic rich domains, which we also believe affects water swelling, as it may translate to lower cohesive energy forces between hydrophobic domains. Figure 3.15 (b) shows proton conductivity as a function of IEC. The P(VDF-co-CTFE_{5.8mol%})-g-SPS_{35} series has a lower percolation threshold for $\sigma$ than P(VDF-co-CTFE_{2.6mol%})-g-SPS_{39}. The $\sigma$-IEC plots are similar in profile but offset by $\sim$0.5 mmol/g which is mirrored by the offset in the water sorption-, proton concentration-, and proton mobility-IEC plots.

**Proton Conductivity as a Function of RH**

Water sorption and proton conductivity as a function of RH for the P(VDF-co-CTFE_{2.6mol%})-g-SPS_{39} and P(VDF-co-CTFE_{5.8mol%})-g-SPS_{35} series are plotted in Figure 3.16. The offset of water sorption described above for the two series exposed to liquid water is not observed under the vapour phase. Membranes having similar degree of sulfonation (i.e., 53% versus 44% and 60% versus 59%) absorb similar quantities of water. In the case of liquid water exposure, P(VDF-co-CTFE_{2.6mol%})-g-SPS_{39} absorbs less water than P(VDF-co-CTFE_{5.8mol%})-g-SPS_{35} for IECs < 3.0 mmol/g. However, with exposure to water vapour, the water uptake increases with higher IECs. For instance, a P(VDF-co-CTFE_{2.6mol%})-g-SPS_{39} membrane with IEC $\sim$2.66 mmol/g (60% DS) yields $\lambda \sim 45$ in liquid water, whereas P(VDF-co-CTFE_{5.8mol%})-g-SPS_{35} membrane with IEC $\sim$ 2.48 mmol/g (59% DS) yields $\lambda \sim 80$, suggesting that IEC is not the major factor affecting $\lambda$, instead, the effect of crystallinity may play a more important role in water sorption properties for the two series in water saturated condition. Nevertheless, the 2.66 mmol/g IEC P(VDF-co-CTFE_{2.6mol%})-g-SPS_{39} membrane possesses a similar $\lambda$ to the 2.48 mmol/g IEC P(VDF-co-CTFE_{5.8mol%})-g-SPS_{35} membrane ($\lambda \sim 9$ and 7, respectively) after
Table 3.7: Properties of P(VDF-co-CTFE-g-SPS) copolymer membranes having different amount of CTFE

<table>
<thead>
<tr>
<th>Membrane</th>
<th>IEC(^a) (mmol/g)</th>
<th>Water uptake(^b) (%)</th>
<th>Water content(^b) (%)</th>
<th>(\lambda)</th>
<th>Conductivity (mS/cm)(^c)</th>
<th>([-\text{SO}_3\text{H}]) (M)</th>
<th>(\mu_\text{eff} \times 10^3) (cm(^2)/s/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(VDF-co-CTFE(<em>{2.6\text{mmol}})-g-SPS(</em>{39}))</td>
<td>1.12 ± 0.01</td>
<td>18 ± 1</td>
<td>15 ± 1</td>
<td>9 ± 1</td>
<td>8 ± 1</td>
<td>1.07 ± 0.01</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>1.72 ± 0.04</td>
<td>47 ± 6</td>
<td>32 ± 1</td>
<td>15 ± 1</td>
<td>47 ± 2</td>
<td>1.34 ± 0.04</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>2.27 ± 0.07</td>
<td>155 ± 8</td>
<td>61 ± 1</td>
<td>38 ± 2</td>
<td>72 ± 2</td>
<td>1.04 ± 0.07</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>2.66 ± 0.06</td>
<td>211 ± 6</td>
<td>67 ± 1</td>
<td>45 ± 2</td>
<td>84 ± 11</td>
<td>0.89 ± 0.02</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>3.02 ± 0.05</td>
<td>278 ± 25</td>
<td>73 ± 1</td>
<td>53 ± 4</td>
<td>77 ± 9</td>
<td>0.77 ± 0.02</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>3.33 ± 0.08</td>
<td>788 ± 33</td>
<td>89 ± 1</td>
<td>136 ± 7</td>
<td>44 ± 2</td>
<td>0.39 ± 0.02</td>
<td>1.12</td>
</tr>
<tr>
<td>P(VDF-co-CTFE(<em>{5.8\text{mmol}})-g-SPS(</em>{35}))</td>
<td>0.64 ± 0.02</td>
<td>9 ± 1</td>
<td>8 ± 1</td>
<td>7 ± 1</td>
<td>2 ± 1</td>
<td>0.62 ± 0.02</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>1.03 ± 0.04</td>
<td>21 ± 2</td>
<td>17 ± 1</td>
<td>11 ± 1</td>
<td>10 ± 3</td>
<td>0.82 ± 0.02</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>1.22 ± 0.02</td>
<td>28 ± 1</td>
<td>22 ± 1</td>
<td>13 ± 1</td>
<td>40 ± 2</td>
<td>1.01 ± 0.01</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>1.59 ± 0.02</td>
<td>89 ± 5</td>
<td>47 ± 3</td>
<td>31 ± 2</td>
<td>75 ± 6</td>
<td>0.89 ± 0.03</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>1.98 ± 0.05</td>
<td>176 ± 5</td>
<td>63 ± 1</td>
<td>53 ± 3</td>
<td>83 ± 2</td>
<td>0.73 ± 0.01</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td>2.48 ± 0.06</td>
<td>358 ± 17</td>
<td>78 ± 1</td>
<td>80 ± 3</td>
<td>65 ± 1</td>
<td>0.52 ± 0.01</td>
<td>1.30</td>
</tr>
</tbody>
</table>

Note. \(^a\)By titration. \(^b\)Room temperature. \(^c\)Soaked in H\(_2\)O overnight and pat-dried with a Kimwipe paper before measurements at room temperature. \(^\ast\)Errors were calculated based on standard deviation of several experiments.
exposure to water vapour at 95% RH and 25°C. These values are half that of Nafion® 117. Moreover, despite \( \lambda \) being much lower than Nafion® 117, their proton conductivities are just as high as Nafion® 117 at 95% RH. This is likely due to the much higher ion content. At lower RH (55% - 85% RH), the higher IEC membranes in the two series possess comparable proton conductivity than Nafion® 117.

Figure 3.15. (a) Water uptake, (b) proton conductivity, (c) analytical acid concentration, and (d) effective proton mobility as a function of IEC for P(VDF-co-CTFE\(_{2.6\text{mol}\%}\))-g-PS\(_{39}\) series, P(VDF-co-CTFE\(_{5.8\text{mol}\%}\))-g-PS\(_{35}\) and Nafion® 117.
Figure 3.16. (a) $\lambda$ and (b) $\sigma$ as a function of RH at 25°C for P(VDF-co-CTFE)\textsubscript{2.6mol%}-g-PS\textsubscript{39} and P(VDF-co-CTFE)\textsubscript{5.8mol%}-g-PS\textsubscript{35} series

3.4. Conclusion

Three series of fluorous-ionic graft copolymers with the same graft density and systematically-controlled graft length were synthesized and characterized. The degree of crystallinity of the membrane due to the fluorous phase decreases from ~24% to ~6% as a result of growing graft PS chains onto the fluorous macroinitiator, suggesting that the graft side chains limit the organization of the fluorous backbone. Sulfonation of the short graft length membranes P(VDF-co-CTFE)\textsubscript{2.6mol%}-g-PS\textsubscript{39} increases degree of crystallinity by a factor of two (to ~12%) relative to its pristine unsulfonated copolymer (~6%). On the other hand, crystallinity of the other two longer side-chain series remains unchanged. This observation indicates that the effect of sulfonation on crystallinity is more pronounced for polymers with shorter graft chains.

A cluster-network morphology was observed for all of the graft copolymers irrespective of graft length. The shorter graft length series possess more defined and better interconnected hydrophobic domains. The shorter graft length series are more
tolerant to swelling when the ion content is high due to its higher PVDF content, more contiguous hydrophobic domains as well as higher degree of crystallinity. With allowance to high ion content, we speculate that the short graft polymers provide purer ionic pathways for high proton mobility and proton conductivity. A wider IEC operating range is observed for the shorter graft length series due to limited water swelling. In water vapour condition between 65% and 85% RH, the graft membranes exhibit lower water content, but provide comparable conductivities to Nafion® membranes. At 95% RH, the highly sulfonated graft membranes exhibit exceptionally high proton conductivities up to 140 mS/cm, which is more than twice that for Nafion® 117 (66 mS/cm). Similarly, proton conductivities at 80°C for graft polymers having IECs larger than 2.3 mmol/g were as high as 340 mS/cm. These results suggest that the high ion content in the graft copolymers can promote well connected hydrophilic conducting channels for higher proton conductivity.

Previously, we concluded that the higher degree of crystallinity and higher PVDF content observed in the short graft length series increases the cohesivity of the fluorous matrix and aids in controlling swelling of the polymer in water. In order to differentiate two factors, another system of a chemically similar polymer, P(VDF-co-CTFE_{5.8mol%})-g-SPS_{35}, prepared by the same method but possessing a higher graft number density, was examined. The degree of crystallinity is significantly higher in the lower-graft-density P(VDF-co-CTFE_{2.6mol%})-g-SPS_{39} series due to the longer sequence length between graft side chains. Furthermore, the number density of ion-rich domains was lower and hydrophobic domains were better connected. The two series possessed similar proton conductivity-IEC profiles, offset by 0.5 mmol/g. The P(VDF-co-CTFE_{2.6mol%})-g-SPS_{39}
membranes are less susceptible to dissolution in water and could be therefore be sulfonated to greater extents.
Chapter 4. Graft Copolymer Blends as Proton Exchange Membranes

4.1. Introduction

Research continues towards the development of proton exchange membranes (PEMs) capable of maintaining proton conductivity under reduced humidity (e.g., ≥0.1 S/cm, ≤50% RH), while retaining limited swelling upon full hydration. State-of-the-art PEMs are based on perfluorosulfonic acid (PFSA) ionomers, where it is established that the nanoscale phase-separated morphology provides contiguous hydrophilic channels for the transport of protons that assist proton conduction under reduced RH and water content. Hydrocarbon-based ionomers, partially fluorinated ionomers, polybenzimidazoles, acid-base blends, and ionomer blends are coming to the forefront because of their variable, controlled composition and microstructure. As with PFSA ionomers, the formation of a desirable channel-supporting morphology appears to be a requirement for maintaining satisfactory proton transport under lower levels of hydration. Clearly, the polymer’s microstructure determines the resultant membrane’s morphology, and consequently water sorption, proton conductivity and mechanical integrity, and while significant advances have been made in this area, the relation of microstructure and blend interactions on these properties are still poorly understood.

Block and graft copolymers are versatile model systems for elucidating structure-property relationships in PEM research because they can be designed to form specific
nanostructures. Previous work on ionic diblock and graft copolymers confirmed that the polymer architecture greatly impacts water sorption and proton transport. Sulfonated block copolymers allow for the alteration of block length and the formation of large lamella-like ionic domains but swelled excessively in water even when the IEC was relatively low. The graft copolymer ionomers on the other hand formed membranes consisting of an interconnected network of disordered, ionic nano-clusters (2-3 nm diam.) which afforded high IEC (> 2 mmol/g) that did not dissolve in water. Modifications to the graft copolymer architecture, including molecular weight, graft length, graft number density, and degree of sulfonation conferred subtle, but impactful, changes on the membrane’s transport properties. For instance, shorter graft side chains yielded larger, but fewer, ionic-rich domains - which reduced swelling and allowed for even greater proton conductivity. In Chapter 3, it was demonstrated that short graft ionomers bearing a lower graft number density allowed for a longer sequence length between graft side chains, which, as a result of increased crystallinity of the fluorous component, afforded even higher IEC membranes (up to 3.3 mmol/g) that resisted aqueous dissolution. Moreover, because of the high IEC attainable, the hydrophilic volume fraction of the membranes remains large, even under reduced humidity, thus facilitating proton conductivity under reduced RH. The caveat of high IEC membranes is still the high swelling behavior and their dependency on RH for high proton conductivity. In addition, they are brittle when dry. The solution to this paradox is to design membranes with an overall low IEC that possess highly localized ion content to suppress excessive swelling of the ionic rich regions in the presence of water, essentially mimicking the morphology of PFSA ionomer membranes.
With the above constraints in mind, blending hydrophobic fluorous polymers with model ionic graft copolymers in order to prepare and examine membranes that possess highly localized ion-rich channels that could potentially afford high proton conductivity under lower RH, improved mechanical properties when dry, and improved resistance to swelling/dissolution when fully hydrated was investigated here. Poly(vinylidene difluoride) (PVDF) was utilized as the blending fluorous polymer because of its chemical and thermal stability, commercial availability, and its tendency to form crystalline domains which impart enhanced mechanical strength.\textsuperscript{77-80} Blending ionic and non-ionic perfluorinated/partially fluorinated polymers has been previously observed to promote a phase-separated morphology and improved mechanical integrity;\textsuperscript{80, 249} however, several studies indicate that blend membranes exhibit a significant decrease in proton conductivity than the parent ionomer.\textsuperscript{81} For example, Nafion\textsuperscript{®}/PVDF blends possess reduced proton conductivity due to the hydrophobic nature of PVDF which restricts water penetrating the membrane surfaces.\textsuperscript{250, 251} In contrast, preliminary work on blends of a low molecular weight (mol. wt.) PVDF (M\textsubscript{n} ~2000 g/mol) with a partially sulfonated graft copolymer showed that the blended membranes were able to maintain proton conduction in spite of a dramatic reduction in ion content due to the formation of an interconnected network of ionic clusters.\textsuperscript{252}

