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Proton-Conducting Sulfonated and Phosphonated Polymers and Fuel Cell Membranes by Chemical Modification of Polysulfones

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Proton-Conducting Sulfonated and Phosphonated Polymers and Fuel Cell Membranes by Chemical Modification of Polysulfones

”An expert is a person who has made all the mistakes that can be made in a very narrow field.”

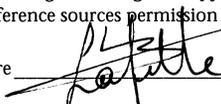
”Un expert est une personne qui a fait toutes les erreurs qui peuvent être faites dans un domaine très étroit.”

Bohr, Niels 1885-1962 (Denmark)

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Abstract The proton exchange membrane fuel cell (PEMFC) is currently emerging as an efficient and environmentally friendly power source. The technology is very complex and relies ultimately on materials and components which need further development. One of the major hurdles for advancing the PEMFC technology is currently the demand for new durable low-cost polymeric membranes that will allow fuel cell operation at high temperatures without extensive humidification requirements. Thus, the design and preparation of functional high-performance proton-conducting membranes with the critical set of properties is a major challenge for polymer and materials chemists around the world today. In this context, major efforts are directed towards different durable aromatic main-chain ionomers. In the present thesis project, new fuel cell membrane materials based on polysulfones (PSUs) functionalized with sulfonated or phosphonated moieties via lithiation chemistry have been designed, synthesized and investigated. PSUs are high performance thermoplastics with excellent chemical, mechanical and thermal properties. By isolating the ionic sites on side chains, away from the polymer main chain, the nanophase separation between the hydrophobic and the hydrophilic domains of the hydrated membrane may be manipulated and influenced, which in turn may provide membranes with balanced water sorption characteristics. Membranes with controlled water uptake were obtained by attaching the sulfonic acid unit to stiff aromatic side chains. This was conveniently achieved by reacting lithiated PSU with 2-sulfobenzoic acid cyclic anhydride in a one-pot reaction. In order to increase the length of the aromatic spacers, a new pathway was developed where lithiated PSU was reacted with 4-fluorobenzoyl chloride. This afforded PSUs with pendant fluorobenzoyl side chains in which the fluoride groups are activated for nucleophilic substitution. As a result, a wide range of nucleophiles may be used to further substitute the polymer. In an initial effort, the activated fluoride groups were replaced by sulfophenoxy or sulfonaphthoxy units in a potassium carbonate-mediated nucleophilic substitution reaction. This reaction proceeded under full conversion and the degree of substitution was easily controlled by the degree of lithiation in the first step. Using a similar methodology, PSUs carrying di- and trisulfonated aromatic side chains were successfully synthesized. In particular, membranes based on a PSU main chain carrying disulfonated naphthoxybenzoyl side chains exhibited a distinct phase separation between the hydrophobic polymer main chain and the hydrophilic sulfonated side chains, and formed a well-defined and efficient network of water-filled nanopores. The latter resulted in excellent proton conductivity at controlled levels of water uptake in contrast to conventional sulfonated aromatic polymers. The investigation of alternative acidic moieties is also of great interest since desulfonation may become a critical issue at high temperatures. This has motivated the search for ionomers based on phosphonic acid units, which generally have a higher hydrothermal stability than sulfonic acid units. Phosphonated PSU was successfully prepared by reacting lithiated PSU with chlorophosphonic acid esters. However, as underlined in a recent literature review, the acidity of phosphonic acid units directly attached to aromatic rings was too low to result in reasonable levels of water uptake. An original approach was therefore developed in which PSU with pendant iodinated benzoyl side chains were prepared via lithiation chemistry. The latter polymer was then further modified to yield the more acidic -CF ₂ PO ₃ H ₂ units located on aromatic side chains. Membranes based on ionomers having 0.90 mmol of phosphonic acid units/g of dry polymer took up 6 wt% water when immersed at room temperature, and levels of conductivity comparable to those reached by a membrane based on a sulfonated polysulfone having 0.86 mmol of sulfonic acid/g of dry polymer were recorded.			
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Proton-Conducting Sulfonated and Phosphonated Polymers and Fuel Cell Membranes by Chemical Modification of Polysulfones

Benoît Lafitte

Division of Polymer & Materials Chemistry

Thesis
2007



LUND UNIVERSITY

Thesis submitted for the degree of Doctor of Philosophy in Engineering, to be defended in public at the Center for Chemistry and Chemical Engineering, Lecture Hall B, on February 26, at 10.15 a.m., as approved by the Faculty of Engineering, Lund University.

Opponent: Dr. Bruno Améduri, Laboratory of Macromolecular Chemistry, UMR (CNRS) 5076, Ecole Nat Sup de Chimie de Montpellier, France.

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Doctoral Thesis

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LIST OF PAPERS

This thesis is a result of the work presented in the following papers, referred to in the text by their respective Roman numerals.

- I. Sulfophenylation of Polysulfones for Proton-Conducting Fuel Cell Membranes**
Benoît Lafitte, Lina E. Karlsson, and Patric Jannasch
Macromol. Rapid Commun., 23, 896-900 (2002)
- II. Proton Conducting Polysulfone Ionomers Carrying Sulfoaryloxybenzoyl Side Chains**
Benoît Lafitte, Mario Puchner, and Patric Jannasch
Macromol. Rapid Commun., 26, 1464-1468 (2005)
- III. Proton-Conducting Aromatic Polymers Carrying Hypersulfonated Side Chains for Fuel Cell Applications**
Benoît Lafitte and Patric Jannasch
Manuscript.
- IV. Phosphonation of Polysulfones via Lithiation and Reaction with Chlorophosphonic Acid Esters**
Benoît Lafitte and Patric Jannasch
J. Polym. Sci. Part A: Polym. Chem., 43, 273-286 (2005)
- V. Polysulfone Ionomers Functionalized with Benzoyl(difluoromethylene-phosphonic Acid) Side Chains for Proton-Conducting Fuel Cell Membranes**
Benoît Lafitte and Patric Jannasch
J. Polym. Sci. Part A: Polym. Chem., 45, 269-283 (2007)
- VI. On the Prospects for Phosphonated Polymers as Proton-Exchange Fuel Cell Membranes**
Benoît Lafitte and Patric Jannasch
Advances in Fuel Cells, 1, 119-186 (2007)

ADDITIONAL PAPERS NOT INCLUDED IN THE THESIS

A Sulfophenylated Polysulfone as the DMFC Electrolyte Membrane - an Evaluation of Methanol Permeability and Cell Performance

Thomas Vernersson, Benoît Lafitte, Göran Lindbergh, and Patric Jannasch

Fuel Cells, 6, 340-346 (2006)

Evaluation of a Sulfophenylated Polysulfone Membrane in a Fuel Cell at 60 to 110 °C

Henrik Ekström, Benoît Lafitte, Jari Ihonen, Henrik Markusson, Per Jacobsson, Anders Lundblad, Patric Jannasch, and Göran Lindbergh

Solid State Ionics, submitted

MY CONTRIBUTION TO THE PAPERS

Paper I. I took an active part in planning the study. I performed all the experimental work and wrote the first draft of the manuscript.

Paper II. I took an active part in planning the study. I performed all the experimental work related to the preparation of the precursor polymers. I carried out the conductivity measurements.

Paper III. I took an active part in planning the study. I performed all the experimental work and wrote the paper.

Paper IV. I took an active part in planning the study. I performed all the experimental work and wrote the paper.

Paper V. I took an active part in planning the study. I performed all the experimental work and wrote the paper.

Paper VI. I took an active part in planning the content of the review. I performed the literature research related to sections 2, 3 and 4. I wrote sections 2, 3 and 4.

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CHAPTER 1

SCOPE OF THE WORK

Proton exchange membrane (PEM) fuel cells, or PEMFCs, are becoming increasingly important as alternative power sources for stationary, automobile and portable applications. PEMFCs generate more power for a given volume or weight of a hydrogen-air fuel cell than any other type of fuel cell. The operating temperature is less than 130 °C, thus allowing rapid start-up. The latter alongside the ability to quickly change power output are some of the characteristics that make the PEMFC the top candidate for several power applications. In addition, PEMFCs have drawn a lot of attention because of their high efficiencies, quiet operation, use of fuel from totally renewable resources, and environmentally friendly processes. Ideally, the only by-product of a hydrogen-powered PEMFC is water. However, there are many challenges that face materials scientists in the preparation of catalyst layers and polymeric materials that can sustain operation in the aggressive in-cell environment for extended times.

It is recognized in the fuel cell industry that cost remains a major issue. Reduction of cost and improving performance are the two major goals of almost all companies developing this technology. Most of these organizations strive to adapt current technology, which is typically accomplished in small steps, but bold improvements are needed. One such approach is to completely replace the costly perfluorinated sulfonic acid membranes with novel polymeric systems that can be prepared more easily and therefore be less expensive. In addition, the largest current limitation for the widespread use of fuel cells in automobiles is perhaps their low operating temperature. Current membrane technology limits the maximum temperature for hydrogen fuel cells to about 80 °C. The small difference between the ambient and operating temperature makes it difficult to remove the excess heat, generated by the

electrochemical reactions in the system. Raising the operating temperature of hydrogen fuel cells simultaneously solves many problems with the current systems in that it, for instance, improves the electrochemical kinetics for both electrode reactions, simplifies water management and increases the CO tolerance of the catalysts. Research efforts are, therefore, aimed at extending the operational conditions of the fuel cells by increasing the cell temperature above 100 °C (typically around 120 °C). This is one aspect of PEMFC operations where the commercial perfluorinated Nafion® membrane has limitations as a PEM. Aromatic polymers are used in many areas such as microelectronics, automotive, structural adhesives and aerospace industries due to their excellent thermal and chemical resistance and superior mechanical integrity. These properties, alongside their generally elevated glass-transition temperature (T_g), suggest that appropriate aromatic polymer systems should be good candidates for high temperature PEMFC applications (i.e. at around 120 °C).

This doctoral thesis was carried out within the framework of the MISTRA programme for fuel cells targeted at high temperature PEMFC operations for the automotive industry. The aim of the thesis project was to investigate the chemical modification of commercially available polysulfones, which are high-performance aromatic polymers, in order to prepare proton-conducting polymer membranes that can operate at elevated temperature. The molecular structure of the ionomer has a profound impact on the macroscopic membrane properties. Therefore, by manipulating the polymeric structure, structure-property relationships can be investigated and important aspects of the synthesis of durable high temperature PEMs may be extracted. Proton-conducting polymers may be prepared by either the copolymerization of sulfonated and non-sulfonated monomers or by the chemical modification of non-sulfonated polymers. One of the principal merits of the chemical modification technique is that it gives access to ionomers where the sulfonic acid units may be placed on side chains to the polymer main chains. Therefore, by using the latter methodology, we investigated the preparation and properties of sulfonated polysulfones where the sulfonic acid units were placed on aromatic side chains of varying lengths and

characters (Papers I-III). Another interesting possibility of the chemical modification approach is that it allows for the preparation of phosphonated polysulfones. Such polymers are in general more complicated to synthesize than 'conventional' sulfonated polymers. The area of phosphonated membranes for fuel cells is still an emerging field and the vast majority of the phosphonated polymers reported in the literature up until now have not been molecularly designed or studied as proton conducting materials (Paper VI). Consequently, it was of interest to investigate the preparation and properties of phosphonated polysulfones (Papers IV & V).

CHAPTER 2

INTRODUCTION

Fuel cells and in particular PEMFCs are actively investigated throughout the world. Several books, book chapters and reviews are available which provide in-depth information regarding the current status of the technology.¹⁻¹¹ PEMFCs and one of its vital components, the proton-conducting polymer membrane, are briefly introduced in the following sections.

2.1 Fuel Cells

A fuel cell is an electrochemical device that converts chemical energy directly into electrical energy. The basic principle of a fuel cell was discovered in 1839 by Sir William Grove.¹² However, fuel cells found their first major application when NASA utilized hydrogen-powered fuel cells to produce electricity and water for the Gemini space missions.¹³ The high cost and short lifetimes of these systems have prevented the use of fuel cells in mass markets. Although the comparison between a fuel cell and a battery is obvious because they serve many of the same functions, a fuel cell differs from a battery since it does not undergo a reversible material change or run down.¹⁴ In principle, it does not require recharging and operates as long as fuel is available.

Fuel cells offer the promise of a low-polluting and highly efficient energy source, which can be designed to utilize an almost limitless abundance of fuel. In its most basic form, the fuel cell uses hydrogen and oxygen from the air to create water and electricity.^{1,13} Such a benign by-product makes the fuel cell an environmentally friendly energy source. Notably, the most efficient heat engines, like internal combustion engines, are limited to a maximum theoretical efficiency of about 40-50%. In contrast, the fuel cell is not a heat engine and it is not subjected to the Carnot Cycle. Therefore, almost all the chemical energy of the fuel may in theory be converted to

Table 1. Different types of fuel cells.

Fuel Cell	Electrolyte	Operating Temperature	Efficiency	Electric Power	Electrochemical Reactions
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	60-90	45-60	Up to 20 kW	Anode: $H_2 + 2(OH)^- \rightarrow 2H_2O + 2e^-$ Cathode: $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$ Cell: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$
Molten Carbonate (MCFC)	Solution of lithium, sodium, and/or potassium carbonates soaked in a matrix	650	45-60	> 1 MW	Anode: $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$ Cathode: $\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$ Cell: $H_2 + \frac{1}{2}O_2 + CO_2 \rightarrow H_2O + CO_2$
Solid Oxide (SOFC)	Solid zirconium oxide with a small amount of yttria	1000	50-65	> 200 kW	Anode: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$ Cathode: $\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$ Cell: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$
Phosphoric Acid (PAFC)	Phosphoric acid soaked in a matrix	175-200	35-40	> 50 kW	Anode: $H_2 \rightarrow 2H^+ + 2e^-$ Cathode: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$ Cell: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$
Proton Exchange Membrane (PEMFC)	Ion Exchange Polymer Membrane	60-130	40-60	Up to 250 kW	Anode: $H_2 \rightarrow 2H^+ + 2e^-$ Cathode: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$ Cell: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$
Direct Methanol (DMFC)	Ion Exchange Polymer Membrane	60-130	40	< 10 kW	Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ Cathode: $\frac{1}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$ Cell: $CH_3OH + H_2O + \frac{1}{2}O_2 \rightarrow CO_2 + 3H_2O$

(see Table 1). This doctoral thesis has focused on PEMFCs. This class of fuel cells currently operates at moderate temperatures (60 to 130 °C) and uses a hydrated PEM to separate the fuel and oxidizer compartments, and to conduct protons from the anode to the cathode.

