Doctoral Thesis

Structure-Property Correlations in Radiation-Grafted Fuel Cell Membranes Investigated on a Polystyrene Based Model System

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Publication Date: 2017

Permanent Link: https://doi.org/10.3929/ethz-a-010898429

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Structure-Property Correlations in Radiation-Grafted Fuel Cell Membranes Investigated on a Polystyrene Based Model System

A thesis submitted to attain the degree of

DOCTOR OF SCIENCES of ETH ZURICH

(Dr. sc. ETH Zurich)

Presented by

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2017
Summary

This work focuses on the investigation of structure-property correlations in radiation grafted membranes. Specific modifications in the architecture of the well-defined model system of (sulfonated) polystyrene grafted onto the base film of ethylene-alt-tetrafluoroethylene (ETFE, ETFE-g-PS(SA)) were analyzed regarding their impact on polymer properties such as proton conductivity. Moreover, the impact on polymer morphology was investigated in collaboration with the laboratory of neutron scattering and imaging at the Paul Scherrer Institute and the Adolphe Merkle Institute in Fribourg.

In the first part an overview of proton exchange membranes (PEMs) and the design principles that can be found in the literature is given. However, most of these studies have been performed on solution cast membranes synthesized by lab-scale techniques such as ATRP. Structure-property correlations in approaches like radiation grafting which can be, on the one hand, easily scaled up and, on the other hand, have the particularity of modifying a preformed film instead of ending with a casting procedure are scarce. As radiation grafted membranes represent a serious alternative to perfluorinated membranes such as Nafion® in polymer electrolyte fuel cells (PEFCs) and were shown to be capable to outlast these membranes while maintaining a comparable performance, it is essential to extend the investigations on structure-property correlations to this type of membranes.

Chapter 3 and 4 focus on the impact of structural parameters of the chosen base polymer. It was shown that not only film inherent structural anisotropy is preserved even in highly functionalized films and has a strong influence on water and proton mobility as well as proton conductivity but also that variations in the arrangement of the crystalline phase in base films that are otherwise chemically identical do have an effect. One of the thereby induced differences was an increased stability upon humidity cycling in the fuel cell.

The water uptake of a membrane is known to be one of the key parameters for a high proton conductivity as a certain amount of incorporated water is needed to form a well-connected network of hydrophilic proton conducting channels. The conductivity of radiation grafted and most non perfluorinated membranes, however, is known to be very sensitive towards relative humidity. Therefore, in Chapter 5 an approach to
increase the water uptake and capability to retain water of radiation grafted membranes is presented. Different amounts of a comonomer that is known for its hygroscopic properties were introduced to the model system. Though the water uptake could be increased this did not translate into an increased proton conductivity. It could be shown that the density of sulfonic acid groups has a higher influence on the proton conductivity of the PEM than an increased water uptake.

Furthermore, a synthetic approach was developed to transfer the tunable design parameters of graft length and number density from “lab-scale” model systems as discussed in the introduction to radiation grafted membranes. Two model compounds were prepared – one comprising long graft chains and a low number density, the other having shorter grafts with a higher number density of grafts. The influence of synthesis parameter, such as applied irradiation dose, reaction temperature and monomer concentration were investigated for their impact on graft distribution. Finally, the optimized systems were compared regarding water uptake and proton conductivity at different relative humidity values and the impact on the phase segregated structure of the model system. The morphology of the system with a high number density of short grafts could be shown to comprise smaller ionic domains that were better connected. This resulted in increased proton conductivity over the whole relative humidity range.