In this study, the blending approach was applied to the high IEC, sulfonated poly(vinylidene difluoride-co-chlorotrifluoroethylene)-g-polystyrene, P[VDF-co-CTFE]-g-PS polymers described in Chapter 3, which have been shown to have fluorous domains embedded in a continuous phase of polystyrene (PS) domains,\textsuperscript{228} and possess small, highly interconnected ionic clusters that give rise to high proton conductivity under reduced RH.\textsuperscript{171} In the first section, blends of a highly sulfonated graft ionomer, which
exhibits high water swelling ($\lambda$, 211; water content, 92%) and different molar masses of PVDF (~2,000 g/mol and 270,000 g/mol) were investigated in order to distinguish the effect of the addition of polymers that induce crystallinity and entanglement from those that simply introduce a higher crystallinity. The degree of crystallinity, morphology and properties (e.g., water sorption and proton conductivity) of the resulting blend membranes in liquid water and under low RH and elevated temperature are reported and discussed. A diagram illustrating the structure of the graft ionomer and schematic representations of the subsequent graft blends are shown in Scheme 4.1. In the second section, blend membranes based on different mass ratios of high mol. wt. PVDF (270,000 g/mol) in liquid water and under reduced humidity and high temperatures were examined and they demonstrate promising proton conductivity from the graft blends in both fully water saturated and reduced humidity conditions.

**Scheme 4.1.** (a) Structure of the graft ionomer; (b) a schematic representation of the graft blend containing 70 wt% of graft ionomer and 30 wt% of PVDF of ~2000 g/mol showing enhance crystallinity, (c) a schematic representation of the graft blend containing 70 wt% of graft ionomer and 30 wt% of PVDF of 270,000 g/mol showing enhanced crystallinity and entanglement.
4.2. Experimental Section

4.2.1. Materials

Vinylidenedifluoride (VDF, Aldrich, 99+%), chlorotrifluoroethylene (CTFE, Aldrich, 98%), potassium persulfate (KPS, Allied Chemical, reagent grade), sodium metabisulfite (Na$_2$S$_2$O$_5$, Anachemia, anhydrous, reagent grade), pentadecafluorooctanoic acid (Aldrich, 96%), 2,2'-dipyridyl (bpy, Aldrich, 99+%), 1,2-dichloroethane (DCE, Caledon, reagent grade), N-methyl-2-pyrrolidone (NMP, Aldrich, anhydrous, 99.5%), sulfuric acid (Anachemia, 95-98%, ACS reagent), cuprous chloride (CuCl, Aldrich, 99%), and acetic anhydride (Aldrich, 99.5%) were used as received. Copper(II) chloride (CuCl$_2$, Aldrich, 99.999%) was purified according to the literature. Styrene (St, Aldrich, 99+%) was washed with aqueous 5% NaOH and water, dried overnight with MgSO$_4$, distilled over CaH$_2$ under reduced pressure, and stored under N$_2$ at -20 °C.

4.2.2. PVDF

Emulsion copolymerization of VDF was performed to prepare PVDF possessing low molar mass. The detailed preparatory procedures were reported previously by Weissbach et al.$^{252}$ A brief description is as followed: the reaction was performed in a 160 mL pressure vessel (Parr Instruments) equipped with a pressure relief valve and a magnetic stir bar. A mixture of water, KPS, Na$_2$S$_2$O$_5$, pentadecafluorooctanoic acid, and chloroform was added. VDF was introduced into the reactor to give a constant pressure of 300 psi and heated at 60 °C. The reaction was carried out approximately 3.5 h. The freezing coagulated polymer latex was melted in warm water followed by rinsing with water four times and with ethanol once. The resulting polymer was dried at 80°C under vacuum for 24 h. The molar mass of the PVDF was measured ~ 2,000 g/mol by gel
permeation chromatography (GPC) using polystyrene standards. High mol. wt. PVDF was purchased from Aldrich, possessing $M_w = 530,000$ g/mol as labeled and $M_n = 270,000$ g/mol analyzed by GPC.

4.2.3. Synthesis of Sulfonated Graft Copolymer

The graft ionomers consist of a hydrophobic backbone P[VDF-co-CTFE] and sulfonated graft styrenic side chains. They were initially synthesized by *graft*-ATRP of styrene from a fluorous macroinitiator, P(VDF-co-CTFE), followed by post-sulfonation to introduce ionicity.\textsuperscript{171} The detailed synthesized procedures regarding preparation of the fluorous macroinitiator and parental graft copolymers and post-sulfonation of graft chains were described in Sections 3.2.2 – 3.2.4. The fluorous macroinitiator P[VDF-co-CTFE] was estimated to contain $2.6 \pm 0.3$ mol\% CTFE and have $M_n \sim 123,000$ g/mol. A highly sulfonated graft copolymer possessing long graft length was chosen for this study because of its high sulfonation level. The average number of styrenes per graft chain of this copolymer was analyzed by $^1$H and $^{19}$F NMR and estimated to possess $\sim 79 \pm 4$ styrenes per graft chain (DP = 79 ± 4). $M_n$ of polystyrenes in the graft copolymer was calculated to be 266,000 g/mol. The graft copolymer was referred as P[VDF-co-CTFE$_{2.6\text{mol\%}}$]-g-PS$_{79}$. The sulfonated graft copolymer possesses IEC $\sim 2.91$ mmol/g and degree of sulfonation (DS) $\sim 56\%$.

4.2.4. Blending and Membrane Preparation

The sulfonated graft ionomer was blended with different molar mass of PVDF: 2,000 and 270,000 g/mol PVDF so as to possess 70 wt\% of graft ionomers and 30 wt\% of PVDF materials. Furthermore, a series of graft blends are prepared using PVDF having $M_n = 270,000$ g/mol in varied mass ratio. The graft blends are prepared by
dissolving the graft ionomer and blending moiety in DMAc solvent until a homogeneous mixture is formed. After reducing the solvent, the membranes were drop cast on a Tefon® sheet. The membranes were initially dried at room temperature, then dried under vacuum at 80°C to remove residual solvent overnight, followed by soaking in 2 M HCl overnight to convert them to the protonic form, and rinsing with Millipore deionized water several times to wash excess acid from the membranes, and finally storing in Millipore deionized water for future use. The typical thickness of the blended membranes was ~50 µm.

4.2.5. Membrane Properties

The water content of membranes in water-saturated state was calculated as the mass percentage of water in the wet membrane according to Equation 2.5. Lambda (λ) of membranes in both water-saturated and water vapour states was calculated according to Equation 2.6 to provide information regarding the average number of water molecular per ion exchange site ([H₂O]/[SO₃⁻]).

Ion exchange capacity (IEC, mmol/g) is represented as the millimoles of ionically exchangeable SO₃H per gram of a dry membrane and was determined by titration. Full description is provided in Section 2.4.3. In short, membranes were initially equilibrated in 2 M NaCl solution to release the protons, which were titrated with standardized NaOH solution to a phenolphthalein end point.

Water vapour sorption at different RH was measured by a DVS-1000 (Surface Measurement Systems, U.K), which can maintain and control the RH and temperature required for the measurements. The sorption isotherm is recorded by the difference in weight of a sample at a given RH relative to its dry weight, which can then be used to
calculate the water uptake of the sample at each tested RH. Detailed description is present in Section 2.4.5.

In-plane proton conductivity was measured using AC impedance spectroscopy with a Solartron 1260 frequency analyzer to obtain Nyquist plots, which were fitted to the standard Randles equivalent circuit to acquire membrane resistance. Proton conductivity is then calculated using Equation 2.8. Detailed description is provided in Section 2.4.4.

Measurements of proton conductivity at reduced RH were performed by both the ESPEC SH-241 environmental chamber and the AC impedance spectroscopy. Membranes were equilibrated at a predetermined RH/temperature in the environmental chamber. Measurements of conductivity were taken inside the environmental chamber until 3 or more conductivity values were consistent over a period of 2 h.

The analytical acid concentration \([\text{-SO}_3\text{H}] \, \text{(M)}\) and effective proton mobility in wet membranes were calculated according to Equation 2.10 and 2.11, respectively. Detailed discussion about the parameters are provided in Section 2.4.6.

For all types of the measurements, membranes were re-cast for reproducibility. The above-mentioned parameters were all calculated from the average of multiple membrane samples and measurements. Errors were calculated based on standard deviation of measurements.

The volume fraction of ionic components (i.e., poly(styrene sulfonic acid) (PSSA)) and fluorous components was calculated using the polymer densities \(\rho_{\text{PSSA}} = 1.44 \, \text{g/cm}^3\), \(\rho_{\text{PS}} = 1.05 \, \text{g/cm}^3\), and \(\rho_{\text{PVDF}} = 1.78 \, \text{g/cm}^3\). The macrorinitiator (VDF-co-
CTFE) was estimated to have similar density to PVDF, thus, the same density was used.

A typical calculation is shown in Equation 4.1 for PSSA.

\[
\text{vol } \% \text{ PSSA} = \frac{(\text{ionomer wt.} \%) \cdot \frac{M_n, \text{PSSA}}{\rho_{\text{PSSA}}} \cdot \frac{M_n, \text{PS}}{\rho_{\text{PS}}} \cdot \frac{M_n, \text{VDF-co-CTFE}}{\rho_{\text{PVDF}}}}{(\text{ionomer wt.} \%) \cdot (\frac{M_n, \text{PSSA}}{\rho_{\text{PSSA}}} \cdot \frac{M_n, \text{PS}}{\rho_{\text{PS}}} \cdot \frac{M_n, \text{VDF-co-CTFE}}{\rho_{\text{PVDF}}})} \cdot 100\% \quad \text{4.1}
\]

**4.2.6. Instruments and Techniques Used for Morphological Study**

In order to obtain ideal TEM images, membranes need to be stained to enhance image contrast, followed by sectioning into ultra-thin slices (60-100 nm) by microtome instrument before the micrographs are taken with a Hitachi H7600 TEM. Quantitative data (e.g., the domain sizes and number density of ionic clusters) was analyzed using software Image J®. Full description of obtaining TEM micrographs and their quantitative data is present in Section 2.4.7 and 3.2.6 under TEM section.

The degree of crystallinity was determined by wide angle X-ray scattering (WAXS) using a Rigaku Rapid Access XRD, performed and analyzed by Dr. Rasoul Narimani. Three Gaussian peaks were fit to each WAXS pattern in order to calculate the degree of crystallinity according to Equation 2.13. The average crystalline domain size was estimated using Equation 2.14 based on Scherrer equation. Detailed information regarding WAXS is provided in Section 2.4.8.
4.3. Results and Discussion

4.3.1. Blending with High Mol. Wt. PVDF vs Low Mol. Wt. PVDF

Membrane Preparation and Characterization

The graft ionomer is composed of a fluorous P[VDF-co-CTFE] backbone and graft sulfonated PS side chains. The fluorous macroinitiator P[VDF-co-CTFE] (M_n ~ 123,000 g/mol) was first synthesized by emulsion polymerization and estimated to contain 2.6 ± 0.3 mol% CTFE. Atom transfer radical polymerization (ATRP) was used to introduce PS graft chains, which were then post-sulfonated to different DS. A detailed synthetic description of the synthesis and characterization was reported previously in Section 3.3.1 in Chapter 3. In Figure 4.1, ¹H NMR spectrum of the macroinitiator (a), the unsulfonated graft copolymer (b) and the partially sulfonated graft copolymer (c) are shown. Additional peaks due to the unsulfonated grafted polystyrene ranging from 6.5 – 7.5 ppm and sulfonated grafted polystyrene at 7.6 ppm were revealed in Figure 4.1 (b) and (c), respectively relative to the macroinitiator shown in (a), indicating successful grafting and sulfonation. By comparing the ratio of protons attributed to VDF and to PS units, PS graft side chain was estimated to contain an average number of 79 ± 4 styrenes (DP_PS = 79) according to Equation 3.3. Afterward, post-sulfonation was performed to a high degree ~ 56% for the copolymer to provide an ionomer possessing IEC ~ 2.91 mmol/g. The degree of sulfonation equal to 56% can be realized as that every other styrene is sulfonated. Upon immersion in water, the membranes swelled 1060 wt%, resulting in a very high water content of 92 wt% (λ, 211). The ionomer was blended with two different mol. wt. PVDF samples (~2,000 and 270,000 g/mol) in a ratio of 70:30 wt%. The graft blend membranes are referred to as G^{70%}B_{2kPVDF}^{30%} and G^{70%}B_{270kPVDF}^{30%}, respectively. The estimated volumetric fraction (vol%) of the PSSA...
decreases from 50 vol% in the pure ionomer membranes to 38 vol% in the graft blend membranes.