2.2 Polymer Electrolyte Membrane Fuel Cells

The idea of using an organic cation exchange membrane as a solid electrolyte in electrochemical cells was first described for a fuel cell by Grubb in 1959.^{15,16} However, the research in the area of PEMFC has only experienced a dramatic increase from the

electricity.¹⁴ In addition, as fuel pumps are likely to be the only moving parts of a fuel cell, high reliability and quiet operations may be achieved. With the goal of obtaining more environmentally friendly power sources that do not rely heavily on fossil fuels, fuel cells have become the leading candidate to replace internal combustion engines and may also replace partially lower energy density power storage devices such as batteries.¹³

A separator or electrolyte, which allows for a flow of ionic charges but prevents the transfer of chemical species, is needed in electrochemical cells such as fuel cells. The temperature of operation, the type of electrolyte, as well as, the type of fuel used distinguishes the various types of fuel cells

1990s and onwards, as represented by the amount of scientific reports published from 1980 to 2005 (see Figure 1).

The main components of a PEMFC power source are (i) single cells containing the porous gas diffusion electrodes, the proton conducting electrolyte, anodic and cathodic catalyst layers and current collectors with the reactant flow fields; (ii) a stack of cells in series, with the current collectors also serving as bipolar plates; (iii) cell stacks connected in series or parallel, depending of the voltage and current requirements for specific applications; and (iv) required auxiliaries for thermal and water management and for the compression of gases.⁷ The power output of a single cell is typically less than 0.5 W and its voltage typically around 0.7 V. A schematic representation of a single-cell PEMFC is given in Figure 2.

The operation of a hydrogen-oxygen PEMFC is relatively straightforward. The “heart” of the PEMFC is the membrane electrode assembly (MEA) (or catalyst-coated membrane) which consists of two electrodes (anode, cathode) separated by an ion-conducting polymer electrolyte. When supplied with fuel (hydrogen) and an oxidant (oxygen), two electrochemical half-cell reactions take place.

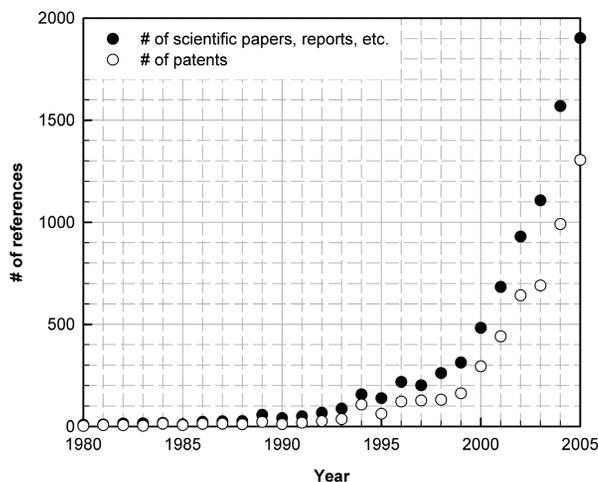
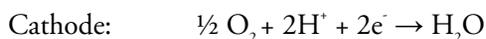


Figure 1. The number of references found in the scientific database 'CAplus' by using the ACS search facility 'Scifinder® Scholar 2006' and a combination of the words: 'polymer', 'fuel' and 'cell'.

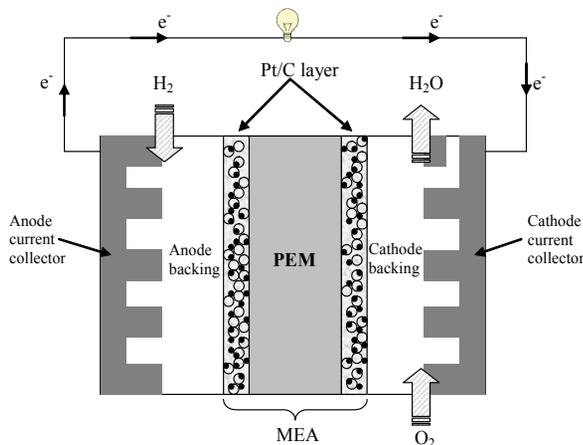
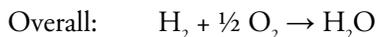


Figure 2. A schematic representation of a single-cell PEMFC.

Hydrogen fed to the anode is oxidized to produce protons and electrons in the presence of a catalyst. The resulting protons are transported in an aqueous environment across the electrolyte to the cathode. Useful electrical energy is harvested by forcing the electrons through an external circuit before allowing them to reach the cathode. At the cathode, gaseous oxygen from the air is reduced and combined with the protons and electrons. The overall cell reaction yields one mole of water per mole of hydrogen and half a mole of oxygen.



Thus far, PEMFCs have shown the most promise in automotive and portable power microelectronics applications.¹ Renewed interest in the commercial development of fuel cells has focused much research into new PEMs. Successful PEMs rely on a set of properties that has to be balanced depending on the choice of fuel, e.g. hydrogen/air or methanol/air. At this time, hydrogen is the fuel of choice for high performance, high power fuel cell applications. Hydrogen powered fuel cells are also potentially one of the most environmentally friendly fuel cells since their only product is water. However, hydrogen has no current distribution infrastructure and is difficult to store under normal conditions. Storage and distribution problems remain to be solved before hydrogen fuel can be used on a large scale. One advantage of hydrogen is that it undergoes easily catalysed reactions under mild conditions. As an example, state-of-

Hydrogen fed to the anode is oxidized to produce protons and electrons in the presence of a catalyst. The resulting protons are transported in an aqueous environment across the electrolyte to the cathode. Useful electrical energy is harvested by forcing the electrons through an external circuit before allowing them to reach the cathode. At the cathode, gaseous oxygen from the air is reduced and combined with the protons and electrons. The overall cell reaction yields one mole of water per mole of hydrogen and half a mole of oxygen.

the-art anode catalysts are alloys of platinum and ruthenium supported on carbon black.³ To date, Nafion® is the most prevalent membrane used in hydrogen fuel cells. Specifically, Nafion® 1135 (1100 equivalent weight, 90 μm thick) and Nafion® 112 (1100 equivalent weight, 50 μm thick) are the products most often used. Thin membranes are preferred since the decrease in cell resistance more than offsets any performance losses associated with the permeability of hydrogen and oxygen through the membrane. Even though perfluorosulfonic acid copolymer membranes are expensive, they are the standard by which other membrane candidates are judged. However, these polymers fail to operate at elevated temperature, which has triggered much research effort into finding alternative systems.¹⁷⁻²² Notably, aromatic hydrocarbon polymers have been recognized as one of the most promising candidates.

Methanol can also be used as a fuel and is currently the most attractive of the hydrocarbon fuels due to the relative ease of oxidation at the anode liberating protons and electrons. In particular, methanol fuel cell research has focused on the direct oxidation of liquid methanol from a methanol/water solution fed to the anode.¹³ The oxidation of methanol can be achieved with nanocrystalline platinum, but alloys of platinum and ruthenium are currently the catalysts of choice.²³ Methanol that is not oxidized at the anode can diffuse through the proton exchange membrane and react at the cathode. This problem is most often called “methanol crossover” and results in the removal of available catalytic sites from the oxygen reduction reaction, thus causing a mixed potential at the cathode. Diffusion of methanol through the membrane acts essentially as “chemical short circuits” in the fuel cell and lowers the open circuit voltage, the voltage efficiency of the cell, and the overall fuel efficiency of the system. Direct methanol fuel cells have not undergone as rapid a development as hydrogen fuel cells, largely because Nafion® membranes are very poor methanol barriers.^{24,25} Typically, a relatively thick Nafion® 117 (1100 equivalent weight, 180 μm thick) is used for direct methanol fuel cells. Any performance penalties associated with the increased resistance of a thicker membrane are more than offset by the complimentary

decrease in methanol crossover. Much fuel cell engineering has been done to reduce the methanol crossover in Nafion®-based direct methanol fuel cells, but the results are still insufficient in promoting direct methanol fuel cells for a wide-ranging commercialization. Consequently, methanol crossover is a central issue of much of the new membrane development in direct methanol fuel cell research. Also here, aromatic hydrocarbon polymers have proved to be suitable candidates.^{24,26-29}

2.3 The Membrane Electrode Assembly

Catalysts and membranes are parts of the basic unit of the fuel cell, the MEA. The MEA consists of two porous electrically and ionically conductive electrodes containing the platinum catalyst bonded to the PEM (see Figure 2). The electrodes can contain either unsupported (methanol fuel cells) or supported (hydrogen fuel cells) catalysts and are usually composed of the same polymer as the PEM.³⁰ The precious metal loading needed is determined by the amount of catalyst per active area and the ionomer content of the electrode can vary between 5-20 wt.%, depending on the application requirements.

Two basic methods commonly used for bonding the electrodes to the PEM involve making a catalyst “ink” composed of the ion conducting copolymer dispersed in a diluent (usually 5% polymer by weight), the catalyst particles, and any other additives to ease processing. In the first method, this ink is painted directly onto the membrane and dried to form the condensed catalyst layer or electrode. This method requires that the ink solution does not dissolve the membrane during painting, or otherwise compromise its integrity during the painting process. After painting, the MEA is ready to be placed into the fuel cell or processed further prior to fuel cell testing. In the second method, the catalyst ink is first painted and dried onto a decal or “blank” with the size of the desired active area. The painted and dried decal is then hot-pressed against the membrane at typically 150-200 °C and pressures of about 20 MPa, so as to bond the composite in the electrode to the membrane. If the correct

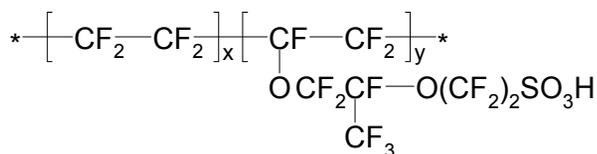
conditions and decal are chosen, the electrode will adhere well to the membrane and the decal can simply be peeled off.

Since the MEA is the heart of a fuel cell, considerable ongoing research is aimed at investigating its exact structure and component interactions.³⁰ The phenomena of “break in” and aging of the MEA structure are of major concern. Break in relates to the slow increase in performance observed over the first 24 h once a fresh MEA is placed in a fuel cell. Aging is the slow degradation of performance during long-term fuel cell operation. Researchers are investigating the electrode and membrane structure, and the interaction between the membrane and electrode for possible physical changes that may occur over time, in order to correlate these physical property changes with the fuel cell performance. In addition, much work has to be carried out for the development of fully integrated MEAs in which newly developed polymers are used both as a component of the porous electrodes and as the electrolyte.^{22,31} Indeed, in most cases these polymers are evaluated against Nafion® impregnated electrodes using slightly modified procedures to those used for the preparation of Nafion® based MEAs. However, the inherent incompatibility between perfluoropolymers and aromatic hydrocarbon polymers results in significant interfacial resistances, and often delamination. It is, therefore, difficult to efficiently evaluate new materials. New methodologies have to be developed in relation to a given new polymer membrane. This represents a crucial step for the successful replacement of Nafion® by aromatic polymer membranes.

2.4 Proton-Conducting Polymer Membranes

A membrane has been defined as “an interphase between two adjacent phases acting as a selective barrier, regulating the transport of substances between two compartments thanks to its unique separation principle, i.e. transport selectivity”.³² Polymer membranes find applications in several important industrial processes such as separation processes for liquid and gaseous mixtures, biomaterials, catalysis, lab-on-chip technologies and fuel cells.³²

Originally, the PEM used in the US space flight program was a sulfonated styrene-divinylbenzene copolymer. These membranes showed very short lifetimes due to oxidative degradation of the polymer backbone. In 1968, DuPont commercialized a PEM based on poly(perfluorosulfonic acid) under the trade name Nafion®.^{33,34} The perfluorinated structure shown in Scheme 1 displays a much greater stability in a fuel cell environment and thus increasingly longer fuel cell lifetimes.



Scheme 1. The chemical structure of Nafion® ($x = 6-10$, $y = 1$).

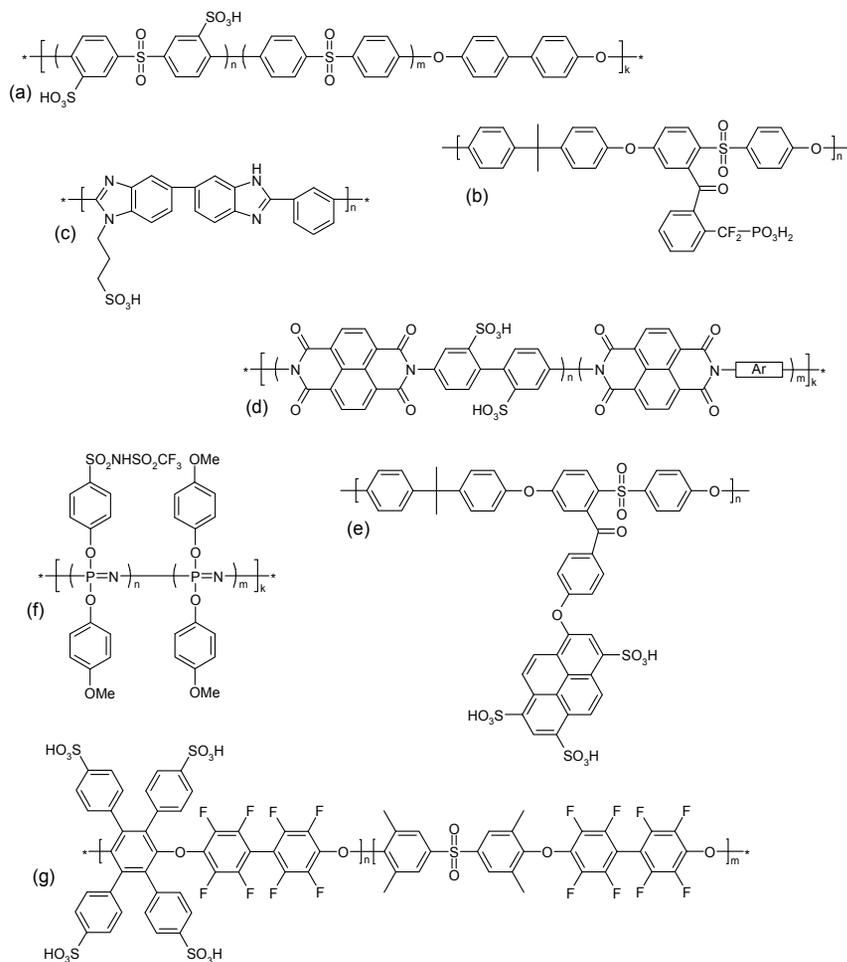
Since then other companies, such as Asahi, Dow and Solvay, have investigated membranes based on poly(perfluorosulfonic acid) structures, but Dow has stopped their activities and Asahi remains a small player. Nafion® has remained the industry standard proton exchange membrane and almost all current PEMFC research from a device standpoint focuses on this type of electrolyte. Major applications for Nafion® also include chlorine synthesis via electrolysis (chlor-alkali processes).³⁵

Moderate operating temperatures for Nafion®-based PEMFCs are required because of the need for aqueous proton transport and the perfluoropolymers used have relatively low T_g , especially when hydrated.³⁶ These systems are currently ongoing further developments in order to improve their characteristics.^{37,38} To increase the operating temperature of PEMFCs to 120 °C, membranes that retain water and conductivity and that are more thermally and mechanically robust at high temperatures, are needed. Another challenge is to produce inexpensive materials that meet the above requirements. Presently, some of the most promising candidates for PEMs are based on high performance aromatic polymers, i.e. polyimides, poly(ether ketone)s, poly(arylene ether sulfone)s, polybenzimidazoles, etc.^{18,19,27,39-41} Advantages of using

these materials include lower cost than perfluorinated membranes, inclusion of polar groups to improve water uptake over a range of temperatures, and the possibility of recycling by conventional methods. Many aromatic polymer systems have been investigated and it is beyond the scope of this introduction to provide a review covering the developments in this area. A number of reviews have recently been published which provide an in-depth information on the current research efforts throughout the world.^{17-20,22,27,39,42-44} Scheme 2 presents some examples of polymeric structures investigated as PEMs. Among others, the preparation of sulfonated poly(arylene ether sulfone)s,⁴⁵⁻⁴⁹ and sulfonated poly(arylene ether ketone)s by direct polymerization,⁵⁰⁻⁵² as well as the chemical modification of polysulfones,⁵³⁻⁵⁹ radiation grafting of polymer membranes,⁶⁰ blending and crosslinking of ionomer membranes,⁶¹ and the synthesis of sulfonated poly(arylene ether)s and polyimides,⁶²⁻⁶⁴ are actively studied.