Finally, swift heavy ion (SHI) irradiation was used to introduce proton conducting domains aligned in the required direction of proton transport. The standard electron or γ-irradiation induced grafting results in the statistical formation of a random morphology with phase-separated hydrophilic / hydrophobic domain structure, in which case the tortuosity of the aqueous phase places an inherent limitation on the conductivity of the material. It could be shown that the SHI approach successfully reduced this limiting factor and resulted in a superior proton conductivity and fuel cell performance. Membranes with various densities of proton conducting channels were synthesized, which were identified via elemental mapping and electrochemical AFM.
Zusammenfassung


Im ersten Teil wird ein Überblick über protonenleitfähige Membranen (PEMs) und die in der Literatur diskutierten Designprinzipien gegeben. Der Grossteil dieser Studien basiert auf aus Polymerlösung gegossenen Membranen, die unter Verwendung von Methoden wie ATRP im Labormassstab hergestellt wurden. Untersuchungen zu den Zusammenhängen zwischen Struktur und Membraneigenschaften in Materialien wie strahlen-gepfropfte Membranen, die über einen Prozess hergestellt werden, der zum Einen einfach auf größere Produktionsmengen umgestellt werden kann und zum Anderen die Besonderheit aufweist Modifizierungen innerhalb eines vorgeformten Polymerfilms durchzuführen anstatt das modifizierte Material über eine Lösung zu einem Film zu giessen, sind dabei selten zu finden. Da strahlen-gepfropfte Membranen in Polymerelektrolyt Brennstoffzellen (PEFCs) eine ernstzunehmende Alternative zu perfluorierten Membranen wie Nafion® darstellen und wie bereits gezeigt wurde diese Membranen bei gleicher Leistung in Beständigkeit überdauern können, ist es unumgänglich die Untersuchungen der Zusammenhänge zwischen Struktur und Membraneigenschaften auf diesen Typ Membran auszuweiten.

Im Zentrum von Kapitel 3 und 4 stehen die Auswirkungen der Struktureigenschaften des gewählten Basisfilms. Es wurde gezeigt, dass nicht nur basisfilminhärente strukturelle Anisotropie selbst noch in stark modifizierten Membranen erhalten bleibt und starken Einfluss auf die Beweglichkeit von Wassermolekülen und Protonen sowie die Protonenleitfähigkeit hat, sondern auch dass Variationen in der Anordnung der kristallinen Phase von anderweitig identischen Basisfilmen Auswirkungen auf
Membraneigenschaften zeigen. Eine dieser Auswirkungen war eine erhöhte Stabilität der Membran gegenüber wiederholten Änderungen der relativen Feuchte in Brennstoffzellen.


Zuletzt wurde Schwerionenstrahlung (SHI) verwendet um protonenleitende Strukturen einzuführen, die in der erforderlichen Richtung des Protonentransports ausgerichtet sind. Das übliche Elektronen oder γ-strahlungsinduzierte Pfropfen führt zu einer statistisch gebildeten willkürlichen Morphologie mit einer phasengetrennten hydrophilen / hydrophoben Domänenstruktur, unter deren Bedingungen die Tortuosität der wässrigen Phase eine inhärente Limitierung der Leitfähigkeit des Materials darstellt. Es konnte gezeigt werden, dass der SHI Ansatz diesen
Limitierungsfaktor erfolgreich verringerte und zu einer ausgezeichneten Protonenleitfähigkeit und Leistung in der Brennstoffzelle führte. Es wurden Membranen mit unterschiedlichen Dichten an protonenleitenden Kanälen hergestellt, welche über EDX und elektrochemisches AFM nachgewiesen wurden.
Acknowledgments

First of all, I would like to thank my supervisor Dr. Lorenz Gubler for his patience with suffering PhD students and comprehensive knowledge in the field of membranes and fuel cells. He always found the right words and was always available for advice.

My gratitude goes also to Professor Thomas Schmidt not only for giving me the opportunity to join his group and work on this interesting topic but also for being the way he is. His humorous and direct manner, his interest in my work and his constant support were very important to me.

Furthermore, I would like to thank Professor Walter Caseri for being so kind to accept co-examining my work.

Besides that, I also want to thank my project partners in the CROSS framework Dr. Gergely Nagy, Dr. Urs Gasser and Dr. Sandor Balog for their effort in characterizing the structural features of my membranes.