Figure 4.1. 600 MHz $^1$H NMR spectra of (a) the macroinitiator P(VDF-co-CTFE$_{2.6\text{mol\%}}$), (b) the unsulfonated graft copolymer P(VDF-co-CTFE$_{2.6\text{mol\%}}$)-g-PS$_{79}$ after 24 h ATRP reaction time, and (c) a highly sulfonated graft copolymer P(VDF-co-CTFE$_{2.6\text{mol\%}}$)-g-SPS$_{79}$, having IEC ~ 2.91 mmol/g and DS ~ 56%

**Degree of Crystallinity**

WAXS spectra of the blend membranes as well as the blending material (i.e., PVDF) and the pristine graft ionomer are shown in Figure 4.2 for comparison. The X-ray spectra are characterized by a broad peak centred at $2\theta = 19^\circ$ and a sharper peak positioned at $20^\circ$, corresponding to amorphous$^{221}$ and crystalline domains$^{222}$ of PVDF, respectively. The crystalline peak for the graft ionomer shows much lower intensity than
that of the graft blends. Three Gaussian peaks were fit to each WAXS pattern and the
degree of crystallinity extracted is shown as an inset in Figure 4.2. The graft ionomer
membrane containing 50 vol% of PSSA, 30 vol% of unsulfonated PS and 20 vol% of
fluorous matrix P[VDF-co-CTFE]) possesses the lowest degree of crystallinity (~4.5%),
which originates from the partially crystalline fluorous backbone. Both graft blends
consist of 38 vol% of PSSA, 22 vol% of unsulfonated PS and 40 vol% of fluorous moiety
(backbone and introduced PVDF combined). The degree of crystallinity of
\(G^{70\%}B_2kPVDF^{30\%}\) and \(G^{70\%}B_{270kPVDF^{30\%}}\) membranes were 15.0% and 12.8%, respectively,
noticeably higher than the pristine ionic membrane due to introduction of crystalline
PVDF. Blending with low mol. wt. PVDF (~2000 g/mol) provides a slightly higher degree
of crystallinity, consistent with lower mol. wt. PVDF being more crystalline.\(^{254}\)
Calculation using the Scherrer equation indicates that the crystalline domains in all
samples are similar, ~6 nm. Relationship between water swelling properties and the
degree of crystallinity will be discussed in later section.

**Observation of Ionic and Fluorous Domains by TEM**

TEM micrographs of the graft ionomer and the graft blends are shown in Figure 4.3. The
graft ionomer possesses an ionic cluster morphology (Figure 4.3 (a)) with ion-rich
domains (dark regions) randomly distributed throughout the fluorous domains (brighter
regions). The average size of ionic clusters was estimated 3.7 ± 0.7 nm in width.
\(G^{70\%}B_2kPVDF^{30\%}\) possesses a similar phase-separated morphology (Figure 4.3 (b))
wherein ion-rich domains are also homogeneously distributed and have similar
dimensions to the pure graft ionomer. Although the fluorous regions are visibly sharper
in \(G^{70\%}B_2kPVDF^{30\%}\) there is no significant change in the dimensions of fluorous domains.
However, \(G^{70\%}B_{270kPVDF^{30\%}}\) displays a distribution of morphologies including spherical
clusters, similar to the pure graft ionomer, and regions where the fluorous domains extend to form contiguous domains (Figure 4.3 (c)). To illustrate this point, the distributions of ion-rich and fluorous-rich domains for $G_{70\%}B_{270kPVDF}^{30\%}$ are highlighted in Figure 4.4. In Figure 4.4 (i), (a) and (b) present fluorous-rich phase (brighter area) and ionomer-rich phase (darker area), respectively. The fluorous-rich phase is further demonstrated in Figure 4.4 (ii,a), presumably mainly consisting of PVDF homopolymer, which can either form amorphous and crystalline regions as shown in Figure 4.4 (ii, c) and (ii, d), respectively. The ionomer-rich phase is illustrated in Figure 4.4 (ii, b), which contains 4 components: (ii, e) amorphous fluorous matrix, (ii, f) crystalline fluorous crystallites, (ii, g) amorphous unsulfonated PS, and (ii, h) the ionic moiety PSSA.

![WAXS spectra](image)

**Figure 4.2.** WAXS spectra of the membranes cast using high mol. wt. PVDF, the graft ionomer and the graft blends consisting of 70 wt% of ionomer and 30 wt% of PVDF. Results for the degree of crystallinity are shown as an inset.

[Due to the intrinsic nature of low mol. wt. PVDF, which is brittle and does not provide much entanglement to hold the membrane together, it was difficult to cast a complete film for further measurement (e.g., WAXS). WAXS experiments were performed and analyzed by Dr. Rasoul Narimani of Department of Physics, Simon Fraser University. Error was calculated based on the standard deviation of five measurements.]
Figure 4.3. Representative TEM images of (a) the graft ionomer, (b) $\text{G}^{70}\% \text{B}_{2k}\text{PVDF}^{30}\%$, and (c) $\text{G}^{70}\% \text{B}_{270k}\text{PVDF}^{30}\%$. 
**Figure 4.4.** The distributions of ion-rich and fluorous-rich domains of G\(^{70}\%) B_{270kPVDF}^{30\%}. (i) TEM image of G\(^{70}\%) B_{270kPVDF}^{30\%}, and (ii) a schematic illustration of ion-rich and fluorous-rich domains, where (a) demonstrates fluorous-rich (PVDF) phase (in blue), also corresponding to (a) in (i); (b) demonstrates ionomer-rich phase (in green), corresponding to (b) in (i); (c) PVDF homopolymer forming amorphous domains, (d) PVDF homopolymer forming crystalline domains, (e) fluorous backbone P[VDF-co-CTFE] forming amorphous domains, (f) fluorous backbone P[VDF-co-CTFE] forming crystalline domains, (g) unsulfonated PS forming amorphous regions, (h) ionic moiety PSSA

[Reproduced by courtesy of Dr. Rasoul Narimani.]

**Water Sorption and Conductivity in Fully Hydrated Membranes**

Properties of membranes (e.g., \(\lambda\), proton conductivity (\(\sigma\)), analytical acid concentration and *effective* proton mobility (\(\mu_{eff}\))) are summarized in Table 4.1 and the relationship between these parameters and IEC are demonstrated in Figure 4.5. IEC values for G\(^{70}\%) B_{2kPVDF}^{30\%} and G\(^{70}\%) B_{270kPVDF}^{30\%}, measured by titration, were 2.17 and 1.96 mmol/g, respectively, despite the only variable being the mol. wt. of the PVDF, and lower than the graft ionomer (2.91 mmol/g) due to dilution with non-ionic polymer. \(\lambda\) correlates with IEC, however, within the narrow window of IEC values examined for the two blend membranes, \(\lambda\) varies significantly, from \(\lambda \approx 150\) (G\(^{70}\%) B_{2kPVDF}^{30\%}) to \(\lambda \approx 68\).
(G<sup>70%</sup>B<sub>270kPVDF</sub>30%). λ for G<sup>70%</sup>B<sub>270kPVDF</sub>30% is half that of G<sup>70%</sup>B<sub>2kPVDF</sub>30%, despite the lower degree of crystallinity of the former. We propose that the longer PVDF chains enable interdigitation of PVDF chains into multiple crystallites or form contiguous fluorous domains, effectively increasing the elastic forces of the membrane that oppose swelling in water.

A significant reduction in water content for the blends did not cause a decrease in proton conductivity with respect to the pristine ionomer (37 mS/cm) (see Figure 4.5(b)); on the contrary, the conductivity of G<sup>70%</sup>B<sub>270kPVDF</sub>30% increased by a factor of 2 (75 mS/cm). Figure 4.5 (c) and (d) present acid concentration and proton mobility as a function of IEC and illustrate that despite being of lower ion content, the acid concentration of the low mol. wt. PVDF blend, G<sup>70%</sup>B<sub>2kPVDF</sub>30% (~0.3 M) is similar to the graft ionomer due to its lower IEC and lower water content, but the concentration increases by almost a factor of two for G<sup>70%</sup>B<sub>270kPVDF</sub>30% (0.66 M) because of its much lower water content. The effective proton mobility of the blends remains exceptional high (> 1 x 10<sup>−3</sup> cm<sup>2</sup> s<sup>−1</sup>V<sup>−1</sup>) relative to Nafion® 117 (0.75 x 10<sup>−3</sup> cm<sup>2</sup> s<sup>−1</sup>V<sup>−1</sup>) indicating that the connectivity of the ionic channels is maintained after blending.

**Table 4.1.** Composition and properties<sup>a</sup> of the graft ionomer and its blends with PVDF

<table>
<thead>
<tr>
<th>Samples</th>
<th>IEC&lt;sup&gt;b&lt;/sup&gt; (mmol/g)</th>
<th>Water content (wt%)</th>
<th>λ</th>
<th>σ (mS/cm)</th>
<th>[-SO&lt;sub&gt;3&lt;/sub&gt;H] (M)</th>
<th>μ&lt;sub&gt;eff&lt;/sub&gt; x1000 (cm&lt;sup&gt;2&lt;/sup&gt;/sV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graft ionomer</td>
<td>2.91</td>
<td>92±1</td>
<td>211±10</td>
<td>36±7</td>
<td>0.28±0.06</td>
<td>1.23±0.08</td>
</tr>
<tr>
<td>G&lt;sup&gt;70%&lt;/sup&gt;B&lt;sub&gt;2kPVDF&lt;/sub&gt;30%</td>
<td>2.17</td>
<td>85±1</td>
<td>151±7</td>
<td>47±4</td>
<td>0.32±0.01</td>
<td>1.39±0.15</td>
</tr>
<tr>
<td>G&lt;sup&gt;70%&lt;/sup&gt;B&lt;sub&gt;270kPVDF&lt;/sub&gt;30%</td>
<td>1.96</td>
<td>71±1</td>
<td>68±1</td>
<td>75±6</td>
<td>0.66±0.09</td>
<td>1.12±0.08</td>
</tr>
</tbody>
</table>

Note.  <sup>a</sup>room temperature.  <sup>b</sup>acid-base titration.
Water uptake, $\lambda$, and proton conductivity increase with increasing RH at 25 °C as expected, shown in Figure 4.6. Generally, the graft ionomer membrane exhibits highest water uptake over the overall RH spectrum. $G^{70\%}B_{2\text{kPVDF}}^{30\%}$ and $G^{70\%}B_{270\text{kPVDF}}^{30\%}$ fall within 5-10% of these values. At 95% RH, the graft ionomer and blend membranes possess similar $\lambda$ values, ranging from 13 to 15; the value for Nafion® 117, in comparison, is ~ 19. At 50% RH, $\lambda$ is 3 – 5 for all of the tested membranes, which meets the minimum requirement for acid association.\(^95\) Nafion® 117 exhibits the highest $\lambda$ (~5);
the graft ionomer membrane, the lowest (~3). It was interesting to observe that the pristine graft ionomer membrane possesses the highest water uptake but lowest λ, which was understood as the result of much higher ion content in the pure graft ionomer. At 95% RH (25°C), the graft ionomer exhibits exceptional proton conductivity in the order of 10^{-1} S/cm, while G^{70%}B_{2kPVDF}^{30%} and G^{70%}B_{270kPVDF}^{30%} exhibit proton conductivities in the order of 10^{-2} S/cm. Specifically, G^{70%}B_{270kPVDF}^{30%} possesses very similar conductivity to Nafion® 117 (56 versus 66 mS/cm, respectively). The relative slopes of the log (σ) versus RH are shown in the inset of Figure 4.6 (c) and reveal the RH dependency of proton conductivity. Proton conductivity at elevated temperatures at 95%, 75%, and 55% RH are plotted in Figure 4.6 (d), (e), and (f), respectively. As generally observed for PEMs, proton conductivity increases with temperature. At 95% RH, the pristine graft ionomer exhibits the highest conductivity (160 mS/cm at 80°C) and the increase in proton conductivity is steady and moderate over the entire temperature range. G^{70%}B_{2kPVDF}^{30%} and G^{70%}B_{270kPVDF}^{30%} yield reasonably high proton conductivity but lower than Nafion® 117. At 55% RH, the graft ionomer and Nafion® 117 are able to possess the order of 10^{-2} S/cm in proton conductivity over the entire temperature range. At 55% RH and 80°C, the graft ionomer and Nafion® 117 possess 20 and 36 mS/cm proton conductivity, respectively. G^{70%}B_{2kPVDF}^{30%} and G^{70%}B_{270kPVDF}^{30%} possess conductivities of 7 and 10 mS/cm, indicating a reasonable conductivity under low RH/elevated temperature conditions. The activation energy for proton conductivity can be extracted through an Arrhenius plot of the data. The activation energy of the graft ionomers,
$G^{70\%B_{5kPVDF}^{30\%}}$ and $G^{70\%B_{270kPVDF}^{30\%}}$ membranes is 13.5, 16.5, and 15.9 KJ/mol, respectively, revealing that the blend membranes require higher activation energy for proton transport under low RH condition. The graft ionomer requires slightly lower activation energy than Nafion® 117 (13.9 KJ/mol). At 25°C, proton conductivity of the blended membranes stays within an order of magnitude for an RH decrease from 95% to 55%. However, at 80°C, both blended membranes exhibit a noticeable decrease in proton conductivity at lower RH (55% RH). This result indicates that the blended membranes are more dependent on RH at higher temperature.
Figure 4.6. (a) water uptake, (b) $\lambda$, (c) proton conductivity as a function of RH at 25°C. Proton conductivity at various temperatures at (d) 95% RH, (e) 75% RH, and (f) 55% for the pristine graft ionomer, $G^{70\%}{B_{2kPVDF}}^{30\%}$, $G^{70\%}{B_{270kPVDF}}^{30\%}$, and Nafion® 117.
4.3.2. Blending with High Mol. Wt. PVDF in Various Mass Ratios