The successful PEM has to combine a number of specific properties, including (i) low cost; (ii) good film-formation; (iii) high proton conductivity (preferably around or above 100 mS/cm), (iv) low electronic conductivity, (v) water retention above 100 °C; (vi) thermal, oxidative and hydrolytic stability; (vii) effective reactant barrier; (viii) possibility of fabrication into MEAs; and (ix) mechanical durability at elevated temperature (80 – 140 °C) for extended durations (typically around 5000 to 10000 h for automobiles).⁶⁵ Unfortunately, many of the desired properties are partly conflicting which further complicates the optimization of the membranes. Thus, the ionomer has to be a high-performing multifunctional material with carefully balanced properties optimized for a quite specific set of operational parameters.

A proton-conducting polymer membrane is typically a poor proton conductor unless water is present. Therefore the hydration of a PEM is very important for the performance of the fuel cell. The water sorption of PEMs has a profound effect on membrane conductivity and mechanical properties. Membranes with little water uptake typically have low proton conductivity, while the mechanical strength is compromised in membranes with too high water sorption.



Scheme 2. Examples of proton-conducting polymers designed for PEM materials: (a) sulfonated poly(arylene ether sulfone); (b) polysulfone carrying benzoyl(difluoromethylene-phosphonic acid) side chains (Paper V); (c) sulfopropylated PBI; (d) sulfonated naphthalenic polyimide (Ar, various aromatic moieties); (e) polysulfone carrying trisulfonated arylene ether side chains (Paper III); (f) poly(aryloxyphosphazene) having sulfonamide units; and (g) partially fluorinated and sulfonated poly(arylene ether sulfone) copolymer.

The water content in ionomers is represented by both the water uptake and the number of water molecules per acid unit, also referred to as the hydration number (λ). The water uptake is calculated by weighing the membrane under both hydrated and dry conditions (Equation 1), and λ can be calculated from the water uptake and the ion-exchange capacity (Equation 2).

$$\text{Equation 1.} \quad \text{Water Uptake (\%)} = [(W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}] \times 100$$

$$\text{Equation 2.} \quad \lambda = 1000 \times [(W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}] / (18 \times IEC)$$

The ion-exchange capacity, or *IEC*, is defined as the moles of exchangeable acidic protons per gram of dry polymer and the *IEC* of membranes can be experimentally determined by potentiometric titration of the acid groups. Another common term used to describe the ionic content is the equivalent weight, which is the inverse of the *IEC*. It is worth mentioning that a complication arises with phosphonic acid units because they carry two acidic protons. In general, only one acidic proton should be considered per phosphonic acid group since the second proton usually does not participate in the proton conduction due to its high pKa value. Yet, both protons might be consumed during the titration depending on the methodology used. In addition, when electron-withdrawing substituents are located in the α position to the phosphonic acid unit, the pKa value of the second proton might be decreased to such a level that both protons should be taken into account. Although there are many other properties of PEMs that have important correlations to fuel cell performance (thermal stability, methanol crossover, electroosmotic drag, etc.), the *IEC*, water uptake and proton conductivity are essential when it comes to evaluating membranes as candidates for PEMFCs.⁶⁶ In addition, the hydrolytic and oxidative stability is also of great importance.^{64,67}

Proton-conducting polymers typically phase separate upon hydration to form a morphology consisting of a percolating network of hydrophilic nano-metric pores

embedded in a hydrophobic polymer-rich phase domain, thus allowing the formation of a continuous pathway for proton conduction.²⁴ The pores contain water and the acid units, and conductivity occurs by transport of dissociated protons via the dynamics of the water, as described in more detail later. The hydrophobic phase domain stabilizes the morphology of the membrane by balancing the swelling pressure of the water against its mechanical strength. Important differences arise when considering perfluorinated polymers such as Nafion® and aromatic main-chain polymers. First of all, they differ in their values of pKa of the sulfonic acid units and also in their microstructures. Structural analyses suggest that the less pronounced hydrophobic/hydrophilic separation of sulfonated polyarylenes such as sulfonated polyetherketones corresponds to narrower, less connected hydrophilic channels and to larger separations between less acidic sulfonic acid units as compared to Nafion® (see Figure 3).²⁴ These morphological features have a profound impact on the macroscopic membrane properties. Large water domains result in a lower degree of water-polymer interaction and more 'bulk-like' water than smaller water domains within a similar chemical environment. The tortuosity (or continuity of the phases) is important for both transport properties and mechanical stability. Most importantly, interanionic distances are a contributing factor to water domain features and primarily affect the proton conductivity of the membrane. Indeed, the energy barriers associated with proton transport are dependant on the distance between anionic sites so that the greater the distance between the sites, the greater are the resistive losses associated with transport.⁶⁸ Notably, it was found that ionic aggregation and phase separation play an important role in the proton conductivity of low *IEC* membranes, but less of a role in high *IEC* membranes.^{69,70}

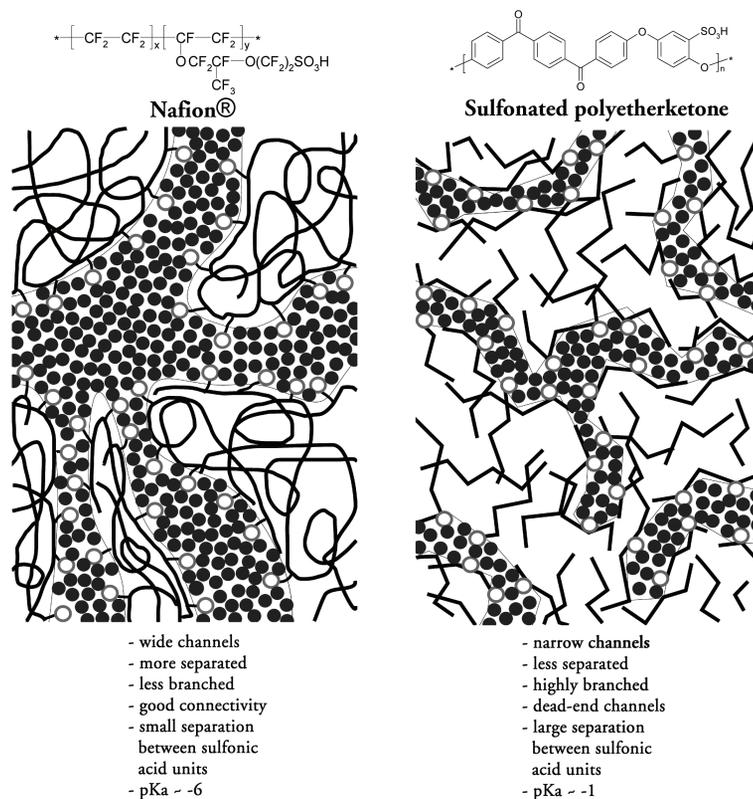


Figure 3. Schematic representations of the microstructures of Nafion® and a sulfonated polyetherketone (adapted from ref. 24). The serpentine black lines, the open circles and the black circles represent the polymer chains, the sulfonic acid units and water, respectively.

In PEMFCs the proton conductivity of the membrane is particularly important since it plays a significant role in the performance of the fuel cell. Higher levels of proton conductivity result in higher power densities. The proton conductivity of hydrated polymer electrolytes dramatically increases with temperature and water content; therefore, it is of importance to report the exact conditions under which the proton conductivity is measured. Currently, automotive companies are pushing for membranes capable of operating in a wide temperature window, typically from sub-

zero degrees up to approx. 120 °C, at low humidification with water vapour partial pressures below 0.5 bar, or with no humidification at all.⁶⁵

The proton conductivity of membranes can be measured by AC impedance spectroscopy. Under true fuel cell conditions, the protons move through the plane of the membrane. However, through-plane conductivity experiments are difficult to perform due to the significant interfacial resistances that may occur during testing. Conversely, it is generally easier to determine membrane conductivities by measuring the resistance in the plane of the membrane.⁷¹ This technique allows for higher and more easily measurable resistances and a simplified set-up. The proton conductivity, σ , is calculated from the impedance data using Equation 3 below. The minimum resistance is derived from the low intersect of the high frequency semicircle on a complex impedance plane with the $\text{Re}(z)$ axis. It is worth noting that two- and four-probe cells are commonly used to study the ionic conductivity of PEMs and that some level of discrepancy arises when comparing the results obtained by the two methods.⁷²

Equation 3. $\sigma = \rho^{-1} = L / (R \times W \times T)$

ρ = resistivity

L = length between electrodes

W = width of sample

T = thickness of sample

R = minimum resistance

The proton is the only ion without an electron shell of its own. Therefore, it interacts strongly with the electron density of its environment (e.g. the valence electron density of one or two nearest neighbours).⁷³ Proton conduction occurs via two main mechanisms in which the protons remain shielded by some electron density along the entire diffusion path.^{73,74} In other words, the existence of a free proton is not needed for the proton conduction to occur. In systems where proton conduction relies on the presence of water molecules, which is the case for the proton conducting

polymer membranes discussed in this thesis, proton migration occurs by the transitional dynamics of larger species referred to as the vehicle mechanism. The proton diffuses together with a vehicle (e.g. H_3O^+) where the counter diffusion of unprotonated vehicles (e.g. H_2O) allows a net proton transport (see Figure 4). Proton transport may also occur via the transfer of protons within hydrogen bonded species from one “carrier” to the other. Such proton hopping is usually termed the Grotthuss mechanism or structure diffusion,⁷⁵ and is responsible for the proton conducting character of anhydrous proton conductors such as imidazoles and benzimidazoles.^{59,76}

⁸² The study of the dynamics of the proton conduction is very complex due to the multi-scale hierarchical structure of ionomer membranes. It has to be investigated in a wide range of relevant correlation times, meaning that different experimental techniques such as quasi-elastic neutron scattering, field-cycling nuclear magnetic relaxation and pulsed field gradient NMR have to be used together with the modelling of proton transport.⁸³⁻⁸⁵

Many bulk properties of the polymer membrane are due to the ionic interactions in sub molecular regions of the polymeric material, and the macromolecular properties of the system are, thereby, critical characteristics.⁶⁶ The polymeric architectures can be different by the position, type and concentration of the ionic groups on the polymer backbone, therefore, producing a large amount of potential systems to study. It is worth noting that other factors such as the conditions used during membrane formation, and post-treatments such as acidification and humidity exposure also influence the nature of the network of nanopores, which in turn influence the macro-

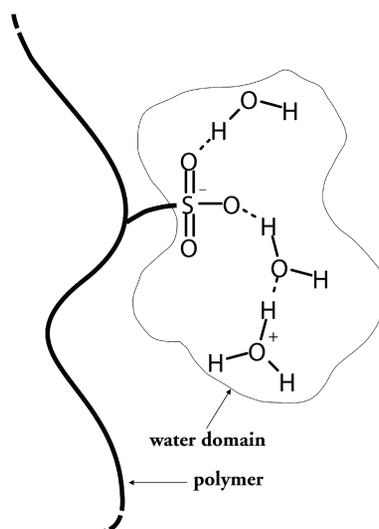


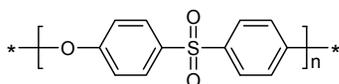
Figure 4. A graphic representation of proton transfer.

scopic membrane properties.^{86,87} Chemical grafting of commercially available polymers, such as polysulfones, gives a high degree of freedom to vary the polymeric structure, the acidic group and the *IEC* of the polymer electrolyte, thus providing membranes with different water domain sizes and shapes, interanionic distances, and tortuosities.⁸⁸ These differences in the structural features of the membranes dictate the proton conductivity, water transport properties, water uptake characteristics, and reactant permeabilities.^{66,89,90} Consequently, we decided to develop synthetic methods to prepare sulfonated and phosphonated polysulfones by chemical grafting using lithiation chemistry, with the goal to prepare and study the properties of durable proton-conducting polymer membranes for high temperature PEMFC applications.

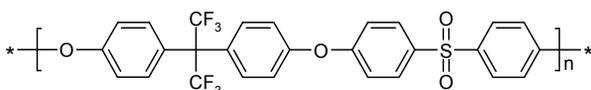
2.5 Chemical Modification of Polysulfones for the Preparation of Proton-Conducting Polymers

2.5.1 Characteristics of Polysulfones

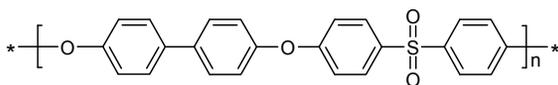
Poly(arylene ether sulfone)s comprise of a class of materials used as engineering thermoplastics because of their excellent properties, such as high T_g and superior thermooxidative stability.^{91,92} Synthetic routes to poly(arylene ether sulfone)s were discovered independently in three laboratories: the 3M Corporation, the Union Carbide Corporation, and the plastics division of ICI. Two main



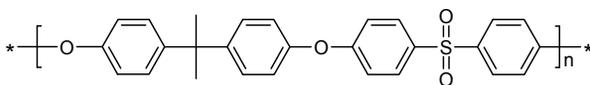
Polyethersulfone, PES



Polysulfone-6F



Polyphenylsulfone, PPSU



Polysulfone, PSU

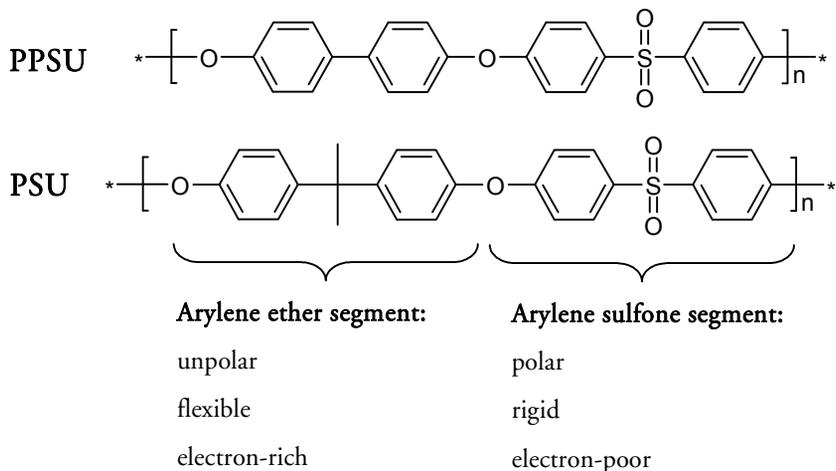
Scheme 3. Examples of poly(arylene ether sulfone)s.

routes have been reported, either a polysulfonation process, which is a classical electrophilic aromatic substitution, or a polyether synthesis, which is a nucleophilic substitution of activated aromatic dihalides. Examples of common poly(arylene ether sulfone)s are given in Scheme 3.