Degree of Crystallinity

Since blending the graft ionomer with high mol. wt PVDF (270,000 g/mol) limited swelling to the greater extent and provided a higher proton conductivity, additional membranes were examined possessing different wt. ratios. Membranes were prepared having 80, 70, 50, and 30 wt% of graft ionomer, referred to as G$^{80\%}$B$_{270kPVDF}^{20\%}$, G$^{70\%}$B$_{270kPVDF}^{30\%}$, G$^{50\%}$B$_{270kPVDF}^{50\%}$, and G$^{30\%}$B$_{270kPVDF}^{70\%}$. The volume fraction of PSSA, decreases from 50 vol% in the graft ionomer to 42, 38, 28, and 18 vol% for the blend samples, which leads the volume fraction of PVDF moiety increases from 20 vol% in the ionomer to 32, 40, 55, 70 vol% for the blend samples. WAXS spectra for this series are shown in Figure 4.7 (a) - the degree of crystallinity increases approximately linearly with PVDF content (see Figure 4.7 (b)). The degree of crystallinity and the volume fraction of PSSA, unsulfonated PS, and PVDF content are summarized Table 4.2.

![WAXS spectra of blend membranes mixed of graft ionomer and high mol. wt. PVDF at various wt. ratios](image)

**Figure 4.7.** WAXS spectra of blend membranes mixed of graft ionomer and high mol. wt. PVDF at various wt. ratios
Table 4.2. Degree of crystallinity of the graft ionomer and blend membranes containing high mol. wt. PVDF

<table>
<thead>
<tr>
<th>Samples</th>
<th>Degree of crystallinity (%)</th>
<th>Estimated volume fraction of PSSA (vol%)</th>
<th>Estimated volume fraction of PS (vol%)</th>
<th>Estimated volume fraction of PVDF (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>270k PVDF</td>
<td>32.0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Graft ionomer</td>
<td>4.5</td>
<td>50</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>G80%B270kPVDF20%</td>
<td>10.4</td>
<td>42</td>
<td>26</td>
<td>32</td>
</tr>
<tr>
<td>G70%B270kPVDF30%</td>
<td>10.5</td>
<td>38</td>
<td>22</td>
<td>40</td>
</tr>
<tr>
<td>G50%B270kPVDF50%</td>
<td>17.0</td>
<td>28</td>
<td>17</td>
<td>55</td>
</tr>
<tr>
<td>G30%B270kPVDF70%</td>
<td>21.6</td>
<td>18</td>
<td>12</td>
<td>70</td>
</tr>
</tbody>
</table>

Water Sorption and Conductivity in Fully Hydrated Membranes

Selected properties of the blends are plotted in Figure 4.8 and summarized in Table 4.3. As expected, ionomer content and IEC decrease proportionally with PVDF content. IECs decrease from 2.91 (graft ionomer) to 0.72 mmol/g as PVDF content increases. The proton conductivities of the blend membranes are higher than the graft ionomer; with the exception of G80%B270kPVDF70%, which is similar in value. The higher proton conductivity observed for the blends can be explained by the much larger acid concentration of the blends ranged between 0.54 and 0.88 M, which is considerably higher than that of the graft ionomer (0.28M) due to a greatly reduced water content. Because of the much higher acid concentration, the connectivity of the hydrophilic channels for the blends is more favorable than the graft ionomer. Proton mobility remained remarkably high for G80%B270kPVDF20%, G70%B270kPVDF30% (>1.1 x 10⁻³ cm² s⁻¹ V⁻¹) - much higher than Nafion® 117 (0.75 x 10⁻³ cm² s⁻¹ V⁻¹), and similar to pristine graft ionomer despite their substantially lower water content.
Figure 4.8. (a) $\lambda$ and proton conductivity, (b) acid concentration and effective proton mobility, vs. ionomer content for graft blend membranes containing high mol. wt. PVDF.

Table 4.3. Properties$^a$ of the ionomer and blend membranes

<table>
<thead>
<tr>
<th>Samples</th>
<th>IEC$^b$ (mmol/g)</th>
<th>Water content (wt%)</th>
<th>$[\text{H}_2\text{O}]/[\text{SO}_3^-]$</th>
<th>$\sigma$ (mS/cm)</th>
<th>$[\text{-SO}_3\text{H}]$ (M)</th>
<th>$\mu_{\text{eff}} \times 10^3$ (cm$^2$/sV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graft Ionomer</td>
<td>2.91</td>
<td>92±1</td>
<td>211±10</td>
<td>37±7</td>
<td>0.28±0.06</td>
<td>1.23</td>
</tr>
<tr>
<td>$G^{80}%B_{270kPVDF}^{20}%$</td>
<td>2.14</td>
<td>82±1</td>
<td>122±4</td>
<td>68±3</td>
<td>0.54±0.04</td>
<td>1.31</td>
</tr>
<tr>
<td>$G^{70}%B_{270kPVDF}^{30}%$</td>
<td>1.96</td>
<td>71±1</td>
<td>68±1</td>
<td>75±6</td>
<td>0.66±0.09</td>
<td>1.18</td>
</tr>
<tr>
<td>$G^{50}%B_{270kPVDF}^{50}%$</td>
<td>1.30</td>
<td>48±1</td>
<td>40±2</td>
<td>64±5</td>
<td>0.72±0.09</td>
<td>0.86</td>
</tr>
<tr>
<td>$G^{30}%B_{270kPVDF}^{70}%$</td>
<td>0.72</td>
<td>26±1</td>
<td>28±1</td>
<td>34±2</td>
<td>0.88±0.18</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Note. $^a$Room temperature.$^b$bacid-base titration.

**Proton Conductivity under Reduced RH**

Under reduced RH, the blended membranes generally absorbed less water across the entire RH spectrum as the ionomer content decreases, as shown in Figure 4.9 (a). Unexpectedly, $\lambda$ values are higher for membranes possessing lower ion content. The $G^{80}\%B_{270kPVDF}^{20}\%$ membrane exhibits 21 wt% higher water uptake than $G^{50}\%B_{270kPVDF}^{50}\%$ at 95% RH. Nevertheless, the same ordering in water uptake versus RH plot is not observed in the plot of $\lambda$ versus RHs. In Figure 4.9 (b), $G^{50}\%B_{270kPVDF}^{50}\%$ exhibits a slightly higher $\lambda$ than the other two samples containing higher ion content, but
all fall within 10% of each other. The explanation for this scenario is that the two higher IEC membranes possess > 1.5 times higher ion content but < 1.5 times water content. Similar phenomena was observed by Weissbach et al., where constant $\lambda$ was observed for membranes with increasing PVDF content (e.g., lower ion content) due to the fact that water sorption scaled with ionomer content. Regardless of the slightly lower $\lambda$, $G^{80\%}_{B270kPVDF^{20\%}}$ exhibits an exceptionally high, 5x higher proton conductivity relative to $G^{50\%}_{B270kPVDF^{50\%}}$. Its proton conductivity is similar to the pristine ionomers although it only contains 80 wt. % of the original ionomer, suggesting that the addition of PVDF does not significantly hinder proton conduction even under low RHs. The relative slopes of the log ($\sigma$) versus RH plots (displayed in the inset of Figure 4.9 (c)) for all of the blended samples are very similar to that of the pristine graft ionomer, with the exception of $G^{50\%}_{B270kPVDF^{50\%}}$.

Proton conductivity versus various temperatures are shown in Figure 4.9 (d), (e), and (f). At a given RH, proton conductivity decrease as temperature decreases, but stays the same order of magnitude. For example, at 95% RH (Figure 4.9 (d)), the proton conductivity of $G^{80\%}_{B270kPVDF^{20\%}}$ decreases from 270 to 200 and 147 mS/cm as temperature decreases from 80$^\circ$ to 50$^\circ$C and 25$^\circ$C, respectively, but the values still remain in the order of $10^{-1}$ S/cm. On the other hand, proton conductivity decreases significantly as RH decreases at a given temperature. For instance, proton conductivity of $G^{80\%}_{B270kPVDF^{20\%}}$ is reduced from the order of $10^{-1}$ to $10^{-2}$ as RH decreases from 95% RH to 75% RH. The results suggest that the proton conductivity of these membranes is more dependent on RH than temperature. Among all of the membranes studied here, $G^{80\%}_{B270kPVDF^{20\%}}$ exhibits superior performance in proton conductivity over the pristine graft ionomer despite its lower ion content (2.14 vs. 2.91 mmol/g) even at lower RHs.
The activation energy of blend membranes (see the inset of Figure 4.9 (f)) increases as PVDF content increases, but not significantly. These results imply that addition of PVDF is not completely detrimental to the resultant blended membranes. In fact, the data illustrates that an appropriate amount of PVDF addition can be beneficial by limiting excessive swelling while maintaining the reasonably high proton conduction.
Figure 4.9. (a) Water uptake, (b) $\lambda$, (c) proton conductivity as a function of RH at 25°C and proton conductivity at various temperature at (d) 95% RH, (e) 75% RH, and (f) 55% RH for the pure graft ionomer, the blend membranes, and Nafion® 117. Note: data for $G^{30\%}B_{270kPVDF}^{70\%}$ not plotted.
4.4. Conclusion

By blending a highly sulfonated graft ionomer with low. mol. wt. PVDF, the degree of crystallinity of the resultant membrane is increased, with concomitttal reduced swelling of the polymer membranes and higher proton conductivity relative to the pristine graft ionomer. Blending with high mol. wt. PVDF leads to a relatively lower enhancement of the crystallinity, but reduces swelling further, with the consequence of greater increase in proton conductivity. In addition to the increase in the crystallinity of the resultant blend membranes, it was speculated that introducing high mol. wt. blending polymer also enhances the connectivity between crystalline domains by virtue of the long polymer chains. Furthermore, PVDF domains (crystalline and amorphous) are more contiguous. These can be verified by TEM images where fluorous-rich domains were interconnected and clearly seen for the high mol. wt. blend. As a result, water uptake is greatly reduced, allowing for higher concentrations of acid, without the proton mobility being compromised. Under reduced humidity, the blend membranes show lower proton conductivity than the pristine graft ionomer. However, the RH dependency of conductivity remains favorable compared to the graft ionomer membrane. The results also show that the blend membranes are more dependent on RH at higher temperature. Blend membrane mixed with high mol. wt. PVDF containing 80 wt% of ionomer and 20 wt% of PVDF exhibits superior proton conductivity in both water-saturated and water vapour conditions compared to any other blend membranes and comparable conductivity to the pristine graft ionomer and Nafion® 117, but possesses significantly lower $\lambda$ values.

This work demonstrates that highly sulfonated graft copolymers when blended with appropriately chosen non-ionic polymer of higher mol. wt. can be utilized to
efficiently alter ion content and effectively control excessive swelling and in turn enhance the mechanical strength and maintain ionic channel formation. Furthermore, such advantages are borne out by a combination of increased crystallinity and connectivity of fluorous domains. While these concepts are examined with model ionomers, they illustrate a strategy of designing PEMs that are characterized by a minimum variation in proton conductivity upon exposure to wide variations in RH and exposure to liquid water.
Chapter 5. Improved Ionic Connectivity in Hydrophilic Channels in the Fully Sulfonated Graft Copolymer Blends


[Contributions: The work described in Chapter 5 resulted from a collaborative study at SFU with graduate exchange student, Mads Nielsen, Department of Chemical Engineering, Technical University of Denmark. I provided mentorship for this project. We worked together in preparing and characterizing the fully sulfonated graft copolymers. I prepared the 40:60 blend series, while Mr. Nielsen prepared the 25:75 blend series. We both performed experiments to obtain IEC, water sorption and proton conductivity of these membranes under water-saturated conditions. Mr. Nielsen also performed experiments under reduced RH. We shared the analytical work on the data. I was responsible for micromilling samples for TEM measurement and obtained the TEM images of fully sulfonated copolymers. Mr. Nielsen and his colleague, Lars Schulte, obtained TEM images of the blend membranes. Mr Nielsen analyzed the TEM images of blend membranes.]

5.1. Introduction

The effects of nanostructure and morphology on proton transport properties of PEMFCs are significant. A common thread among all of the PEMs systems is the existence of hydrophilic and hydrophobic phase separated domains. Hydrophobic domains contribute to the mechanical stability of the membrane, while hydrophilic moieties provide proton conductivity. Examining the structure-property relationships by applying model systems is thus crucial for tailoring PEMs for specific applications. Understanding the relationship between polymer architecture, morphology, and transport properties has been a focus of the Holdcroft group. It was realized that the degree of sulfonation (DS) and the length of diblock sequences and graft side chains play a considerable role on the size of ionic clusters.
More specifically, an increase in sulfonation resulted in an increase of ionic cluster size, which in turn led to an increase in both ionic connectivity and connectivity of proton-conducting channels. The effect of graft density is also impactful on the morphology and properties as described in Chapter 3. A recent study using small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) on the graft copolymer systems revealed that the ionic content is a primary parameter affecting water uptake when the polystyrene (PS) content is > 75 vol%, whereas other factors (PVDF volume ratio and the degree of crystallinity) are more relevant when the PS content is < 75 vol%. Recently, studies on PVDF blends with partially sulfonated diblock/graft copolymer systems demonstrated that the resulting nanostructured morphology of the graft copolymer after blending did not alter the ionic network and therefore were better suited for blending than diblock copolymers. The blending concept was utilized and extended in Chapter 4 by blending a highly sulfonated graft ionomer with (i) a low mol. wt. crystalline fluorous polymer that could induce the degree of crystallinity, and (ii) a high mol. wt. crystalline fluorous polymer that could increase both crystallinity and the entanglement of the fluorous domains. It was surmised that both blend membranes greatly reduced water swelling when exposed to liquid water, leading to improved proton conductivity. The high mol. wt. blend especially decreased water swelling to a higher extent and resulted in 2x higher proton conductivity than the pure graft ionomer. A major trend has emerged throughout the above works: the high ionic content of the ion-rich domains facilitates phase separation and the non-sulfonated component restricts water swelling, overall enhance proton transport. A high ion content in PEMs is favoured but it may lead to
excessive swelling. One solution is to prepare materials with an overall low IEC but retain highly localized ion content in channels to promote ionic connectivity.

This chapter examines the influence of tuning the ionic content of membranes by blending fully sulfonated poly([vinylidene fluoride-co-chlorotrifluoroethylene]-graft-styrene) [P(VDF-co-CTFE)-g-SPS], with the high mol. wt. PVDF. The graft copolymers were synthesized by atom transfer radical polymerization (ATRP) of styrene, followed by post-sulfonation as described in Chapter 3. A completely sulfonated P(VDF-co-CTFE)-g-SPS as well as three other completely sulfonated graft copolymer blends were prepared so as to contain the same hydrophilic to hydrophobic volume contents (40 vol% poly(styrene sulfonic acid) (PSSA) and 60 vol% PVDF) to investigate formation of ionic channels and the resulting proton transport behavior.

Scheme 5.1 illustrates the composition of the pure graft ionomers and the blends, as well as the relationship between added PVDF content and the relatively resultant IECs. Additional series of graft blends containing even higher PVDF content: 25 vol% PSSA and 75 vol% PVDF were also prepared to examine the proton transport properties of low ion content polymers (Scheme 5.1 (e), (f), and (g)). Furthermore, the effect of lowering the overall ion content in the membrane by different strategies: reducing the DS of the graft copolymers or blending fully sulfonated graft copolymers with PVDF on morphology and properties is examined here. An important feature of this work is that it represents an advancement of previous studies because it demonstrates the benefit of blending a fully sulfonated graft copolymer in order to promote ionic channels that are less likely to contain organic material (e.g., unsulfonated PS), that may play a role in hindering connection between ionic domains. It also demonstrates that the volumetric
PSSA content can be lowered without isolating ionic domains, as is the case when the PSSA content is lowered by reducing the DS.

**Scheme 5.1.** Schematic diagrams of membranes examined for this work, demonstrating the relationship between PVDF homopolymer content and the resultant IECs. (a) fully sulfonated graft copolymer Graft40:60, (b) fully sulfonated short graft blend SB40:60, (c) fully sulfonated medium graft blend MB40:60, and (d) fully sulfonated long graft blend LB40:60. Another series containing even higher PVDF content was prepared: (e) SB25:75, (f) MB25:75, and (g) LB25:75. (h), (i), and (j) represent the fully sulfonated graft copolymer Graft2.6-short, Graft2.6-medium, Graft2.6-long, respectively. (k) represents a partially sulfonated short graft ionomer with a relatively low IEC value.
5.2. Experimental

5.2.1. Materials

The following chemicals were purchased from Aldrich and used as received unless otherwise stated: vinylidene difluoride (VDF, 99+%), chlorotrifluoroethylene (CTFE, 98%), 2,2-dipyridyl (bpy, Aldrich, 99+%), styrene (Aldrich, 99+%) (washed with aqueous 5 wt% NaOH and water, dried overnight with MgSO₄, distilled over CaH₂ under reduced pressure, and stored under N₂ at -20 °C), acetic anhydride (99.5%), hexanes, ethanol, dimethyl acetamide (DMAc, anhydrous, 99.8%), calcium chloride (CaCl₂), acetone-δ₆, potassium persulfate (KPS, Allied Chemical, reagent grade), N-methyl-2-pyrrolidone (NMP, Aldrich, anhydrous, 99.5%), sodium hydroxide (NaOH), aqueous hydrochloric acid solution (HCl), 1,2-dichloroethane (DCE, Caledon, reagent grade), sulfuric acid (H₂SO₄, Anachemia, 95-98%, ACS reagent), copper (I) chloride (CuCl, 99%) and copper (II) chloride (CuCl₂, 99.999%), which were purified according to literature.²¹⁶ poly(vinylidene fluoride) (PVDF, Mₚ = 530,000 g/mol, Mₙ = 270,000 g/mol). Lead (II) acetate trihydrate (Pb(OAc)₂ • 3 H₂O) and Spurr’s epoxy resin for preparation of membranes for TEM measurements.

5.2.2. Synthesis of P(VDF-co-CTFE)-g-PS

Two groups of poly([vinylidene difluoride-co-chlorotrifluoroethylene]- graft-styrene) [P(VDF-co-CTFE)-g-PS] possessing different graft density (i.e., different sequence length between graft side chains) were prepared. The linear macroinitiators P(VDF-co-CTFE) containing molar percentages of ATRP-initiating CTFE units of 2.6% and 1.1% were used to initiate ATRP of styrene, yielding the grafted PS copolymers. The two series of parent graft copolymers are referred as Graft₂.₆ and Graft₁.₁. Three copolymers
with different graft length, possessing DP$_{\text{PS}}$ ~ 39, 62, and 79, were obtained for the high
graft density series, and are referred as Graft$_{2.6,\text{short}}$, Graft$_{2.6,\text{medium}}$, Graft$_{2.6,\text{long}}$. The
detailed synthetic procedure of the series was provided in Section 3.2.3. The lower graft
density copolymer was similarly prepared. The synthetic procedure of P(VDF-co-
CFFE$_{1.1 \text{mol\%}}$)-g-PS is described as followed. The macroinitiator P(VDF-co-CTFE$_{1.1 \text{mol\%}}$)
(0.9996 g) was dissolved in 40 mL NMP in a predried round bottom flask, followed by
adding bpy (3.0009 g), purified styrene (40 ml), CuCl (0.6406 g), and CuCl$_2$ (0.0887 g).
The flask was sealed tight with a septum and degassed over three freeze-pump-thaw
cycles to remove oxygen and water from the reactor. The reaction mixture was heated
at 110 °C for a total reaction time of 45 h. Finally, the resulting brown polymer mixture
was precipitated in methanol to obtain solid polymers. Soxhlet extraction with
cyclohexane was performed to remove PS homopolymer. A final precipitation from
methanol was carried to obtain the purified solid polymers, followed by drying under
vacuum at 60°C overnight. Characterization of the synthesized graft copolymer was
performed using GPC, $^{19}$F and $^1$H NMR spectroscopy. The low graft density copolymer
was estimated to have a DP$_{\text{PS}}$ ~ 24.

5.2.3. Sulfonation of P(VDF-co-CTFE)-g-PS

A typical sulfonation reaction was performed to prepare graft copolymers with
complete degree of sulfonation. Briefly, P(VDF-co-CTFE)-g-PS (0.2 g) was dissolved in
DCE (5 ml) under a blanket of argon at 40-50 °C. Sulfonating agent was prepared in a
separate flask, where acetic anhydride (0.6 ml) was mixed with DCE (1.0 mL) in a N$_2$-
purged vial, cooled in a chilled 10% CaCl$_2$ solution, followed by adding sulphuric acid
(0.2 ml). The resulting acetyl sulphate was immediately transferred to the polymer
mixture, in which the colour changed from yellowish to brown as the reaction proceeded.
The reaction was heated at 40°C for a total reaction of 24 h. The reaction was terminated and precipitated by pouring the mixture into 1:1 ethanol/hexanes (ethanol terminates the reaction). After removing the solvent, the precipitate was washed with Millipore water until neutral pH was reached, and then dried under vacuum at 60 °C overnight. Complete sulfonation for all of the copolymers studied here was determined by $^1$H NMR spectra (acetone-$d_6$) recorded on a 400 MHz Varian MercuryPlus spectrometer. $^1$H NMR (400 MHz, acetone-$d_6$, δ): 7.65 (2H, Ar H ortho to –SO$_3$H), 6.81 (2H, Ar H meta to –SO$_3$H), 2.96 and 2.35 (2H, CH$_2$-CF$_2$, PVDF), 1.89-1.64 (2H, CH$_2$-CH, PS), 1.44-1.27 (1H, CH-CH$_2$, PS). More detailed of analysis will be discussed in results and discussion section.

5.2.4. Blending and Membrane Preparation

A commercially available high mol. wt. PVDF ~ 270,000 g/mol was used as the blending material. After successful ATRP, Graft$_{1,1}$ was estimated to have a DP$_{PS}$ ~ 24. Followed by post-sulfonation, it was estimated to possess 40 vol% of PSSA and 60 vol% of fluorous matrix according to Equation 4.1. The complete sulfonated Graft$_{1,1}$ is termed Graft$_{40:60}$. In order to prepare blends with similar PSSA-PVDF ratios, fully sulfonated graft copolymers from the three Graft$_{2,6}$ series were mixed with the high mol. wt. so as to contain 40 vol% of PSSA and 60 vol% of fluorous moiety (fluorous backbone and blending PVDF combined). Three resulting blend membranes contain fully sulfonated graft ionomers of varying graft length but overall equal molar ionic content embedded in fluorous phase. They are abbreviated as SB$_{40:60}$, MB$_{40:60}$, and LB$_{40:60}$, for short (DP$_{39}$), medium (DP$_{62}$), and long (DP$_{79}$) graft lengths, respectively. A second blend series, possessing even higher PVDF content was prepared to examine the effect on water sorption and proton conductivity on very low IEC membranes. The resulting membranes
in this series contain a PSSA: PVDF molar ratio of 25:75, abbreviated SB\textsubscript{25:75}, MB\textsubscript{25:75} and LB\textsubscript{25:75}.

The predetermined masses of polymer and PVDF were dissolved in DMAc, concentrated and cast on a levelled Teflon\textsuperscript{®} sheet at room temperature. The resulting polymer films were dried at 80 °C in vacuum oven overnight. Upon drying the membranes, 50-75 μm thick, were cut into rectangular shapes of typically 10 mm by 5 mm after which they were protonated by immersion in 2M HCl. The protonated membranes were washed multiple times with Millipore deionized water to remove excess acid, and then stored in Millipore deionized water between two glass microscope slides to prevent coiling until use.

5.2.5. Membrane Properties

IEC was determined by acid-base titration. The detailed experimental procedures are presented in Section 2.4.3. Generally, exchangeable protons were released by equilibrating the membranes in 2 M NaCl, followed by titrating the protons with standardized NaOH solution to a phenolphthalein end point. IEC was calculated by Equation 2.7. IEC values determined by titration are referred to as IEC\textsubscript{act} (actual IEC), whereas theoretical IEC values are referred to as IEC\textsubscript{th}. Lambda (λ), also known as the hydration number, was determined to represent the number of water molecules per sulfonic acid group according to Equation 2.6. Reported IEC and λ are average values from several measurements on duplicate membranes. Errors are calculated as the standard deviations of the data. Nafion\textsuperscript{®} 117 membranes were used as internal reference among all measurements.
In-plane proton conductivity was measured by AC impedance spectroscopy by using a Solartron 1260 frequency response analyzer, utilizing a two-electrode configuration, according to Section 2.4.4. A membrane (typically 10 mm by 5 mm) was placed between two Pt electrodes in a Teflon® conductivity cell. By applying a 100 mV sinusoidal AC voltage over a frequency range of 10 MHz – 100 Hz, Nyquist plots could be obtained. The Nyquist data were fitting to the standard Randles equivalent circuit to determine the membrane resistance, which was then used to calculate proton conductivity according to Equation 2.8. The reported proton conductivity was calculated as the average of several measurements.