Poly(arylene ether sulfone)s are useful engineering plastics since processing is feasible in the melt and in solution, and since the polymers possess a high thermal stability. Even in air, slow degradation is only detectable at temperatures above 420–450°C. The incorporation of sulfone groups into the macromolecular chain often generates interesting properties, such as an increased T_g . Indeed, the T_g of a polymer depends on both chain rigidity and polarity. The polar arylene sulfone segment has an inherent chain rigidity, which arises from the phenyl groups, and from the presence of the inductive polar sulfone groups.⁹¹ The high polarity of the sulfone group leads to an electron-withdrawing effect, which delocalizes the π -electrons from the aromatic rings, producing some of a double-bond character in the neighbouring links. Such delocalization considerably enhances the rotational barrier around the C-S link and consequently the chain rigidity. A T_g of 272.5 °C was obtained by extrapolation to infinite number-average molecular mass for PES as suggested by the Flory-Fox theory.⁹³ This value is in good agreement with the T_g of 269.5°C obtained using Carlier *et al.*'s concept of the percentage of rigid chain length.⁹³ In contrast, the ether links have a comparatively low rotational barrier. This provides flexibility to the arylene ether segments. In addition, the unpolar 2-propylidene link of PSU also contributes to the overall chain flexibility.

In poly(arylene ether sulfone)s, the valence angle for C-SO₂-C is 105° and for C-O-C it is 124°.⁹¹ This substantial difference in the inter-ring bond angles reduces the packing density of the unit cell. This corresponds to a substantial decrease in the melting enthalpy and in T_m . As a result, the ($T_m - T_g$) interval is quite narrow for poly(arylene ether sulfone)s, and the crystallization is, in most cases, inhibited. Devaux and Carlier have observed that a percentage of rigid chain length greater than 60 is necessary to obtain crystallizable poly(arylene ether sulfone)s.⁹¹ Consequently

most poly(arylene ether sulfone)s are amorphous materials in spite of exhibiting a symmetrical chain structure. In contrast, poly(arylene ether ketone)s are generally semicrystalline.⁹¹



Scheme 4. Molecular characteristics of the PSU and PPSU main chains.

PSU and PPSU are both commercially available from Solvay Advanced Polymers under the trade marks Udel® and Radel-R®, respectively. They are completely amorphous and have T_g s at 190 and 208 °C, respectively, and decomposition temperatures at 500 and 540 °C, respectively, under inert atmosphere. These two polymers are interesting for the preparation of PEMs by chemical modification because they can be dissolved in common organic solvents. The inherent chemical stability of PSU and PPSU, from now on referred to by the generic term polysulfones, implies that only a few options are available for efficient chemical modification. Nevertheless, the chemical structure of the polysulfone backbone is such that two dissimilar repeating segments may be distinguished depending on the chemical reactivity (see Scheme 4). The ether groups, as well as, the 2-isopropylidene group, are electron-donors to the neighbouring phenylene rings. In contrast, the electron-withdrawing effect of the sulfone groups in the polysulfones is strong enough to give an acidic character to the *ortho*-to-sulfone hydrogens. Consequently, polysulfones may be modified

by electrophilic substitution reactions, which include nitration, chloromethylation, halogenation, and sulfonation, or by the use of lithiation reactions. The latter reactions, originally described by Beihoffer *et al.*⁹⁴, and further developed by Guiver *et al.*⁹⁵, offer the possibility of modifying the molecular structure of the polymer with a high degree of freedom.

2.5.2 Direct sulfonation of polysulfones

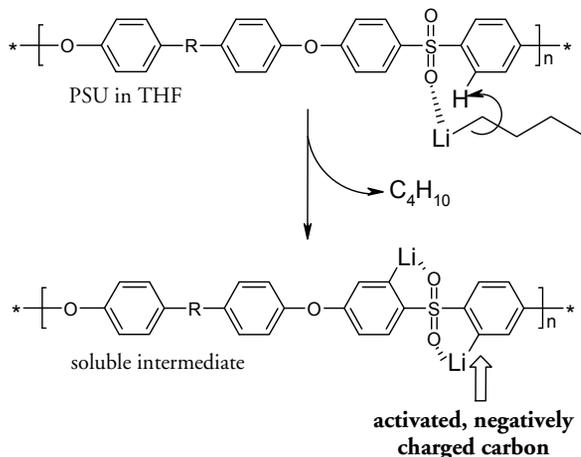
The perhaps most simple and widely used method to prepare sulfonated polysulfones concerns the direct sulfonation of the main chain using chlorosulfonic acid or fuming sulphuric acid in chlorinated solvents.⁹⁶ Since this is an electrophilic substitution reaction, positions *ortho* to the ether groups are favoured. As mentioned earlier, these positions are electrophilically activated by the oxygen atoms giving an electron-rich character to the arylene ether segments, which in turn make them the most favourable sites for substitution. However, because the sulfonation reaction is a reversible reaction, the ease of sulfonation also implies that these positions are activated for desulfonation under acidic aqueous conditions.⁹⁷ This might prove detrimental for the successful use of such polymers in PEMFCs. Of particular concern to the polymer chemists are the harsh conditions needed for the sulfonation of the polymer main chain, which can lead to partial cleavage of the polymeric main chain. Another complication is that directly sulfonated polymers characteristically exhibit extensive swelling and lose their mechanical stability when a certain critical degree of sulfonation, or temperature, is exceeded under immersed conditions. For example, directly sulfonated polysulfones with a degree of sulfonation of 80% have been found to be water-soluble at room temperature, therefore limiting the *IEC* of the polymers that can be used as membranes in fuel cells.⁹⁸

2.5.3 Lithiation of polysulfones

In 1986, Beihoffer *et al.* demonstrated for the first time the feasibility of lithiating PSU.⁹⁴ In their study, PSU was metalated and carboxylated by a reaction with *n*-

butyllithium (*n*-BuLi, 1.6 M in hexanes) and carbon dioxide at room temperature in dry tetrahydrofuran (THF). After acidification with HCl the product was recovered via precipitation in water. It was reported that the lithiated PSU precipitated from the reaction mixture at relatively low levels of metallation, and that an uneven carboxylation occurred. No indication regarding the sites of the substitution was reported at that point. It was not until 1988, based on reports by Guiver *et al.*, that the mechanism of the lithiation of polysulfones was understood.⁹⁹ In addition, the lithiation of polysulfones proved to be a fast and selective way of modifying the main chain. In their study, Guiver *et al.* reacted lithiated PSU with D₂O and iodomethane in order to identify the reactive sites on the PSU backbone by analyzing the resulting polymers using ¹H NMR spectroscopy. In contrast to the methodology used by Beihoffer *et al.*, the lithiation reaction was carried out at low temperature, typically at -78 °C in THF using a 2-propanol / dry-ice bath. Guiver *et al.* indicated that the temperature had to be maintained in the temperature range -10 °C to -78 °C. Higher temperatures resulted in the precipitation of the polymer caused by intramolecular rearrangements. The formation of lithiated polysulfone was observed by the appearance of a greenish brown to reddish brown viscous solution. Analyses by ¹H NMR spectroscopy indicated that the reaction proceeded rapidly and homogeneously in high yields and required little or no excess of reagent or catalyst. In addition, the site of lithiation was at the *ortho*-to-sulfone position and the degree of lithiation (*DL*), i.e. the number of metalated carbons per repeating unit of the polysulfone, could be conveniently controlled by the amount of *n*-BuLi added to the reaction mixture up to a *DL* = 2.

The direct lithiation of polysulfones using organolithium reagents such as *n*-BuLi is possible due to the strong *ortho*-directing power of the sulfone groups. As mentioned above, the electron-withdrawing power of the sulfone group gives an acidic character to the *ortho*-tosulfone hydrogens allowing their replacement using strong



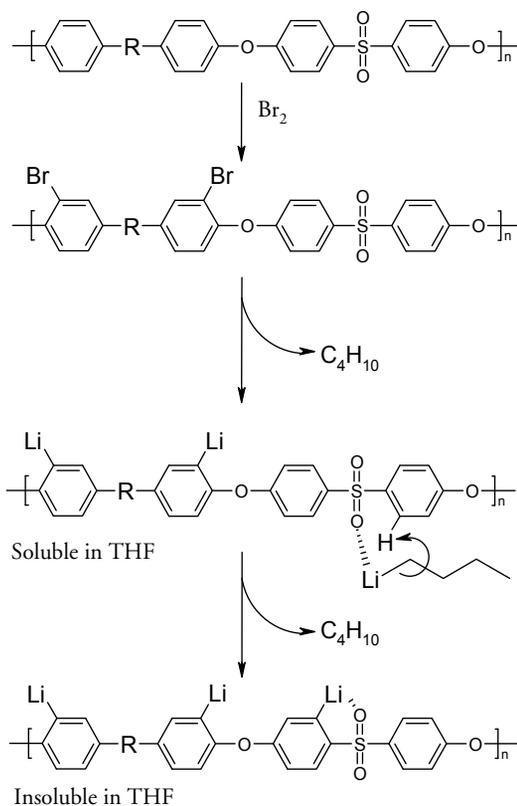
Scheme 5. Direct lithiation of the polysulfone main chain using *n*-butyllithium.

organic bases. In addition, the lone electron pairs of the sulfone groups stabilize the lithium cations in the form of complexes (see Scheme 5). These two effects activate exclusively the positions *ortho* to the sulfone linkage for substitution via direct lithiation. In another contribution, Guiver *et al.* reported that lithiated sites *ortho*-to-ether could be accessed via a two-step bromination-lithiation reaction.¹⁰⁰ Bromination of polysulfones occurs readily in the presence of elemental bromine without the presence of a catalyst. The reactive substitution positions are located *ortho*-to-ether as for the direct sulfonation reactions. Since the metal-halogen exchange was the dominant reaction over the acid-base reaction, *ortho*-to-ether positions could be selectively metalated. Notably, *DL* values up to three can be obtained since *ortho*-to-sulfone positions may be lithiated when all the bromine atoms had been consumed (see Scheme 6). Because of its high solubility in THF, high concentration of PSU in THF may be used for lithiation reactions. However, one must consider that highly viscous solutions are obtained, especially at high levels of *DL*. This means that the electrophilic reagent should react readily with lithiated PSU without the occurrence of side reactions that may lead to crosslinking. PPSU, on the other hand, has a limited solubility in THF.

Consequently, lower concentrations should be used. Notably, the solubility of PPSU in THF increases when the temperature of the solution is lowered.

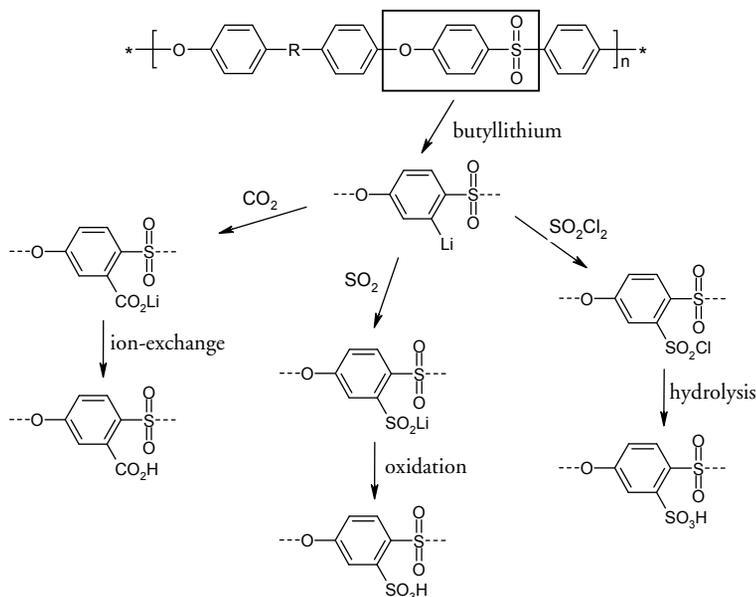
The great advantage of using lithiation chemistry is that, after lithiation, the polysulfone main chain is activated for reactions with numerous different electrophilic reagents, of which many are commercially available.^{88,95} Negatively charged carbon atoms on the polysulfone main chain react with electrophilic carbons or heteroatom centres, either by addition reactions (e.g. with CO_2 , SO_2) or by replacement of a leaving group (e.g. with activated halogenated compounds, esters). Complex functional groups

may be introduced by a judicious choice of the electrophile. When the electrophile has the potential for inducing crosslinks, it has to be added rapidly in excess at an optimum temperature and under the appropriate conditions in order to efficiently quench the reactive carbanions. Factors such as the rate of addition, temperature, crosslinking potential, viscosity and mixing of the reagents are of particular importance. It is worth noting that polymer membranes may be lithiated heterogeneously.¹⁰¹ Guiver *et al.* found that the optimum conditions for membrane functionalization were 0.2 M *n*-butyllithium in hexane at room temperature and that the reaction rate



Scheme 6. Bromination and lithiation of the polysulfone main chain.

increased substantially in the presence of 2% THF.¹⁰¹ The surface-lithiated membranes can be derivatized, potentially with a wide variety of functional groups.