The analytical acid concentration [-SO₃H] (M) in a wet membrane was calculated using IEC values obtained by titration based on Equation 2.10. The effective proton mobility, \( \mu_{\text{eff}} \) [cm² sV⁻¹] in the wet membrane was estimated using Equation 2.11, representing the “normalized” proton conductivity, which the effects of acid concentration are removed. Proton mobility provides insights on acid dissociation, ionic channel tortuosity, and special proximity of neighbouring acid groups, serving an important property for PEMFCs. Detailed descriptions of analytical acid concentration and proton mobility are provided in Section 2.4.6. Both of acid concentration and proton mobility are reported as the average value of duplicate measurements.

Proton conductivity under various temperature and RH were conducted by the AC impedance spectroscopy in an ESPEC SH-241 temperature/humidity environmental chamber. Proton conductivity data was taken until the membrane was fully equilibrated and a constant result was reached. This usually takes ~ 5 hours. Membranes were recast and their proton conductivities measured multiple times.
Gravimetric water vapour sorption technique was used with using a DVS-1000 (Surface Measurement System, UK) to obtain the isothermal water vapour sorption at different RH. The RH was reached by using a mixed gas flow of saturated water vapour and dry nitrogen, maintained and controlled by a dew-point sensor. Typically, the membranes were equilibrated at 25 °C in an RH range of 0 – 95% with step of 10%. The mass of the membrane was recorded every 10 seconds until a stable mass was obtained, which was used to calculate the water sorption. The slope of a linear fit to the data points is a useful measure of the dependency of temperature and humidity respectively on proton conductivity. Smaller slope indicates that the membrane performance remains constant regardless of fluctuations in temperature and humidity, revealing relatively lower sensitivity of proton conductivity on temperature and humidity.

5.2.6. Transmission Electron Microscopy for Morphological Study

Samples were stained with lead acetate and embedded in Spurr’s epoxy before they were microtomed into ultra-thin slices and collected on a copper grid before they were measured under TEM. A Hitachi H7600 TEM was used to obtain micrographs by applying an accelerating voltage of 100 keV. The blend membranes were also cryo-microtomed using a Leica Ultracut UCT with a Cryo 35° Waterblade. Electron micrographs were obtained with a Tecnai T20 G² operated at an accelerating voltage of 200 keV. Full description about the instrument is provided in 2.4.7. Determination of the ionic domain sizes was performed using the software Image J®, measuring the average cluster size in width and standard deviation from 100 measurements of multiple images for each sample. The 2D number density and standard deviations was determined by counting the clusters enclosed in a predetermined 1 x 1 cm area as described in Section
3.2.6. The average number density of ionic clusters was calculated as the average of 30 measurements.

5.3. Results and Discussion

5.3.1. Preparation and Characterization of Fully Sulfonated P(VDF-co-CTFE)-g-PS

Three graft copolymers consist of the macroinitiator of 2.6 mol% of ATRP-initiating CTFE were synthesized successfully as previously described in Section 3.3.1. Three series possess different graft length, $D_{PS} \sim 39$, 62, and 79 for short, medium and long, and referred as Graft$_{2.6,short}$, Graft$_{2.6,medium}$, Graft$_{2.6,long}$, respectively. The other graft copolymer was synthesized using a macroinitiator of lower CTFE density (1.1 mol%), and estimates to have a $D_{PS}$ of 24. After post-sulfonation, Graft$_{1.1}$ was estimated to exhibit 40 vol% of PSSA and 60 vol% of PVDF and is referred Graft$_{40:60}$.

The degree of sulfonation was confirmed by $^1$H NMR spectroscopy, as illustrated in Figure 5.1, where $^1$H NMR spectra of the unsulfonated long graft copolymer Graft$_{2.6,L}$, its partially sulfonated graft copolymer (DS $\sim$ 56%) and fully sulfonated graft copolymer (DS $\sim$ 100%) are shown as examples. The pristine unsulfonated copolymer exhibits peaks at $\delta = 6.5 - 6.8$ ppm (peak “a”) and $\delta = 6.9 - 7.4$ ppm (peak “b”) corresponding to polystyrenic ortho- and meta/para- protons, respectively. The partially sulfonated copolymers exhibit an additional peak at $\delta = 7.6$ ppm, which corresponds to protons adjacent to the sulfonated group (peak “c”), suggesting successful sulfonation occurred. The fully sulfonated Graft$_{2.6,L}$ has no remaining meta/para- $^1$H NMR peaks shown in Figure 5.1 (c). Fully sulfonated Graft$_{2.6,M}$ ($IEC_{th} = 4.05$ mmol g$^{-1}$) and Graft$_{2.6,L}$ ($IEC_{th}$ =
4.29 mmol g\(^{-1}\)) partially dissolved in water due to their increased ionicity, which precluded the determination of IEC by titration.

5.3.2. Preparation of Fully Sulfonated Blends

Graft\(_{40:60}\) was estimated to contain 40 vol% of PSSA and 60 vol% of fluorous matrix. In order to have a fair comparison, fully sulfonated Graft\(_{2.6-S}\), Graft\(_{2.6-M}\), and Graft\(_{2.6-L}\) were blended with high mol. wt. PVDF so as to have similar PSSA-PVDF ratios. They are referred as SB\(_{40:60}\), MB\(_{40:60}\), and LB\(_{40:60}\), for short (DP\(_{39}\)), medium (DP\(_{62}\)), and long (DP\(_{79}\)) graft lengths, respectively. A second blend series, having even higher PVDF content was prepared to examine the consequences on water sorption and proton conductivity when PVDF phase was increased to a greater extent. The resulting membranes in this series contain a PSSA: PVDF molar ratio of 25:75, abbreviated SB\(_{25:75}\), MB\(_{25:75}\), and LB\(_{25:75}\). The chemical composition of the fully sulfonated Graft\(_{40:60}\) copolymer and the blends of Graft\(_{2.6-short}\), Graft\(_{2.6-medium}\), and Graft\(_{2.6-long}\) are summarized in Table 5.1. Diagrams illustrating the vol. fraction of polymer components for samples containing 40 vol% of PSSA and 60 vol% of PVDF are shown in Scheme 5.1 (a) – (d). In (a), a cartoon of Graft\(_{40:60}\) is illustrated, where approximately 40 vol% of ionic moiety (i.e., PSSA) is embedded in the 60 vol% of fluorous backbone (light grey). Scheme 5.1 (b) – (d) display the vol. fraction of membrane components for the 40:60 blend membranes. For SB\(_{40:60}\), shortest SPS chains and small amount of fluorous backbone are embedded in the PVDF homopolymer (dark grey); similarly, medium and longest SPS chains and the polymer backbone are embedded in the PVDF matrix for MB\(_{40:60}\) and LB\(_{40:60}\), respectively. The 25:75 blend series exhibiting half of IEC values of 40:60 blend series are illustrated in Scheme 5.1 (e)-(g).
Figure 5.1. 400 MHz $^1$H NMR spectra of grafted polystyrene of (a) unsulfonated Graft$_{2.6}$-L, (b) its partially sulfonated graft copolymer, DS = 56%, and (c) its fully sulfonated graft copolymer, DS = 100%.
Table 5.1. Chemical composition of fully sulfonated graft blends and fully sulfonated Graft copolymer

<table>
<thead>
<tr>
<th>Ionomer CTFE (mol%)</th>
<th>Blend PS-PVDF (vol %)</th>
<th>GD (mol%)</th>
<th>DP_{PS}</th>
<th>M_{n} \text{PVDF-co-CTFE} (kg/mol)</th>
<th>M_{n} \text{PSSA} (kg/mol)</th>
<th>wt% Ionomer</th>
<th>wt% PVDF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graft_{2.6}</td>
<td>SB_{40.60}</td>
<td>1.68</td>
<td>39</td>
<td>123</td>
<td>230</td>
<td>48.3</td>
<td>51.7</td>
</tr>
<tr>
<td>Graft_{2.6}</td>
<td>MB_{40.60}</td>
<td>1.68</td>
<td>62</td>
<td>123</td>
<td>365</td>
<td>42.0</td>
<td>58.0</td>
</tr>
<tr>
<td>Graft_{2.6}</td>
<td>LB_{40.60}</td>
<td>1.72</td>
<td>79</td>
<td>123</td>
<td>466</td>
<td>39.7</td>
<td>60.3</td>
</tr>
<tr>
<td>Graft_{2.6}</td>
<td>SB_{25.75}</td>
<td>1.68</td>
<td>39</td>
<td>123</td>
<td>230</td>
<td>24.0</td>
<td>76.0</td>
</tr>
<tr>
<td>Graft_{2.6}</td>
<td>MB_{25.75}</td>
<td>1.68</td>
<td>62</td>
<td>123</td>
<td>365</td>
<td>21.0</td>
<td>79.0</td>
</tr>
<tr>
<td>Graft_{2.6}</td>
<td>LB_{25.75}</td>
<td>1.72</td>
<td>79</td>
<td>123</td>
<td>466</td>
<td>19.7</td>
<td>80.3</td>
</tr>
<tr>
<td>Graft_{1.1}</td>
<td>-</td>
<td>0.68</td>
<td>24</td>
<td>154</td>
<td>70</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

Note.  

- Measured by $^{19}$F NMR; number of ATPR-initiating CTFE units per 100 backbone repeat units.  
- According to Equation 4.1, using wt\% and the densities of the components.  
- Graft density, calculated from $X_{\text{CTFE}}$ multiplying by the grafting efficiency.  
- Average number of styrene per graft chain, calculated from the St:VDF ratio divided by graft density.  
- Measured by GPC calibrated with PS standards.  
- Calculated from DP_{PS}.  
- Calculated from the compositions and the densities of the ionomer and fluorous components.
5.3.3. Observation of Ionic and Fluorous Domains by TEM

TEM images of Graft$_{2.6}$ – PVDF blends as well as their corresponding fully sulfonated copolymers and Graft$_{40:60}$ are shown in Figure 5.2 for comparison. Quantitative data such as size of ion-rich clusters and 2D number density is summarized in Table 5.2. All of the membranes exhibit a phase-separated morphology, in which the ion-rich clusters, appearing as dark areas, are randomly distributed in the fluorous matrix, appearing as bright areas. Among all of the fully sulfonated graft ionomers (i.e., Graft$_{2.6,short}$, Graft$_{2.6,medium}$, Graft$_{2.6,long}$, and Graft$_{40:60}$), Graft$_{40:60}$ has lowest cluster size (e.g., 3.7 ± 0.6 nm for Graft$_{40:60}$ vs. 3.8 – 4.7 ± 0.6 nm for Graft$_{2.6}$ series), but no significant difference in size was observed (all fall within the error range) – suggesting a negligible influence of graft length on the ion-domain size when the copolymers are fully sulfonated. The average 2D number density of ion-rich clusters is considerably lower for Graft$_{40:60}$ than the Graft$_{2.6}$ series (e.g., 40 per 10$^4$ nm$^2$ vs. 53 – 56 per 10$^4$ nm$^2$), which is attributed to its lower graft density and low PSSA content. Unlike the pure graft membranes, which exhibit consistent disordered cluster morphology, inhomogeneous morphology was observed for all of the blend membranes. This can be demonstrated in Figure 5.3. Three TEM images under different length scales are displayed here. In (a), fluorous domains are dominant in the display area, confirming the higher vol. fraction over the ionic domains in the blended membrane. Although fewer ionic regions are shown, ion-rich phase is able to form continuous networks. In (b) under higher magnifications, primarily ion-rich domains appear in the display area. In (c), a higher magnified image is present, showing the boundary between the ion-rich (left) and fluorous domains (right) and a close-up of the disordered cluster morphology. Besides, for the 40-60 blend membranes under high magnification of the images (scale bar 20 nm) (Figure 5.2b, for example), continuous disordered clusters distributed in a
predominantly PVDF containing network was observed, which can be seen to form interconnected ion-rich networks in the size order of hundreds of nm under lower magnification (scale bar 200 nm). The size of the clusters was estimated to be 1.5 ± 0.3 nm, 1.6 ± 0.4, and 1.7± 0.4 for SB40:60, MB40:60, LB40:60, respectively. The sizes of the ion-rich clusters are not significantly different from each other, but noticeable smaller than that of their pure graft copolymers. The 25-75 series also phase-separate into ion-rich domains and PVDF-rich domains as seen under lower magnification. Surprisingly, ion-rich networks (channels) are observed even the blended membranes consist mostly fluorous moiety over the ionic component (75 vol% vs 25 vol%, respectively).
Figure 5.2. TEM images of (A) Graft$_{2.6}$-Short, (B) SB$_{40-60}$, (C) SB$_{25-75}$, (D) Graft$_{2.6}$-medium, (E) MB$_{40-60}$, (F) MB$_{25-75}$, (G) Graft$_{2.6}$-long, (H) LB$_{40-60}$, (I) LB$_{25-75}$ and (J) Graft$_{40:60}$. PVDF-rich and ion-rich domains are shown in bright and dark, respectively.

[Cryo-microtoming and TEM were performed by Lars Schulte of Department of Chemical and Biochemical Engineering, Technical University of Denmark.]
**Figure 5.3.** TEM images of SB$_{40:60}$ at three different length scales
[Reproduced by courtesy of Dr. Mads M. Nielsen.]

**Table 5.2.** The sizes of ionic clusters and the number densities for pure graft copolymers and their blends

<table>
<thead>
<tr>
<th>Polymer</th>
<th>IEC$_{th}$ (mmol g$^{-1}$)</th>
<th>IEC$_{act}$ (mmol g$^{-1}$)</th>
<th>DS (%)$^d$</th>
<th>Width of ionic clusters (nm)</th>
<th>2-D number density (per 10$^4$ nm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Graft$_{2.6}$-short</td>
<td>3.52</td>
<td>3.48</td>
<td>100</td>
<td>3.8 ± 0.6</td>
<td>56 ± 3</td>
</tr>
<tr>
<td>(B) SB$_{40:60}$</td>
<td>1.72</td>
<td>1.22 ± 0.18</td>
<td>×</td>
<td>1.52 ± 0.31</td>
<td>×</td>
</tr>
<tr>
<td>(C) SB$_{25:75}$</td>
<td>0.85</td>
<td>0.60 ± 0.02</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>(D) Graft$_{2.6}$-medium</td>
<td>4.05</td>
<td>×</td>
<td>100</td>
<td>4.1 ± 0.7</td>
<td>55 ± 2</td>
</tr>
<tr>
<td>(E) MB$_{40:60}$</td>
<td>1.72</td>
<td>1.31 ± 0.10</td>
<td>×</td>
<td>1.59 ± 0.32</td>
<td>×</td>
</tr>
<tr>
<td>(F) MB$_{25:75}$</td>
<td>0.85</td>
<td>0.75 ± 0.09</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>(G) Graft$_{2.6}$-long</td>
<td>4.29</td>
<td>×</td>
<td>100</td>
<td>4.7 ± 0.6</td>
<td>53 ± 1</td>
</tr>
<tr>
<td>(H) LB$_{40:60}$</td>
<td>1.72</td>
<td>1.15 ± 0.09</td>
<td>×</td>
<td>1.74 ± 0.37</td>
<td>×</td>
</tr>
<tr>
<td>(I) LB$_{25:75}$</td>
<td>0.85</td>
<td>0.64 ± 0.02</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>(J) Graft$_{40:90}$</td>
<td>1.72</td>
<td>1.10 ± 0.07</td>
<td>100</td>
<td>3.7 ± 0.6</td>
<td>40 ± 1</td>
</tr>
</tbody>
</table>

Note.  
$^a$Not available due to partially membrane dissolution when immersed in water.  
$^b$The 25-75 series is difficult to quantify unambiguously and thus excluded from the table.  
$^c$Due to inhomogeneous morphology observed, it is difficult to determine the number densities of the blend membranes, thus also excluded from the table.
5.3.4. Effect of Lowering IEC by Blending with PVDF vs. Reducing Degree of Sulfonation.

Upon the addition of PVDF to the blend membranes, their IECs are effectively lowered compared to the pure graft ionomers. Theoretical and actual IEC values of the graft copolymers and their blends are summarized in Table 5.2. The IEC$_{th}$ of the 40-60 and 25-75 series are 1.72 and 0.85 mmol g$^{-1}$, respectively, but IEC$_{act}$ are in the range of 1.15 – 1.31 and 0.60 – 0.75 mmol g$^{-1}$, respectively. Generally, IEC$_{act}$ are lower than IEC$_{th}$ by 10 - 35%, indicating partial inaccessibility of acidic groups in the fluorous matrix. The IEC$_{act}$ for Graft$_{40:60}$ is also lower than its theoretical value (1.10 and 1.72 mmol g$^{-1}$, respectively), but similar to the 40-60 blend series membranes.

The morphology-related properties such as water sorption and proton transport properties under liquid-saturated conditions for the three 40-60 blend membranes are summarized in Table 5.3. These properties of the three Graft$_{2.6}$ series including partially and fully sulfonated graft copolymers are reported previously in Table 3.4. Relationships between the properties and IEC$_{act}$ for the pristine graft ionomers and the blend membranes are plotted in Figure 5.4 to examine the effect of reduced IEC by blending or by changing the DS on the properties. Lambda ($\lambda$) vs. IEC$_{act}$ is plotted in Figure 5.4 (a), where the blends exhibit a factor of 3 – 5 increase in $\lambda$ compared to the partially sulfonated grafts containing similar IEC values. The partially sulfonated grafts require twice as high an ionic content to obtain similar water uptake. This suggests that the blend membranes allow for an increase in water percolation due to the elimination of the restricting effect of unsulfonated PS. In addition, the blends possess up to 2 – 3 times more water than Nafion® 117.
**Table 5.3.** Properties\(^a\) of graft and blend membranes

<table>
<thead>
<tr>
<th>Sample</th>
<th>IEC(_{act}) (mmol g(^{-1}))</th>
<th>(\lambda) ([H(_2)O]/[SO(_3)H])</th>
<th>(\sigma) (mS cm(^{-1}))</th>
<th>[-SO(_3)H] (M)</th>
<th>(\mu_{eff} \times 10^3) (cm(^2) sV(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graft(_{40:60})</td>
<td>1.10±0.07</td>
<td>62</td>
<td>46±3</td>
<td>0.49±0.02</td>
<td>0.97</td>
</tr>
<tr>
<td>SB(_{40:60})</td>
<td>1.22±0.18</td>
<td>30</td>
<td>63±3</td>
<td>0.71±0.02</td>
<td>0.92</td>
</tr>
<tr>
<td>MB(_{40:60})</td>
<td>1.31±0.10</td>
<td>41</td>
<td>62±1</td>
<td>0.68±0.08</td>
<td>0.95</td>
</tr>
<tr>
<td>LB(_{40:60})</td>
<td>1.15±0.09</td>
<td>44</td>
<td>62±4</td>
<td>0.72±0.01</td>
<td>0.89</td>
</tr>
<tr>
<td>SB(_{25:75})</td>
<td>0.60±0.02</td>
<td>29</td>
<td>48±6</td>
<td>0.97</td>
<td>0.51</td>
</tr>
<tr>
<td>MB(_{25:75})</td>
<td>0.75±0.09</td>
<td>30</td>
<td>49±5</td>
<td>0.90</td>
<td>0.57</td>
</tr>
<tr>
<td>LB(_{25:75})</td>
<td>0.64±0.02</td>
<td>21</td>
<td>51±6</td>
<td>0.90</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Note. \(^a\)Measured at room temperature and membranes were immersed in water before their properties were measured.

The proton conductivity vs. IEC is shown in Figure 5.4 (b). For a given IEC, the blends exhibit at least 4 times higher conductivities than the partially sulfonated grafts (62 - 63 mS cm\(^{-1}\) vs. 1 - 15 mS cm\(^{-1}\)). The partially sulfonated system requires 2 - 3 times more ionic content to obtain equivalent conductivities. The analytical acid concentration is plotted against IEC shown in Figure 5.4 (c). The blends possess [-SO\(_3\)H] \(\sim\) 0.68 - 0.72M, which are 35% lower than the values of the partially sulfonated ionomers for similar IECs and \(\sim\) 30% lower than the [-SO\(_3\)H] of Nafion\(^\circledR\) 117. The effective proton mobility, \(\mu_{eff}\), vs. IEC is shown in Figure 5.4 (d). The blends exhibit \(\mu_{eff}\) that are much higher than the partially sulfonated grafts (0.89 \(\times\) 10\(^3\) - 0.95 \(\times\) 10\(^3\) cm\(^2\) sV\(^{-1}\) vs. 0.01 \(\times\) 10\(^3\) - 0.14 \(\times\) 10\(^3\) cm\(^2\) sV\(^{-1}\)) for a given IEC \(\sim\) 1.25 mmol g\(^{-1}\) and slightly higher than that of Nafion\(^\circledR\) 117 (0.75 \(\times\) 10\(^3\) cm\(^2\) sV\(^{-1}\)). The significant differences in \(\mu_{eff}\) suggest a morphological gain by blending. In order to obtain a similar \(\mu_{eff}\), the partially sulfonated system requires 2 – 3 times higher ionic content.
A schematic diagram illustrates the effects of changing ion content by reducing DS (left) or by blending with PVDF (right) in Figure 5.5. The fully sulfonated short graft membrane displayed in the centre has highest PS volumetric content (77 vol\% ionic PS) and possess a IEC of 3.52 mmol g\(^{-1}\). Ionic domains are well connected. However, this leads to excessive swelling in water, diluting the acid concentration and losing in mechanical integrity. Consequently, proton conductivity is compromised (41 ± 3 mS/cm). If reducing DS ~ 18\%, the partially sulfonated graft membrane shown on the
left has a 65 vol% PS content and possess an IEC of 1.12 mmol g\(^{-1}\). The large portion of unsulfonated PS encapsulates ionic domains, causing low water sorption and poor connectivity between ionic domains (Figure 5.5, left). This is confirmed by the water sorption results, in which \( \lambda \) decreases from 283 to 9 water molecules per acid site when DS is reduced from 100 to 18%, resulting in very low proton mobility (0.07 cm\(^2\) sV\(^{-1}\)). Furthermore, the isolated ionic domains cause poor proton conductivity. The fully sulfonated blend shown on the right, on the other hand, has 40 vol% PS and possesses similar IEC (1.22 mmol g\(^{-1}\)) as the partially sulfonated graft copolymer. The fully sulfonated PS content is embedded in the PVDF homopolymer matrix. The absence of unsulfonated PS (Figure 5.5, right) promotes and retains continuous ionic domains for effective proton transport, thus maintain high ionic connectivity in the hydrophilic channels. More, the PVDF homopolymer matrix helps reduce excessive water swelling and enhance mechanical property effectively.

**Figure 5.5.** Schematic presentation of the effect of reducing IEC by decreasing the degree of sulfonation (left) and by blending with PVDF (right)
5.3.5. Comparison Between a Pure Graft Copolymer and Fully Sulfonated Graft Blends Having Similar Ion Content

Graft\textsubscript{40:60} and the three 40:60 blend membranes are to be examined in the following section to study the effect of membrane morphology on properties. The blend membranes were purposely prepared so that they contain equivalent volumetric content of PSSA and PVDF relative to Graft\textsubscript{40:60}, thus theoretically have equivalent IECs. Another series containing 25 vol\% of PSSA and 75 vol\% PVDF was prepared to investigate the proton transport properties for low ion content polymers. The properties of these membranes are tabulated in Table 5.3 and the relationship between the properties and IECs are plotted in Figure 5.6. For a similar IEC, the pure graft ionomer Graft\textsubscript{40:60} exhibits higher $\lambda \sim 62$, while the 40:60 blend membranes possess $\lambda$ of 30, 41 and 44 as graft length increases. $\lambda$ for the 25-75 blend series is even lower. The striking feature observed here is that the 25-75 blend series exhibit slight lower IEC values than Nafion\textsuperscript{®} 117, but contain slightly higher $\lambda$. The lower water content in both blend series results in higher acid concentration than the Graft\textsubscript{40:60}. Consequence, the proton conductivities of the 40:60 blend series are 35\% higher than the Graft\textsubscript{40:60} and comparable to Nafion\textsuperscript{®} 117. Surprisingly, the 25:75 blend series possess only half of IEC as Graft\textsubscript{40:60} and the 40:60 blend series, but exhibit comparable proton conductivity than the Graft\textsubscript{40:60} (48 – 51 ± 6 mS/cm vs. 46 ± 3 mS/cm) and only 20\% lower than the 40:60 blend series. The effective proton mobility is plotted in Figure 5.6 (d). Blend membranes and Graft\textsubscript{40:60} exhibit similar proton mobility: $0.89 \times 10^3$ cm$^2$ sV$^{-1}$ – $0.95 \times 10^3$ cm$^2$ sV$^{-1}$ vs. $0.97 \times 10^3$ cm$^2$ sV$^{-1}$, which are all higher than that of Nafion\textsuperscript{®} 117 ($0.75 \times 10^3$ cm$^2$ sV$^{-1}$). The effect of increasing PVDF content in the 25:75 blend series causes half reduction of proton mobility.

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Figure 5.6. (a) $\lambda$, (b) proton conductivity, (c) analytical acid concentration and (d) effective proton mobility as a function of IEC for pure ionomer $\text{Graft}_{40:60}$, $\text{Graft}_{2.640:60}$ and 25:75 blend series in water-saturated condition.