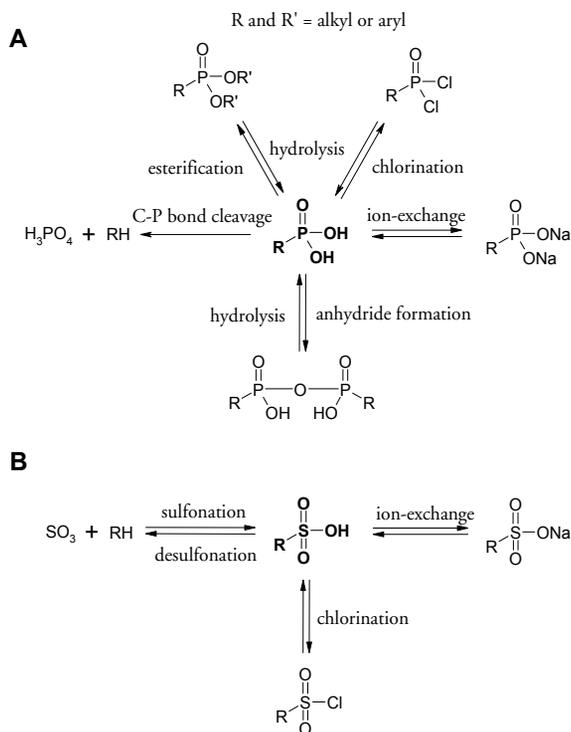
Scheme 7. Carboxylation and sulfonation of polysulfones using lithiation chemistry.

The lithiation of polysulfones gives possibilities to prepare sulfonated polysulfones in which the sulfonic acid units are located on the electron-poor segments of the backbone in contrast to the direct sulfonation method discussed above (see Scheme 7). As a result, the former units are expected to be less prone to desulfonation. In particular, Kerres *et al.* have prepared sulfonated PSU by first reacting the lithiated polymer with sulphur dioxide to produce sulfinated PSU. In a second step, the sulfinate groups were oxidized to sulfonate groups by the use of various oxidizing agents including H₂O₂, NaOCl, and KMNO₄. Ionomers with *IEC* values between 0.5 and 3.2 meq/g were obtained and an ionomer having 2.4 meq of SO₃H/g dry sample was found to be water soluble.¹⁰² Karlsson *et al.* extended the use of the sulfinated PSU intermediate to prepare ionomers where the sulfonic acid groups are placed on

alkyl spacers of different lengths.⁵⁴ Sulfinated PSU was grafted with sulfoethyl and sulfopropyl units by reaction with an excess of the sodium salts of 2-bromoethyl sulfonate and 3-bromopropyl sulfonate, respectively, in *N*-methyl pyrrolidinone at 40 °C. Correspondingly, sulfobutylated PSU was prepared by reaction of sulfinated PSU with 1,4-butane sultone.

2.6 Phosphonated Polymers for Fuel Cell Applications

The search for alternative proton-conducting membranes capable of operating at high temperatures has widened the focus of the research area, and increased the interest of investigating alternative acidic or “protogenic” groups which have the ability to facilitate proton conductivity under low-humidity conditions.^{21,103,104} These groups include for example the phosphonic acid and various heterocycles such as imidazole and benzimidazole, and are perhaps best described as amphoteric. Thus, polymers carrying these groups have quite different properties than sulfonated polymers. For example, phosphonated polymers generally show a higher degree of hydrogen bonding and lower water uptake than their sulfonated analogues at comparable *IECs*. Moreover, phosphonated model compounds have recently been shown to possess an attractive combination of properties that further motivates investigations of phosphonated polymers as proton conductors under low-humidity conditions.²¹ However, the area of phosphonated membranes for fuel cells is still an emerging field. Since this is a relatively new topic, some key characteristics of the phosphonic acid unit as compared to the sulfonic acid unit have to be underlined. The reader is referred to Paper VI, in this thesis, for in-depth information regarding phosphonic acid units and the prospects of phosphonated polymers for fuel cell applications.



Scheme 8. A comparison of important transformations of phosphonic acid units (A) and sulfonic acid units (B).

When it comes to the preparation of novel ionomers for fuel cells, one major difference between polymers based on phosphonic acid units and conventional sulfonated polymers is the important chemical transformations that the former acidic units may undergo (see Scheme 8). Phosphonic acids possess two ionizable acid moieties. For aryl- and alkylphosphonic acid the pKa values are typically between 2-3 and 7-8 for the first and second protons, respectively (see Table 2). The first acidic moiety has an ionization potential intermediate to those of sulfonic and carboxylic acids. Because of the intermediate acid strength of the first acid moiety and

the higher IEC of the phosphonic acid, as compared to sulfonic and carboxylic acids at the same acid concentration, many of the properties of ionomers based on phosphonic acid may be found intermediate to the properties of sulfonated and carboxylated ionomers or, perhaps, even comparable to sulfonated ionomers.

As outlined in Scheme 8, one characteristic of the phosphonic acid unit is that it may be obtained by the hydrolysis of the corresponding phosphonate ester. The synthesis of phosphonate esters is often the only route to polymers functionalized with phosphonic acid units. It is therefore of importance to find suitable chemical reactions for the conversion of phosphonate esters into their acidic form. Figure 5 presents different possibilities found in the literature. The use of trimethylchlorosilane is

particularly advantageous for polyfunctional molecules as it reacts with phosphonate ester units under mild conditions, therefore avoiding side-reactions and allowing for a selective conversion into phosphonic acid units.

Table 2. Acid dissociation constants in water for selected acidic compounds.

Acid	pKa ₁	pKa ₂
CF ₃ P(O)(OH) ₂	1.2	3.9
C ₆ H ₅ CH ₂ P(O)(OH) ₂	2.3	7.6
CH ₃ P(O)(OH) ₂	2.4	7.5
(HO) ₂ (O)PCH ₂ P(O)(OH) ₂	<2 and 2.6	6.9 and 10.3
C ₆ H ₅ P(O)(OH) ₂	1.8	7.1
C ₆ H ₅ SO ₃ H	<1	-

The published data on fuel cell membranes based on phosphonated polymers is still very limited. However, a careful examination of the results obtained up until now indicates that these membranes may potentially show some advantages over sulfonated polymer membranes. This is perhaps particularly true when it comes to operation under low humidity conditions at high temperatures. At high water contents, the protons may be transported through the dynamics of the water, much in the same way as in conventional membranes based on sulfonated polymers. In addition, because of the amphoteric nature of the phosphonic group, there seems to be a possibility of transporting protons through structure diffusion within the hydrogen bonded phosphonic acid networks at low water contents. Moreover, phosphonated polymers generally show a higher hydrolytic and thermal stability than sulfonated polymers due to the strength of the C-P bond.

A survey of the literature indicates that phosphonation of polymers is in general more difficult than the corresponding sulfonation. The difference is perhaps most striking when it comes to attaching acid groups on aromatic rings. In addition, the water uptake of phosphonated polymer membranes is generally much more moderate

than for corresponding sulfonated polymer membranes. In this respect, most of the polymers studied up until now tend to have an insufficient degree of phosphonation for use as fuel cell membranes. An alternative way to increase the water uptake may be to enhance the acidity by attaching the phosphonic acid via $\text{CF}_2\text{-P}$ bonds. This will obviously change the acid-base character in relation to phosphonic acid units attached through aromatic or alkyl C-P bonds.

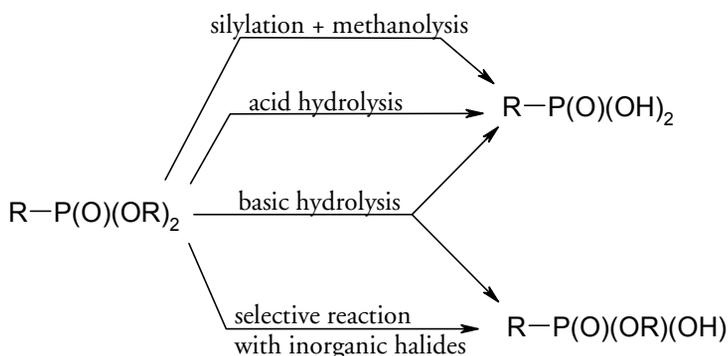


Figure 5. Schematic representations of various pathways yielding monoacid monoester phosphonate and/or phosphonic acid groups from phosphonate esters.

CHAPTER 3

THESIS WORK

In order to study structure-property relationships, we have first investigated new methods to prepare durable proton-conducting polymers functionalized with sulfonic acid groups placed on aromatic side chains of varying lengths and character, and studied their properties as PEMs (Papers I to III). As mentioned already in the introduction, placing the sulfonic acid units away from the hydrophobic polymer main chain may prevent excessive water uptake and the loss of the mechanical integrity of the polymer membrane when a certain degree of sulfonation or a certain temperature is exceeded, as in the case of directly sulfonated PSU. In addition, minimizing the local inter-acid distance might also prove beneficial to promoting a distinctly phase separated morphology. Finally, phosphonated polymers may potentially exhibit interesting properties as PEMs, especially for high temperature operation. Therefore, we have investigated new synthetic pathways to phosphonated polysulfones. Our first attempt has consisted in attaching phosphonic acid units directly onto the polymer main chain (Paper IV). Then, PSUs tethered with phosphonic acid units with increased acidity located on aromatic side chains to the polymer main chain were prepared and studied (Paper V). Figure 6 represents a graphic overview of the research work introduced above.

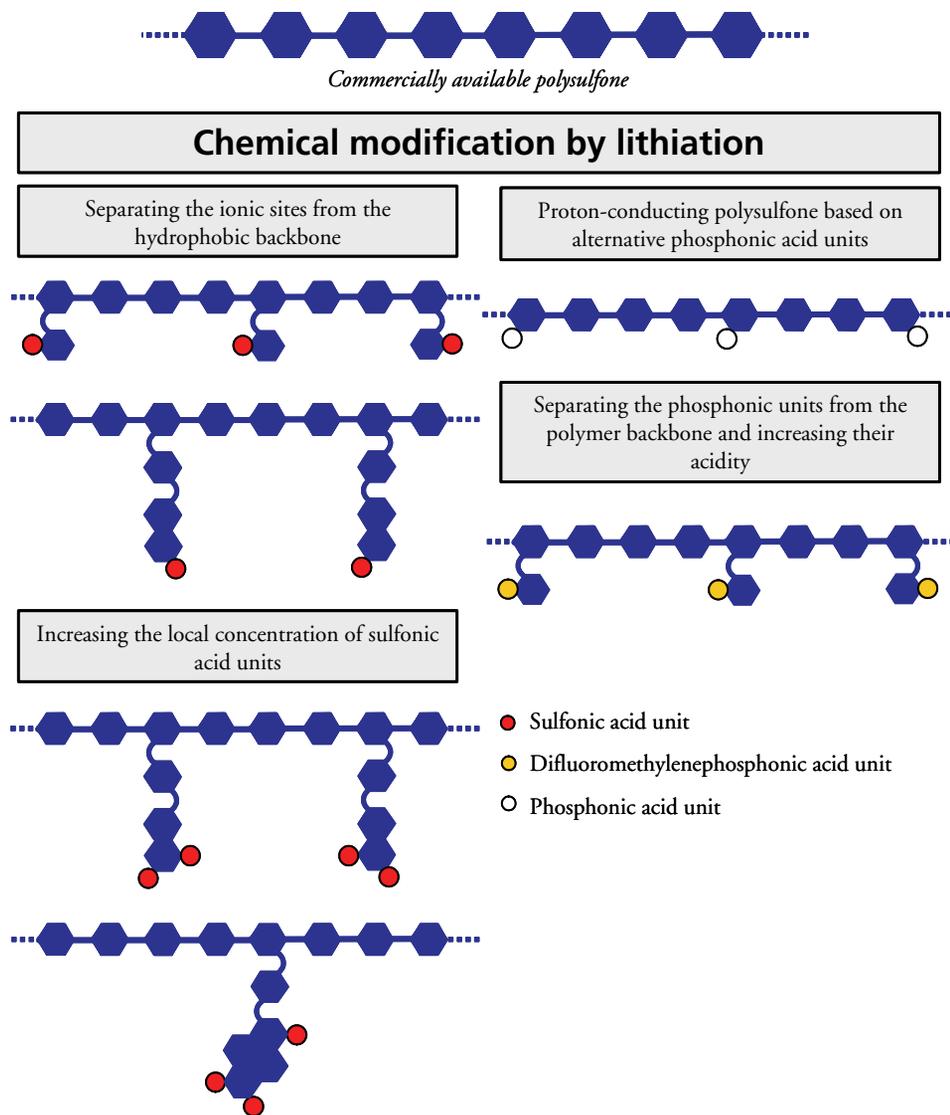
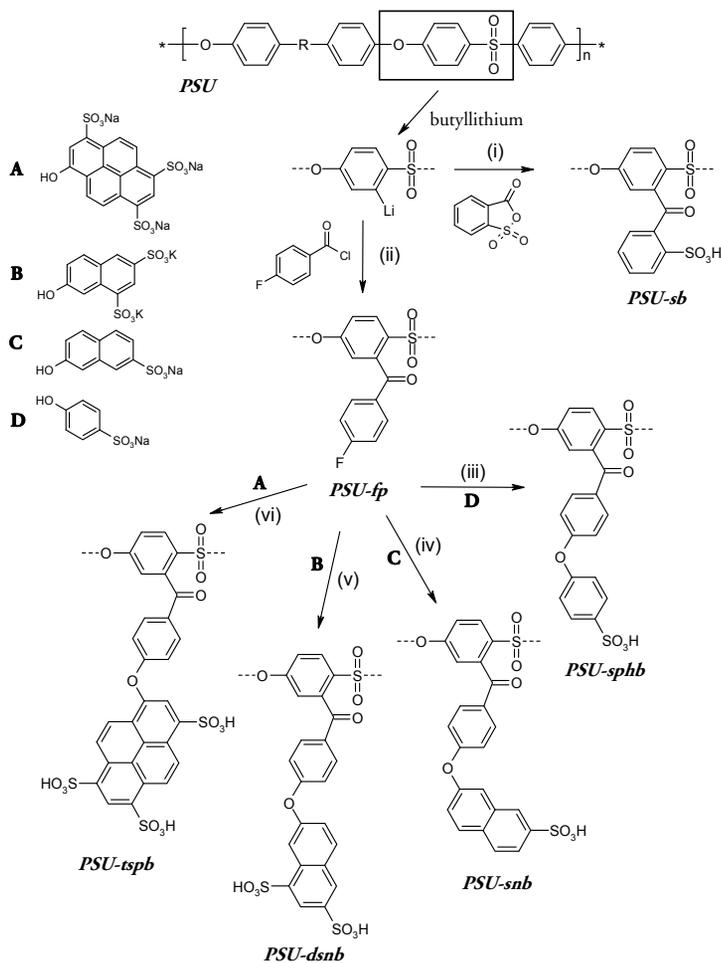


Figure 6. A graphic representation of the synthetic approaches to new ionomer membrane materials employed in the present doctoral thesis.

3.1 Polysulfones Carrying Sulfonated Aromatic Side Chains (Papers I-III)

3.1.1 Preparation

The different sulfonated polymer structures covered by this thesis project are shown in Scheme 9.



Scheme 9. Synthetic pathways to polysulfones carrying sulfonated aromatic side chains.

In the initial effort to separate the acid unit from the backbone polymer, polysulfones carrying short aromatic sulfonated side chains were conveniently synthesized via a one-pot synthesis. Lithiated PSU was left to react with 2-sulfobenzoyl acid cyclic anhydride at low temperature for approx. 45 min before quenching and precipitation in 2-propanol [pathway (i) in Scheme 9]. 2-Sulfobenzoyl acid cyclic anhydride is a commercially available and relatively inexpensive mixed cyclic anhydride containing a carboxylic acid and a sulfonic acid part. Upon reaction between the negatively charged carbon atoms of the lithiated PSU and the electrophilic C=O groups, arylsulfonate groups tethered to the PSU main chain via ketone links were

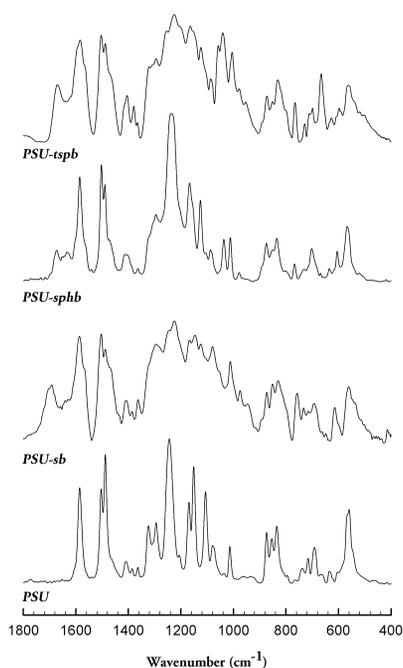


Figure 7. FTIR spectra of pristine PSU, sulfobenzoyl PSU, sulfophenoxybenzoyl PSU and PSU tethered with trisulfopyrenoxybenzoyl side chains.

obtained in one step. The grafting of the sulfobenzoyl side chains to PSU was confirmed by FTIR and ^{13}C NMR spectroscopy. For instance, a vibrational band at 1675 cm^{-1} arising from the carbonyl stretch of the side chains was observed in the spectrum of sulfobenzoyl PSU, referred to as PSU-sb (see Figure 7) and its intensity increased with the degree of substitution (DS). As the reaction proceeded, the polymers precipitated from the THF solution due to the formation of the ionic groups. This implied that an efficient stirring must be kept to limit the precipitation to only small particles. Both PSU and PPSU can be tethered with sulfobenzoyl side chains, as reported by Karlsson *et al.*⁵⁵ A maximum of 0.9 sulfobenzoyl side chains per repeating polymer unit was obtained, implying that ionomers with IEC up to approx. 1.5 meq/g can be prepared. Careful

purification of the solvent and reactants afforded a good control on the *DS* of the final polymers by the *DL* selected.

In order to extend the length of the aromatic side chains, and to vary their nature, lithiation chemistry was used to prepare fluorinated precursor polymers with grafting possibilities. PSUs with pendant reactive fluorinated aromatic groups (PSU-*fp*) were conveniently prepared by reaction between lithiated PSU and 4-fluorobenzoic acid chloride as presented in Scheme 9 – pathway (ii). This was achieved using a one-pot synthesis employing *n*-butyllithium as a metalating agent in THF at -78 °C. No crosslinking reactions were observed and fluorinated PSUs with *DS* up to 1 were conveniently prepared. The presence of the fluorine atoms was readily confirmed using ^{13}C NMR spectroscopy (see Figure 8). Shifts arising from the carbon atom carrying the fluorine substituent were found in the form of a doublet at δ 164.7 and δ 167.3 ppm. The signal at δ 193.6 ppm was attributed to the carbonyl carbon atom of the ketone link. Carter has shown that it is possible to evaluate the reactivity of fluorinated monomers towards aromatic nucleophilic substitution reaction by ^{13}C and ^{19}F NMR spectroscopy.¹⁰⁵ The ^{13}C and ^{19}F NMR chemical shifts were found to be equal to δ 166 ppm and δ -104.5 ppm, respectively, for the fluoro groups in PSU-*fp*. By comparing these values to those tabulated by

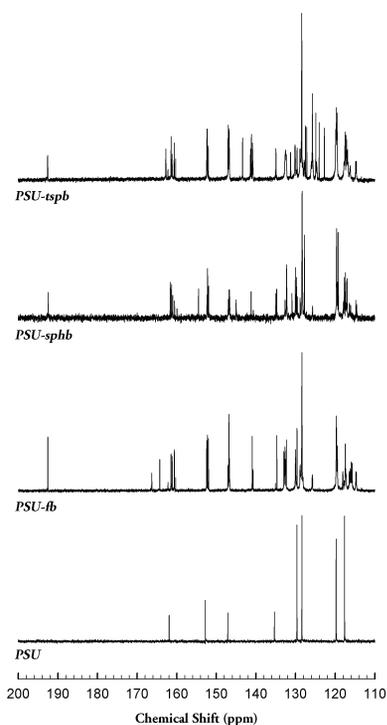


Figure 8. ^{13}C NMR spectra of pristine PSU, fluorobenzoyl PSU (*fp*), sulfophenoxybenzoyl PSU (*sphb*) and PSU tethered with trisulfonyloxybenzoyl PSU (*tspb*).

Carter, it was found that the reactivity of the precursor polymer was in the range of the highly reactive 4,4'-difluorodiphenyl sulfone monomer and superior to the difluorodiphenyl ketone monomer. This finding indicated that the carbonyl groups linked to the electron-poor diaryl sulfone segments of the PSU main chain had an electron-withdrawing power in the order of a sulfone group, and superior to a ketone group.

We first investigated the synthesis of sulfophenoxy- and sulfonaphthoxybenzoyl PSUs, referred to as PSU-sphb and PSU-snb, respectively, via such a route [pathways (iii) and (iv) in Scheme 9]. These reactions were typically carried out in *N,N*-dimethylacetamide (DMAc) under reflux using a methodology commonly employed in the polycondensation reactions of polysulfones. This reaction proceeded under full conversion and the *IEC* was easily controlled by the *DL* in the first step. The grafting of the sulfophenolate and sulfonaphtholate groups was confirmed by the complete disappearance of the peak arising from the fluorinated carbon atoms in the ^{13}C NMR spectra (see Figure 8), and by the presence of a strong absorption band at 1036 cm^{-1} in the FTIR spectra accounting for the S-O stretching of the sulfonated side chains (see Figure 7). One limitation arose from the fact that a maximum of one side chain per repeating polymer unit could be obtained, thereby limiting the *IEC* of the resulting ionomers to approx. 1.4 meq/g.

One way to increase the *IEC* of the ionomers consists of selecting reactants that carry more than one sulfonic acid units. This was done by selecting 2-naphthol-6,8-disulfonate and 8-hydroxy-1,3,6-pyrenetrisulfonate salts to carry out the syntheses in pathways (v) and (vi), respectively, in Scheme 9. The resulting side chains were defined as *hypersulfonated* since two sulfonic acid units were concentrated on one aromatic ring. Initial attempts to employ the same reaction conditions as in the study presented above proved unsuccessful because of the limited solubility of the highly charged salts in DMAc. After studying solvents with higher dielectric constants capable of solvating the salts, the reactions were successfully carried out in dimethylsulfoxide (DMSO). The temperature was kept quite low at $90\text{ }^{\circ}\text{C}$ to suppress chain-

breaking transesterification reactions which are detrimental to the molecular weight. The decreased reactivity at the low temperature was at least partly compensated for by the highly activated fluorine atoms during the reactions. After careful purification, the sulfonated polymers were characterized by ^1H NMR, ^{13}C NMR and FTIR spectroscopy. Figure 8 shows a representative ^{13}C NMR spectrum of trisulfopyrenoxybenzoyl PSU (PSU-tspb), along with a spectrum of a precursor polymer (PSU-fp). As seen, signals originating from the fluorinated carbons were completely absent in the former spectrum, indicating that all the fluorine atoms had been displaced during the reactions. In addition, characteristic peaks arising from sulfonated carbon atoms were clearly identified. Chemical shifts at δ 143.4, δ 141.1, and δ 140.9 ppm for the PSU-tspb samples. FTIR spectroscopy further confirmed the successful substitution of the fluorine atoms by sulfonated aryl ether groups. Characteristic absorption bands of the symmetric S=O stretching of the sulfonate groups were found at 1056-1042 cm^{-1} for the PSU-tspb samples (see Figure 7). The conversion of the substitution reaction was calculated from ^1H NMR data by comparing the integral of the signals originating specifically from the di- or trisulfonated groups, respectively, with the integral of the isopropylidene group of the polymer main chain at δ 1.67 ppm. It was found that the conversions were in the range of 60-75%, indicating that a substantial reactivity was retained at 90 °C. Notably, conversions of approx. 70-75% were obtained with the disulfonated reactant. The fact that the reactions were not driven to full conversions may be partly explained by the slow removal of water during the reaction at low temperature. Nucleophilic hydroxide anions, formed under the basic conditions, may have partly displaced the fluorine atoms. Such side reactions may thus explain the incomplete conversions while the C-F groups were completely consumed.

3.1.2 Properties

Membranes were prepared by a solvent-casting methodology. Typically 5-10% solutions of the polymers in polar aprotic solvents, such as DMSO or DMAc, were used to prepare 100 μm -thick membranes by evaporation of the solvent. Membranes

based on PSU-sph and PSU-sphb were successfully prepared from DMAc solutions at 60 °C. Notably, it was not possible to obtain mechanically strong membranes from PSU-snb. This might be a consequence of the occurrence of chain-breaking transesterification reactions that lowered the molecular weight, coupled with a decrease of the chain flexibility of the sulfonaphthoxy derivatives in comparison with the sulfophenoxy derivatives. Due to their poor solubility in DMAc, membranes based on disulfonaphthoxy- and trisulfonypyrenoxybenzoyl PSU were cast from DMSO solutions at 100 °C to obtain membranes. All the polymers were cast in the salt form before being ion-exchanged to the protonated form by immersion in an aqueous 1M HCl solution for 24 h. The *IEC* of each polymer membrane was evaluated by acid-base titration.

The thermal stability of the PEMFC membranes is a key property that indicates the durability under fuel cell operation. The latter was investigated by thermogravimetric analysis (TGA) by heating the membranes in their protonated form at 1 °C/min under air or at 10 °C/min under N₂. The temperature at which the membranes based on PSU-tspb retained 95 wt% of their initial weight decreased gradually from 284 °C to 203 °C, in air, as the *IEC* of the membranes based on the polymers with trisulfonated aromatic side chains increased from 0.87 to 2.28 meq/g. Furthermore, it was found that at a given *IEC* the polymer membranes containing disulfonated aryl side chains had a somewhat higher thermal stability than the membranes containing trisulfonated aryl side chains. This was in line with the results obtained from the TGA measurements under N₂. Indeed, onsets of degradation were recorded in the temperature ranges 233-280 °C and 260-420 °C, under N₂, for PSU-tspb and PSU-dsnb, respectively. PSU-sphb typically degraded around 285 °C and PSU-sph at temperatures >300 °C, indicating that increasing the length of the aromatic side chains leads to a slight decrease of the thermal stability of the polymer. Nonetheless, these onsets of degradation are in the range of other sulfonated non-fluorinated polymer membranes that typically degrade at around 250 °C due to the loss of –SO₃H groups.²⁷

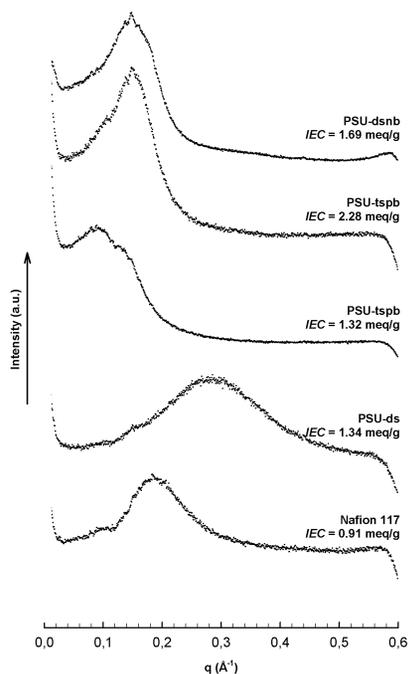


Figure 9. SAXS data recorded using polymer membranes stained by ion-exchange with lead acetate.

The morphological features of the membranes based on PSU-dnsb and PSU-tspb were studied by small-angle X-ray scattering (SAXS) on lead-ion exchanged membranes to enhance the contrast by selectively staining the ionic domains. The SAXS profiles of three different membranes based on the polymers with hypersulfonated side chains are shown in Figure 9. The SAXS profiles of Nafion® 117 and a conventionally sulfonated PSU (PSU-ds, $IEC = 1.34$ meq/g) with the acid units attached directly onto the polymer main chain were also studied for comparison. The synthesis of the latter polymer has been described elsewhere.¹⁰² In general, the characteristic separation lengths between the ion-rich domains and the hydrophobic polymer-rich domains in ionomers can be observed in terms of the values of q corresponding to the so-called ionomer peak. As seen in Figure 9 the ionomer peak of the conventionally sulfonated polymer membrane was broader and shifted towards higher q value, as compared to the profile of the Nafion® membrane. This indicated a smaller characteristic separation length with a wider distribution in the former membrane. By comparing the SAXS traces of membrane PSU-ds and the membranes based on the polymers with hypersulfonated side chains, it is clear that the latter polymers showed larger characteristic separation lengths, indicating the formation of larger ionic clusters. Moreover, the relatively narrow peak profiles of membranes based on the side-chain sulfonated PSUs suggested that the ionic clusters were quite uniform in size. In addition, it was found that the

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polymers with higher ionic side-chain concentrations gave membranes with smaller distance between the ionic domains. Finally, the similarities of the SAXS traces of membranes PSU-tspb, PSU-dsnb and Nafion® 117 indicated that a high local concentration of sulfonic acid groups, and their separation from the polymer main chain, promoted a high degree of phase segregation. This finding is of interest because it shows that distinctly phase separated systems may be obtained also with sulfonated hydrocarbon polymer systems with a proper molecular design.

The water uptake of sulfonated polymer membranes has a profound effect on membrane conductivity and mechanical properties. Membranes with a low water uptake typically have low proton conductivity, while the mechanical strength is compromised in membranes with high water uptake. As mentioned in the introduction, placing the sulfonic acid units away from the hydrophobic polymer main chain may prevent excessive water uptake and the loss of the mechanical integrity of the polymer membrane when a certain degree of sulfonation or a certain temperature is exceeded.