Proton Conductivity as a Function of RH and Temperature

Water sorption behaviour and proton transport properties under various RH for $\text{Graft}_{40:60}$ and the 40-60 blend series are shown in Figure 5.7. The 25:75 blend series is excluded because it exhibited poor conductivities at reduced RH. As RH increases, $\lambda$ increases for all of the membranes. At 45% RH, the $\lambda$ values are in the range of 1-3 for both 40:60 blends and $\text{Graft}_{40:60}$, whereas N117 exhibits $\lambda = 5$. At 95% RH, the values increase and range from 9 to 14 for the blends, 13 for $\text{Graft}_{40:60}$ and 19 for N117. The
blends appear to follow a trend that the longer graft blend exhibits higher $\lambda$ values, which are similar to that of Graft$_{40:60}$. Generally, Nafion® 117 exhibits the highest $\lambda$ for a given IEC. Similarly to water sorption trend, as RH increases, proton conductivity increase proportionally. The slopes of the plots of proton conductivity vs. RH are similar for Graft$_{40:60}$ and the 40-60 blend series, suggesting similar dependencies on RH. Proton conductivity of Graft$_{40:60}$ and the blends are comparable but generally 4 – 7 times lower than that of Nafion® 117 at reduced RH.

Figure 5.7 (c) displays the relationship between conductivity and temperature for Graft$_{40:60}$ and the 40:60 blend series at 95% RH. Proton conductivity increase as the temperature increases. Generally, all of the membranes consisting of 40 vol% PSSA exhibit very similar $\sigma$ – temperature profiles, which are obviously lower than Nafion® 117. At 80°C, these membranes have $\sigma$ ~ 36 – 45 mS/cm, while Nafion® 117 has $\sigma$ ~ 165 mS/cm. However, it is worthwhile noting that even when the PVDF content is higher than the ionic content, these blend membranes can still exhibit reasonable proton conductivity at reduced RH. This may be associated to the good ionic connectivity in the graft copolymers due to their continuous disordered cluster morphology, promoting well connected hydrophilic conducting channels.

The activation energy for proton transport can be obtained through an Arrhenius plot of the data. According to Arrhenius plots, the activation energy of Graft$_{40:60}$ was calculated as 15.8 KJ/mol, which is slightly lower than the 40:60 blends (16.5 – 24.3 KJ/mol). The results suggest that the blend series require higher energy for proton transport, likely due to their high PVDF contents that are strongly hydrophobic and limit the water sorption at reduced RH. However, the absolute proton conductivity of the pure graft ionomer Graft$_{40:60}$ is very similar to that of the blend series, suggesting that the high
localized ion content in the blend membranes promotes ionic connectivity for effective proton transport.

Figure 5.7. (a) $\lambda$, (b) proton conductivity as a function of RH at 25 °C, (c) conductivity as a function of temperature for $\text{Graft}_{40:60}$ and the 40:60 blend membranes.
5.4. Conclusions

Membranes consisting of fully sulfonated graft copolymers mixed with high mol. wt. PVDF were prepared to examine the effect of lowering ion content by reducing DS or blending with PVDF on morphology and the morphology-related properties. TEM images reveal that after blending with PVDF, the homogeneously disordered cluster morphology observed for the pure graft ionomers changes to an inhomogeneous morphology, where fluorous and ionic phases dominate in different regions across the display area of the image. Nevertheless, ion-rich domains are well connected, forming a continuous ionic network even for the blend series containing 25 vol% PSSA and 75 vol% PVDF. Promising proton conductivities were observed for both blend series: 40:60 and 25:75 PSSA:PVDF vol%. For a given IEC, the fully sulfonated blends exhibit 4x higher proton conductivity than the partially sulfonated copolymers. This is likely associated to the unsulfonated styrenic moieties enclosing the ionic domains in the partially sulfonated copolymer, causing poor connection between ionic regions, thus poor proton conductivity. On the other hand, the ionic domains in the fully sulfonated blends are well connected for high proton conductivity comparable to Nafion® 117. The PVDF moiety act effectively to control excessive swelling, preventing severe acid dilution and enhancing mechanical integrity of the membranes. The 40:60 blend series also display higher proton conductivity than a pure graft ionomer Graft40:60, exhibiting similar vol% of PSSA and PVDF. Therefore, reducing ion content by blending is shown to be a more effective approach to limit water swelling while maintain promising proton conductivity. The strategy helps confine and localize ionic domains so as to facilitate proton transport under reduced humidity.
Chapter 6. Thesis Summary and Outlook

This thesis focuses on the elucidation of structure-property relationships in proton exchange membranes. Emphasis is particularly given to the strategies used to control the polymer microstructure, i.e., chemical composition and ion content, and their influence on membrane morphology, crystallinity, formation of ionic domains and, consequently, membrane properties. Model graft polymers have the ability to self-assemble into a variety of nano-scaled morphological structures through the process of microphase separation. Furthermore, the nanostructure of the polymer systems can be systematically controlled and tailored, resulting in controlled phase-separated morphologies. The polymer systems serve as excellent model systems, allowing for relationships between polymer structures, morphology, crystallinity, and proton transport properties to be examined in order to elucidate preferred structures for the design of new-generation membranes.

In Chapter 3, the synthesis and characterization of three series of fluorous-ionic graft copolymers, poly[[vinylidene difluoride-co-chlorotrifluoroethylene]-graft-styrene) [P(VDF-co-CTFE)-g-PS], possessing distinctive graft lengths - but systematically-controlled graft density - are described. These polymers were sulfonated to different degree and served as a platform to study the effect of graft length and sulfonation degree on membrane morphology and properties. WAXS data revealed that the degree of crystallinity of the membrane formed decreased due to the presence of graft polystyrene chains grown from the macroinitiator - indicating the grafts restrict the
organization of the fluorous backbone. After sulfonation of the parent graft copolymers, the crystallinity increased for the short graft length copolymers but remained unchanged for the two longer graft length series - demonstrating that the effect of sulfonation on crystallinity is more pronounced for shorter graft lengths. A disordered cluster morphology was observed for all of the graft copolymers. The short graft length series appeared to possess more defined and interconnected hydrophobic domains. This series was more tolerant to swelling (for high ion contents) because of the higher degree of crystallinity, higher PVDF content, and the more contiguous nature of the fluorous domains. The limited water swelling of the short graft copolymers promoted acid concentrations (less acid dilution) and high proton conductivity over a wider range of IEC. For the medium and long graft series, the range of IEC that led to high proton conductivity was very narrow. Under reduced RH (95% RH), the graft copolymers exhibited high proton conductivities (> 0.1 S/cm) for IECs > 2.3 mmol/g. Proton conductivity up to 0.3 S/cm was observed at 80°C, which is twice as large as Nafion® 117. These promising results suggest that the high ion content achieved for the graft copolymers allowed establishment of well-connected hydrophilic conducting networks for exceptionally high proton conductivity.

The effect of graft density was investigated by comparing the short graft copolymer with an analogous graft copolymer which possessed a similar weight fraction of PS to fluorous polymer but lower degree of crystallinity. The study also aided to differentiate the effect of crystallinity and PVDF content on membrane properties (different degree of crystallinity but similar PVDF content). The short graft copolymer possessed significantly higher crystallinity due to the longer sequence length between graft side chains (i.e., a lower graft density). Furthermore, the number density of ion-rich
domains was lower and the cohesivity of the fluorous matrix was higher, rendering the short graft series less susceptible to dissolution in water even when the graft chain was fully sulfonated.

In Chapter 4, the highly sulfonated long graft ionomer described in Chapter 3 was blended with two different mol. wt. PVDF samples in order to examine the effect of blending on membrane morphology and properties. When blended with low mol. wt. PVDF, the degree of crystallinity of the blend membrane increased 2.5x with significantly reduced swelling and higher proton conductivity compared to the pristine graft ionomer. When mixed with high mol. wt. PVDF, a relatively lower enhancement of the crystallinity was observed (2x), but water swelling was reduced further and a greater increase in proton conductivity observed. It is speculated that the addition of high mol. wt. PVDF not only increased in crystallinity but enhanced the connectivity between fluorous domains by virtue of the long fluoropolymer chains. Water uptake was greatly reduced, eliminating high dilution of the acid functionality, yet the proton mobility remained high. A blend membrane containing 80 wt% of ionomer and 20 wt% PVDF exhibited high proton connectivity in both water-saturated and water vapour conditions. Under reduced RH (~95%), it possessed 0.14 and 0.27 S/cm at 25°C and 80°C, respectively, which is comparable to the pristine graft ionomer (despite an overall lower ion content) and double that of Nafion® 117.

It is demonstrated that a highly sulfonated graft copolymer can provide continuous, highly localized ion domains that promote high proton connectivity even when the overall ion content is diluted with a non-ionic polymer (PVDF). Blending with non-ionic polymer of higher mol. wt. can be used to effectively alter ion content and effectively limit water swelling and, in turn, improve the mechanical strength of the
membranes. Such advantages are demonstrated by a combination of increased crystallinity and connectivity of fluorous domains.

Chapter 5 further illustrates the importance of confined and high localized ionic domains on the formation of ionic channels and on the membrane properties. Three graft copolymers, described in Chapter 3, were sulfonated to their maximum degree (DS ~ 100%) and blended with high mol. wt. PVDF. This work was an advancement of research presented in Chapters 3 and 4, as blending with a fully sulfonated graft copolymer eliminates the uncertainty of the effect of having unsulfonated polystyrenes remaining in the structure of (partially) sulfonated graft copolymers, and allows for a more precise examination on formation of ionic networks. Moreover, complete sulfonation was believed to promote higher connectivity between ionic domains, consequently increasing the localization of ions to even larger extents than previously described.

TEM images demonstrated slight changes in morphology after blending with PVDF. The consistent disordered cluster morphology observed for the pure graft ionomers evolved to an inhomogeneous morphology, where fluorous and ionic phases aggregated in different regions across the entire display area of the image. Nevertheless, ion-rich clusters still appear to be randomly distributed and connected, forming a continuous ionic network even for blend membranes containing 75 vol% PVDF (25 vol% PSSA). It was determined that for a given IEC, the fully sulfonated blends possessed 4x higher proton conductivity than the partially sulfonated copolymers. It is speculated that the unsulfonated styrenic moiety in the partially sulfonated copolymers encapsulated the ionic domains, resulting in poor connectivity between the ionic regions; and consequently, a lower proton conductivity. The extended PVDF domains in the
blend membranes served to limit excessive swelling, leading to higher acid concentrations and enhanced mechanical integrity of the membranes. Reducing the ion content by blending is shown to be an effective approach to controlling water swelling while still retraining high proton conductivity.

This thesis primarily concentrates on polymer synthesis and the influences of nanostructure and morphology on the water sorption and proton conductivity of PEMs. While these properties are critical features of PEMFCs, other properties such as water transport, mechanical strength, and chemical stability are also important. The above properties of the blend membranes prepared in this work are of great interest as the blends were found to be less brittle when dry than the pure graft copolymers and appeared to possess greater mechanical strength. This, coupled with the high proton conductivities observed both in water-saturated and water vapour conditions, indicates that their examination in fuel cells applications is warranted.

The effect of the polymer architecture is understood to have great impact on membrane morphology and properties. To further this understanding, research efforts should continue towards the development of copolymers with different architectures such as tri-block, multi-block, and star-block copolymers, which can self-assemble into a larger variety of complex morphological structures. In order to accomplish this, however, more advanced synthesis methods will have to be developed.

Expanding upon the limited insight gleaned by the TEM results, a precise investigation regarding the phase separation between hydrophobic and hydrophilic domains of the membranes prepared in this thesis can be very useful and are in fact in progress. Narimani et al. have recently published the results of SAXS, SANS and
WAXS studies performed on the pristine sulfonated graft copolymers presented in this thesis. These results indicate that spherical, fluorous and water-rich domains are embedded in a continuous polystyrene matrix. The phase separation between the hydrophobic backbone and hydrophilic graft side chains and the aggregation of ionic groups contribute the formation of hydrophobic and ionic domains. Graft copolymers with 0 and 100% degree of sulfonation exhibit the highest degree of phase separation. For partially sulfonated grafts, phase separation of fluorous component is restrained by the aggregation of sulfonic acid groups. In Chapter 3, it was observed that sulfonation caused an increase in the degree of crystallinity for the short graft copolymers yet resulted in no change for the other two longer graft series. A question that remains unanswered is: whether sulfonation plays a role in affecting the degree of crystallinity. Does change in phase separation after sulfonation have an impact on the organization of fluorous backbones? Synthesizing systematically controlled copolymers with a variety of block lengths can help to clarify this uncertainty. Furthermore, in order to gain more insight into blending methodologies, additional efforts can be made by using SANS and SAXS to investigate the effect of blending on phase separation. Investigations using fully sulfonated graft blends can be particularly useful since the fully sulfonated graft copolymers exhibit well-controlled highly localized ionic domains, which are less likely to contain organic materials (i.e., unsulfonated polystyrene). A deeper understanding of phase separation behaviour will provide significant information about structure-morphology-property relationships in PEMFCs, thus, promoting the development of advanced membranes with desirable properties that meet the requirements for widespread commercialization of PEMFCs.
References