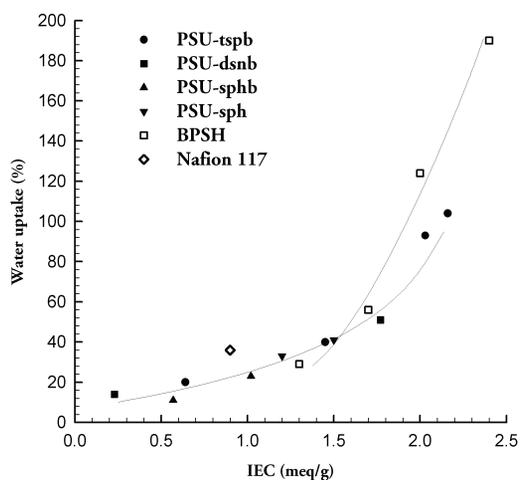


Figure 10. Water uptake of polymer membranes measured at room temperature as function of the IEC value.

It was found that membranes based on PSU-sph retained a nearly constant level of water uptake at temperatures up to 120 °C.⁵⁵ Figure 10 presents the water uptakes at room temperature of the different polymer membranes prepared in Papers I-III, together with those of membranes based on Nafion® 117 and sulfonated poly(arylene ether sulfone) random copolymers (referred to as BPSH), prepared by McGrath *et al.*⁴⁶ In the latter copolymers, the sulfonic acid units were located directly

onto to the polymer main chain. It is clear that placing the sulfonic acid units on side chains to the polymer main chain is advantageous for retaining reasonable levels of water uptake, especially at high *IEC* values. The segregation between the hydrophobic polymer main chain and the hydrophilic hypersulfonated side chains appears to provide the morphology needed to balance the swelling pressure.

Table 2. Selected membrane properties. The values regarding BPSH and PSU-sph were taken from ref. 66 and 55, respectively.

Membrane	IEC (meq/g)	$w^{[a]}$ (%)	λ	$\sigma^{[b]}$ (S/cm)
Nafion® 117	0.9	36	22	0.058
BPSH30	1.3	29	12	0.050
BPSH50	2.0	124	34	0.111
PSU-sph	1.2	33	15	0.026 ^[c]
PSU-sph	1.5	41	15	0.024 ^[c]
PSU-sphb	0.6	11	11	0.011
PSU-sphb	1.0	23	12	0.320
PSU-dsnb	0.2	14	15	0.003
PSU-dsnb	1.8	51	16	0.086
PSU-tspb	0.6	20	16	0.020
PSU-tspb	2.0	93	26	0.095

[a] Water uptake in liquid water at room temperature.

[b] Proton conductivity measured under immersed conditions at room temperature.

[c] Proton conductivity measured under 100% relative humidity at room temperature.

The number of water molecules per sulfonic acid units, λ , in the membrane is an important parameter. As seen in Table 2, the λ values of PSU-tspb increase when the *IEC* increases. Such behaviour is commonly observed in membranes based on sulfonated aromatic polymers like the BPSH copolymers,⁶⁶ and indicates the formation of wider water-filled nanopores as the *IEC* increases. On the other hand, it was found that λ remained seemingly constant with the *IEC* in the case of the membranes based on PSU-dsnb and PSU-sph. Holdcroft *et al.* showed that such a difference is indicative of random and more organized systems, respectively.¹⁰⁶ In other words, retaining low λ values at high *IEC* is a result of the formation of a more effi-

cient channel network that is not necessarily coupled to the formation of wider water-filled channels. The results obtained by SAXS indicated that the cluster formation in membranes based on PSU-tspb and PSU-dsnb was rather similar. The fact that PSU-dsnb was able to form a more efficient and organized percolating network upon hydration as compared to PSU-tspb is most likely a consequence of the greater mobility of the disulfonaphthoxybenzoyl side chains as compared to the trisulfopyrenoxybenzoyl side chains. The former side chains are, thereby, able to reorient more efficiently upon hydration.

Figure 11 shows the proton conductivity at different temperatures measured under immersed conditions in a sealed cell. All the sulfonated side-chain polymers exhibited an Arrhenius-like behaviour and similar activation energies were found for

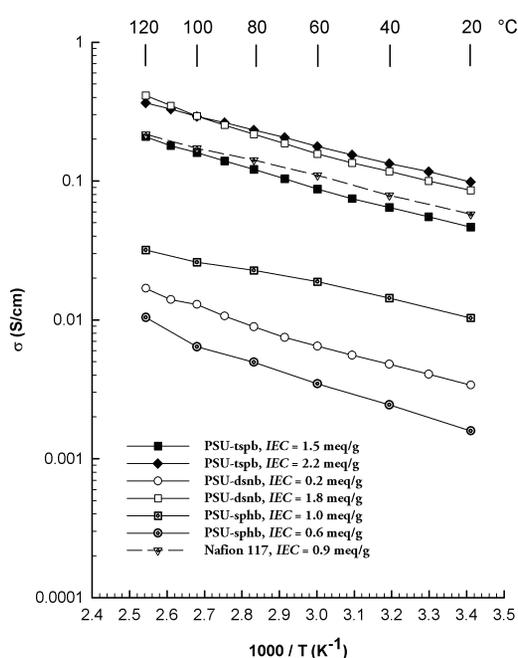


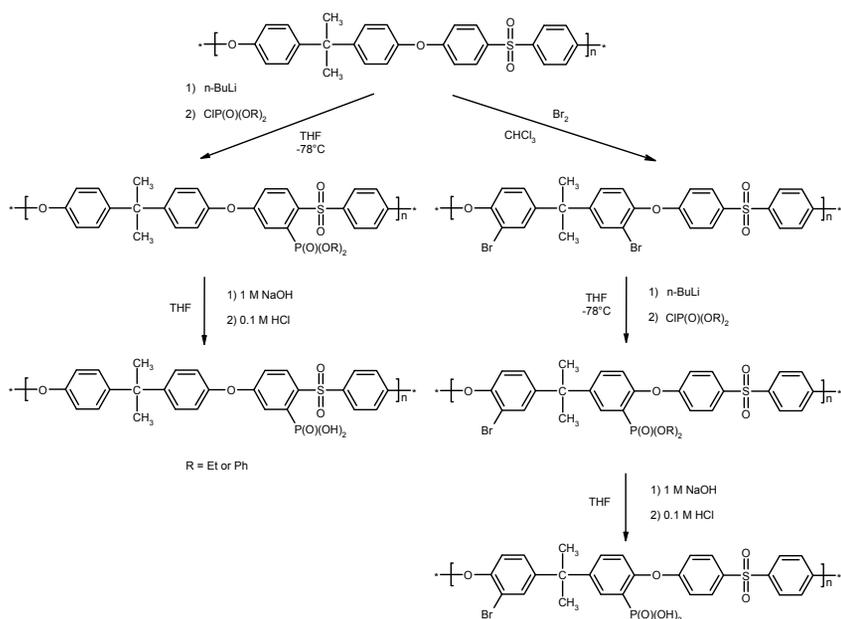
Figure 11. Arrhenius plots of proton conductivity data measured by electrochemical impedance spectroscopy with membranes immersed in water.

Nafion® 117. In particular, conductivities up to 0.4 S/cm at 120 °C were measured for membranes based on PSU-dsnb 2 and conductivities well above Nafion® 117 were obtained for the membranes PSU-dsnb 2, PSU-tspb 3 and PSU-tspb 4. In addition, membranes based on PSU-tspb 2, having a moderate IEC of 1.45 meq/g, reached a level of conductivity in range of Nafion® 117. All the conductivities recorded on membranes based PSUs carrying hypersulfonated side chains were in the range to those obtained by McGrath et al. on the BPSH membranes.⁴⁶ It is worth noting that the conductivity

of PSU-dsnb with an $IEC = 0.2$ meq/g is higher than the conductivity of PSU-sphb with an $IEC = 0.6$ meq/g. This is most likely a result of the efficient ionic cluster formation in membranes based on PSU tethered with hypersulfonated side chains that results in a reasonable water uptake and the formation of a relatively efficient percolating network even at low IEC .

3.2 Polysulfones With Phosphonic Acid Units Grafted on the Main Chain (Paper IV)

We investigated the feasibility of employing an $S_NP(V)$ reaction between lithiated polysulfones and either diethylchlorophosphate or diphenylchlorophosphate. $S_NP(V)$ reactions are nucleophilic attacks at a relatively electropositive quinquivalent phosphorus centre by an anionic specie with the displacement of a good or moderately good leaving unit. Scheme 10 presents the chemical pathways used in that study.



Scheme 10. The phosphonation of PSU via lithiation and reaction with chlorophosphonic acid esters.

The different reaction parameters such as the reaction temperature and time, the excess of electrophile and rate of addition, etc. are, in this case, of particular importance since the electrophile has a potential for crosslinking via the displacement of phenoxy or ethoxy units. Allcock *et al.* reported that a large excess (approx. 200%) of chlorophosphonic acid ester was required in order to suppress crosslinking reactions in polyphosphazenes.¹⁰⁷ A systematic study of the reaction was carried out to identify the experimental conditions favouring this carbanionic displacement reaction.

FTIR and NMR spectroscopy were used to characterize the synthesized polymers synthesized. Typical FTIR spectra of phosphonated PSU (PSU-p) in the ester and the acid forms are shown in Figure 12 (b) and (c), respectively. Characteristic bands at 1184 cm^{-1} and at 933–943 cm^{-1} in Figure 12 (b) were assigned to (P)-O-C stretching and to P-O-(C) vibrations, respectively. These observations indicated the successful grafting of diphenyl phosphonate ester units onto PSU. A qualitative characterization with FTIR spectroscopy was carried out through the normalization of each spectrum to the band originating from the asymmetrical stretching of the main-chain ether linkages at 1014 cm^{-1} in order to assess the degree of substitution (*DS*) obtained after each reaction. The quantitative assessment of *DS* was carried out by ^1H NMR spectroscopy. The actual attachment on the main chain was confirmed by ^{31}P NMR

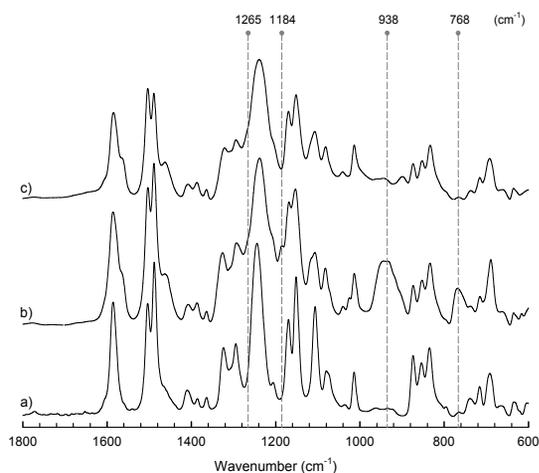


Figure 12. FTIR spectra of a) pristine PSU, b) PSU tethered with diphenylphosphonate ester units, and c) PSU tethered with phosphonic acid units.

characterization with FTIR spectroscopy was carried out through the normalization of each spectrum to the band originating from the asymmetrical stretching of the main-chain ether linkages at 1014 cm^{-1} in order to assess the degree of substitution (*DS*) obtained after each reaction. The quantitative assessment of *DS* was carried out by ^1H NMR spectroscopy. The actual attachment on the main chain was confirmed by ^{31}P NMR

spectroscopy through a chemical shift found at δ 6.18 ppm for the phosphorus atom after reaction (see Figure 13).

It was found that the overall conversion of the lithiated sites was limited to 40% at $DL < 1$. Regardless of the reaction conditions, all attempts to introduce two lithiated sites per repeating unit led to crosslinking after addition of diphenyl or diethyl chlorophosphate. The temperature had to be kept at -70°C in order to avoid the reaction of unreacted lithiated sites with already grafted phosphonate units. The limited reactivity of *ortho*-to-sulfone lithiated sites with chlorophosphonic acid ester can partially be explained by sterical hindrance and the electron-withdrawing power of the sulfone group which may to some extent deactivate the lithiated sites. In an attempt to increase the reactivity of these sites, the PSU main chain was brominated and selectively lithiated by transmetalation with *n*-BuLi to achieve activated *ortho*-to-ether lithiated sites as described in the introduction. In this way, the degree of phosphonation was slightly enhanced to reach 50%. Notably, FTIR, ^1H and ^{31}P NMR (see Figure 13) spectroscopy confirmed that a complete conversion of diphenyl ester to phosphonic acid occurred during basic hydrolysis, although such hydrolysis procedure normally yields the monoacid/monoester. Phosphonation of PSUs via an $\text{S}_\text{N}\text{P}(\text{V})$ reaction provides a non-catalytic reaction that is quite simple to accomplish, although its ef-

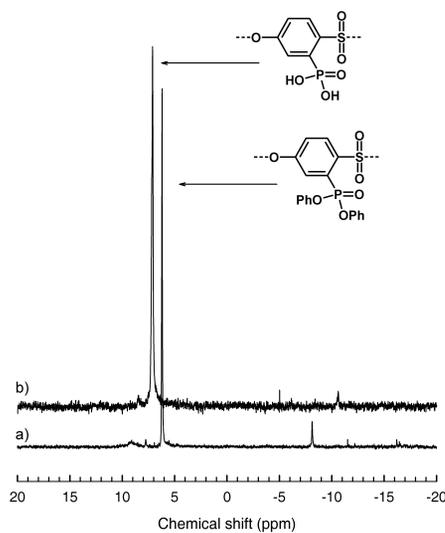


Figure 13. ^{31}P NMR spectra of a) PSU tethered with diphenylphosphonate ester units and b) PSU tethered with phosphonic acid units.

efficiency for converting lithiated sites to phosphonate units is limited. PSUs with degrees of phosphonation up to 0.4-0.5 and the phosphonic acid placed either on the bisphenol-A or the biphenyl sulfone segments were, however, conveniently synthesized.

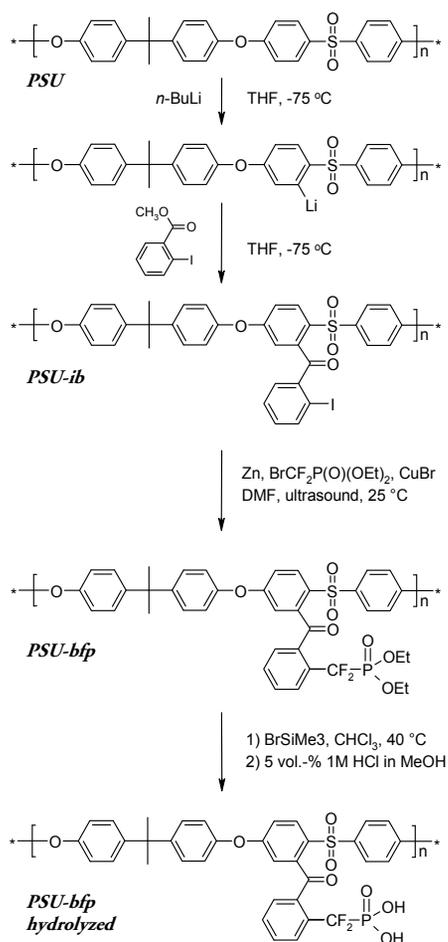
Thermogravimetric analysis showed that an initial small loss of mass occurred between 200 and 320 °C for phosphonated PSUs where the phosphonic acid was located *ortho*-to-ether and *ortho*-to-sulfone. This initial weight loss was attributed to the formation of anhydrides by the creation of P-O-P linkages, as shown in Scheme 8. The main decomposition step of PSU with *ortho*-to-ether phosphonic acid units occurred above 350 °C, while PSU with phosphonic acid units *ortho*-to-sulfone started above 375 °C. This may be explained by both the slightly lower value of *DS* of the latter sample and by the stabilization effect originating from the localization of the acidic units on electron-poor segments of the PSU main chain.

Finally, the phosphonated polymers possessed a good membrane-forming property. However, the low level of *IEC* of the polymer membranes obtained in this study did not lead to water uptake levels sufficient enough to promote proton conduction. An original approach was attempted in which the phosphonated polymer was used as a component, together with phosphoric acid and *m*-sulfophenylphosphonic acid, in the preparation of precursor solutions of hybrid polymer membranes using the procedure developed by Alberti *et al.*^{108,109} Such a methodology may provide a system in which the polymer contributes to the mechanical integrity of the membrane while the inorganic layer provides the proton conduction. Notably, upon casting of the precursor solutions, totally transparent and strong membranes were obtained at levels up to 50 wt.% of inorganic filler. The incorporation of the phosphonated polymer within the organically modified zirconium phosphate layer was confirmed by immersing the membranes in DMAc which is a solvent for the polymer. Interestingly, the membranes retained their integrity and were insoluble even after 48h of stirring. These preliminary results may serve as a basis for a more detailed and thorough study on new hybrid polymer membranes for fuel cells.

3.3 Polysulfones Carrying Highly Acidic Phosphonated Aromatic Side Chains (Paper V)

One conclusion from the study presented in Section 3.2 is that the water uptake of the phosphonated ionomers is much lower than that of the corresponding sulfonated ionomers. One way to increase the water uptake of the former ionomers is to enhance the acidity of the phosphonic acid in order to favour the formation of a morphology of a percolating network of water-filled hydrophilic nanopores embedded in a hydrophobic polymer-rich phase domain. Consequently, we prepared and investigated novel PSUs carrying benzoyl(difluoromethylene-phosphonic acid) side chains (PSU-bfp) via the preparation of iodinated PSUs (PSU-ib) which served as precursors for the preparation of the phosphonated polymers (see Scheme 11).

The iodinated polymers were characterized by ^1H and ^{13}C NMR and FTIR spectroscopy. The ^{13}C NMR spectra of PSU-ib and pristine PSU are presented in Figure 14. As expected, several new peaks were present in the spectrum of PSU-ib, including the peak at δ 193.1 ppm. This is typically the chemical shift at which carbonyl groups belonging to benzoyl side-chains at-



Scheme 11. Synthetic pathway to *o*-benzoyl(difluoromethylene-phosphonic acid) PSU.

tached *ortho* to the sulfone groups of the PSU main chain resonate. The presence of the aryl iodide group was also confirmed by a peak at δ 94.1 ppm, which is characteristic of iodinated aromatic carbons. A maximum of approx. 0.6 *o*-iodobenzoyl side chains per repeating unit of the PSU was reached. The limited reactivity might be a consequence of the steric effects induced by the bulkiness of the iodine atom located *ortho* to the reactive carbonyl group. Indeed, when methyl 4-iodobenzoate was used for the preparation of iodobenzoyl PSU, a value of *DS* of nearly 0.9 was obtained.

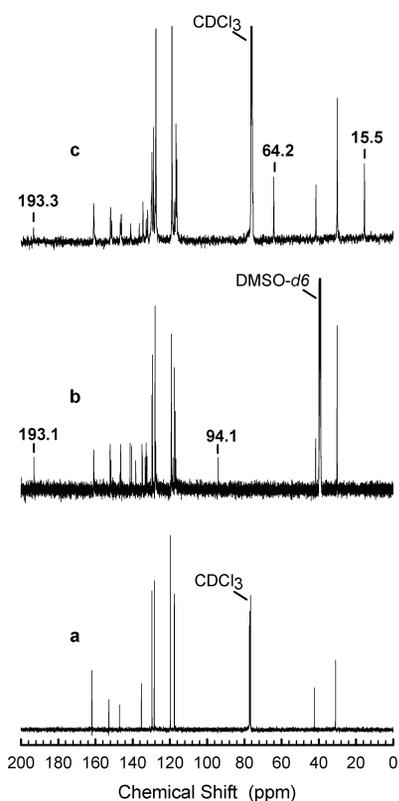


Figure 14. ^{13}C NMR spectra of (a) prisine PSU, (b) PSU-ib, and (c) PSU-bfp in the ester form.

In the present study, we used an efficient and low-cost CuBr-mediated cross-coupling reaction of [(diethoxyphosphinyl)difluoromethyl] zinc bromide with iodoaryl initially developed by Yokomatsu *et al.* for the preparation of aryl-(difluoromethylenephosphonate)s.¹¹⁰ The iodobenzoyl PSUs were left to react for 24 h under ultrasonic treatment with a two-fold excess of [(diethoxyphosphinyl)-difluoromethyl]zinc bromide created *in situ* by the transmetalation of the corresponding Grignard reagent with a stoichiometric amount of CuBr. Analysis of the ^{13}C NMR spectrum of PSU-bfp confirmed the complete replacement of the iodine atoms by $-\text{CF}_2\text{-P}(\text{O})(\text{OEt})_2$ units since no peaks were found at δ 94.1 ppm in the spectra of the phosphonated polymers [see Figure 14 (c)]. Instead, two new peaks were present at δ 64.2 and

δ 15.5 ppm and were attributed to the signals arising from the ethoxy groups of the diethyl phosphonate ester units. The phosphonation reaction proceeded with an excellent yield of approximately 90% when *o*-iodobenzoyl PSU was used. However, in the case of *p*-iodobenzoyl PSU the yield decreased to 48%.

The complete hydrolysis of PSU-bfp was achieved by reaction of the phosphonated polymers with BrSiMe_3 at 40 °C for 24 h. ^{31}P NMR spectroscopy confirmed the successful hydrolysis (see Figure 15). The phosphorus atom of the diethyl phosphonate ester unit resonated at δ 6.47 ppm in a triplet as a result of the coupling with CF_2 . After hydrolysis, only a single triplet was visible at δ 3.92 ppm, accounting for the phosphonic acid units.

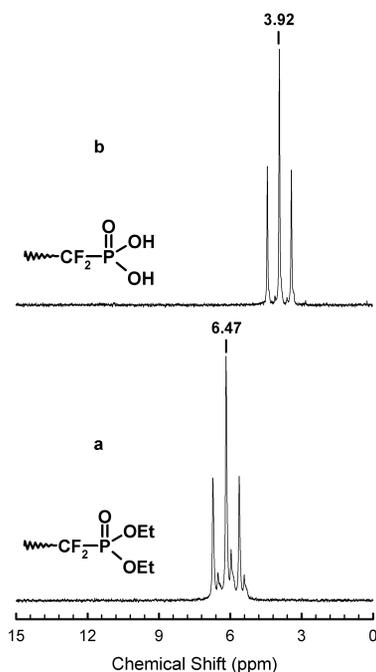


Figure 15. ^{31}P NMR spectra of PSU-bfp in (a) ester and (b) acid forms.

It was found that the thermal decomposition of the phosphonated polymers in their ester form proceeded via two distinctive degradation steps. The weight loss connected with the first degradation step, which occurred between 200 and 320 °C, corresponded to the weight of all the $-\text{CF}_2\text{P}(\text{O})(\text{OEt})_2$ units. The thermal decomposition of the samples in the acid form also proceeded in two steps, which is typical of polymers containing phosphonic acid. In this case, the first weight loss started at $T_d \sim 230$ °C and corresponded to the weight of all the phosphonic acid units. As described in Paper VI, alkyl-P bonds are usually weakened by the presence of electron-withdrawing units, whereas aryl-P bonds are weakened by electron-donating units. This

might explain the lower thermal stability of the phosphonic acid unit in the present case because of the strong electron-withdrawing character of the CF_2 group. Still, despite the detrimental effects of the aryl- CF_2 -P configuration on the stability, the thermal stability remained reasonably high and T_g s above 220 °C were recorded.

Membranes with an IEC of 1.79 meq/g took up 6 wt.% of water per g of dry polymer at room temperature. As a basis for comparison, a phosphonated poly(arylene ether) synthesized by Meng *et al.*, with 1.93 mmol of phosphonic acid units per g of dry polymer, took up 7.5 wt.% water when immersed in hot water.¹¹¹ In addition, membranes based on the phosphonated PSU described in Section 3.2 and with 0.84 mmol of phosphonic acid unit per g of dry polymer took up less than 2 wt.% at room temperature. It is likely that the increase of the acidity of the phosphonic acid unit acts in two ways. First, because the protons are more dissociated, there is an increase in the entropy gain resulting from the solvation of these protons

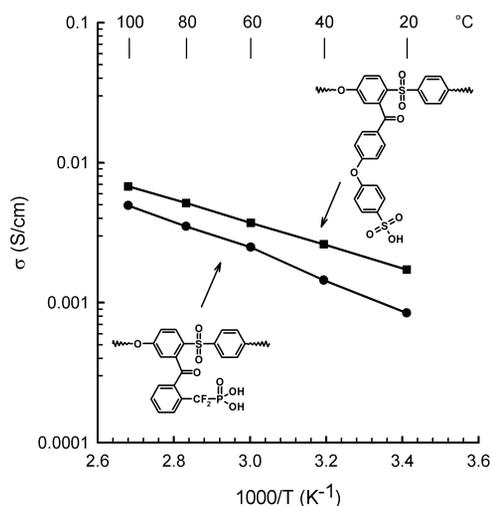


Figure 16. Arrhenius conductivity plots of membranes based on PSU-bfp and PSU-sphb with 0.9 acidic units per g of dry polymer.

by water molecules. In addition, the increased acidity depresses the amphoteric character of the phosphonic acid units which reduces the self-hydrogen bonding between these units. Consequently, they become more available for hydrogen bonding with water.

Reasonable levels of proton conductivity up to 5×10^{-3} S/cm at 100 °C were repeatedly measured for membranes with 0.90 mmol of phosphonic acid unit per g of dry polymer. Interestingly, as shown in Figure 16, such a level of conductivity is in the range of conductivity of membranes

based on sulfophenoxybenzoyl PSU with approximately the same content of acid units per g of dry polymer, i.e., 0.86 mmol of sulfonic acid unit per g of dry polymer. The slightly lower level of conductivity of the phosphonated polymer membranes may be explained by the lower water uptake of these membranes as compared to the sulfonated polymer membranes; 6 wt.% of water at room temperature versus 11 wt.% for the sulfonated polymer membranes.

CHAPTER 4

SUMMARY & OUTLOOK

New pathways to phosphonated and sulfonated polysulfones have been established by new lithiation-grafting techniques. Such a methodology afforded polymers with pendant phosphonic acid units, or pendant phosphonated or sulfonated aromatic side chains. In particular, polysulfones carrying short aromatic sulfonated side chains were conveniently synthesized via a one-pot synthesis. Access to longer side chains was possible thanks to the preparation of a precursor polymer tethered with highly reactive fluorobenzoyl side chains that were activated for nucleophilic aromatic substitution reactions. Consequently, by a careful choice of reactants and reaction conditions, polysulfones carrying hypersulfonated aromatic side chains were synthesized and studied. In general, it was difficult to obtain more than one side chain per repeating unit of the polysulfone due to problems of reactivity connected with sterical hindrance and side reactions. Finally, phosphonated polysulfones were also successfully prepared via either $S_NP(V)$ reactions between lithiated polysulfones and chlorophosphonic acid esters or via a two step reaction involving the preparation of polysulfones tethered with iodobenzoyl side chains. The iodine atoms were then replaced by $-CF_2-PO_3H_2$ units via a CuBr-crosscoupling reaction.

It was found that membranes with controlled water uptake were obtained by attaching the sulfonic acid unit to short and stiff aromatic side chains, demonstrating that by placing the cohesion of the hydrophobic main-chain polymer phase was retained despite the formation of a highly water-swollen phase. Placing the sulfonic acid units on side chains proved particularly advantageous to retain reasonable water uptakes at high *IECs*. Of particular interest, membranes based on a polysulfone main chain carrying disulfonated naphthoxybenzoyl side chains exhibited a distinct phase separation and formed a well-defined and efficient network of water-filled nanopores.

This afforded excellent proton conductivity at controlled levels of water uptake in contrast to conventional sulfonated aromatic polymers. In addition, it was found that a certain level of flexibility of the side chains is necessary for the formation of an efficient percolating network. Increasing the local concentration of sulfonic acid units as well as separating the hydrophilic moieties from the hydrophobic polymer main chain enabled the stabilization of the morphology of the water-swollen membranes and a promotion of the proton conduction.

The investigation of alternative acidic moieties is also of great interest as desulfonation may become a critical issue at high temperatures. However, the acidity of phosphonic acid directly attached to aromatic rings was found to be too low to result in reasonable levels of water uptake. An original approach was therefore developed in which PSU with pendant iodinated benzoyl side chains were prepared using lithiation chemistry. The latter polymer was then further modified to yield the more acidic $-\text{CF}_2\text{PO}_3\text{H}_2$ units located on aromatic side chains. Membranes based on ionomers with 0.90 mmol of phosphonic acid units/g of dry polymer took up 6 wt.% water when immersed at room temperature, and levels of conductivity comparable to those reached by a membrane based on a sulfonated polysulfone with 0.86 mmol of sulfonic acid per g of dry polymer were recorded, indicating that phosphonated polymers may be used in the context of water-assisted proton-conducting polymer membrane systems.

This work may efficiently serve as a basis for new projects as many aspects need to be investigated further. First, it would be interesting to devote a study to the direct comparison of the different sulfonated side chain polysulfones in order to elucidate the exact morphological features of these membranes, especially in the swollen state. High local concentrations of sulfonic acid units might also prove to be beneficial for the preparation of composite polymer membranes based on zirconium phosphate using the precipitation methodology. Indeed, the high conductivity of the neat polymer membrane implies that suitable stabilizing inorganic fillers may be added without suffering from detrimental performance losses. Furthermore, the phospho-

nated polymers have shown promise as PEMs and the chemical modification approach has proven to be an efficient route to phosphonated polymers with various architectures. Of particular interest, phosphonated polymers may be included into the formation of zirconium phosphate layers. Consequently, hybrid polymer membranes in which the polymer main chain is covalently linked to the inorganic filler may be formed. Such an approach should be investigated further as it may provide highly stable morphologies resulting in PEMs capable of operating efficiently at elevated temperatures. Finally, membranes based on polysulfones tethered with disulfonaphthoxybenzoyl side chains appeared to combine a unique set of properties that make them interesting for testing in PEMFC and DMFC environments.

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