I cannot mention all the people that enriched the past years of my thesis but I deeply cherish all the support and laughter I found not only in my group but also in the whole PSI. Thank you. I am really grateful for this.
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This PhD thesis is a cumulative doctoral thesis that contains 3 peer-reviewed published manuscripts and three manuscripts that were prepared for submission to the indicated journals. Some new parts have been written (Chapter 1, 2 and 9). Chapters 3, 4, 5, 6, 7 and 8 comprise a short summary followed by the reproduced publication. The publications accumulated in this thesis are enumerated in the following table:

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The individual contributions of all co-authors are given here:

- **V. Sproll** performed and designed experiments, analyzed and illustrated data (P1-P6) and wrote the manuscripts (P1-P4, P6).
- **N. Gergely** performed SANS experiments, analyzed scattering data and discussed results (P1, P2, P5). Co-wrote manuscript P2 and wrote manuscript P5.
- **M. Obiols-Rabasa** performed SAXS experiments and discussed results (P2).
- **U. Embs** supervised QENS experiments and assisted in the analysis of the corresponding data, discussed results (P2).
- **S. Gustavsson** performed PFG-NMR experiments and discussed results (P1).
- **S. Balog** assisted in scattering experiment design and supervised the analysis and interpretation of the corresponding data, discussed results, evaluated and edited manuscripts (P1, P2, P5). Co-wrote manuscript P2 and wrote manuscript P5.
- **U. Gasser** discussed results, evaluated and edited manuscripts (P1, P2, P5).
- **L. Gubler** and **T.J. Schmidt** discussed results, supervised the work, evaluated and edited manuscripts.
- **A. Handl** performed EC-AFM experiments and discussed results (P6).
- **R. Hiesgen** and **K.A. Friedrich** discussed EC-AFM results, evaluated and edited manuscripts (P6).

The chapters in this thesis contain excerpts and/or ideas (chapter 1, 2 and 9) or reproductions (chapter 3 – 8) of the indicated manuscripts as indicated in the following table:

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Chapter 1. Introduction
1. Introduction

1.1. Motivation

During the last decades polymer electrolyte membranes attracted more and more interest due to their wide range of potential applications in solid-state and electrochemical devices, including batteries, chemical sensors, super capacitors and polymer electrolyte fuel cells (PEFC).\(^1\)\(^-\)\(^9\) The advantages of the polymer electrolyte membranes compared to conventional liquid electrolytes triggered the improvement of the existing technology concerning modular, safer and more robust systems.\(^10\)

With the challenges arising from an increasing energy demand and problems associated with a fossil fuel based energy system (e.g. rising CO\(_2\) concentration in the atmosphere, climate change with rise in average temperature and sea level, fossil fuel shortage),\(^11\)\(^,\)\(^12\) fuel cells have attracted great attention. Together with electrolyzer systems fuel cells are in the center of the concept of a “hydrogen economy” that promises an accessible and sustainable energy cycle with hydrogen as energy carrier.\(^13\)\(^-\)\(^15\)

Regarding PEFCs, the proton exchange membrane (PEM) plays a key role and is therefore the target of extensive investigations in order to obtain commercially attractive fuel cells. Such a membrane is required to meet several specifications, such as good chemical (oxidative and hydrolytic) and mechanical stability and gas barrier properties (low permeability to fuel and oxidant). Moreover, high proton conductivity along with no electrical conductivity and balanced water transport are prerequisites and, of course, the cost factor has a major impact.\(^1\)\(^,\)\(^3\)\(^,\)\(^16\)

Today’s state of the art membranes, such as Nafion\(^\text{®}\) (DuPont) and other structurally analogous materials (Aciplex, Aquivion, Flemion), on the other hand are considered to be very expensive (Figure 1.1).\(^17\)

![Figure 1.1](image)

Figure 1.1: Chemical structure of perfluorosulfonic acids such as Nafion\(^\text{®}\). For more information about different PFSA membranes cf. Figure 1.6.

In perfluorosulfonic acid (PFSA) membranes the combination of a hydrophobic backbone and a proton conducting moiety is realized in the same macromolecule. Due to their spatial arrangement they have the possibility to form hydrophilic clusters which
swell upon sufficient hydration in a way to produce hydrophilic channels through the hydrophobic bulk material.\textsuperscript{18,23}

These PFSA membranes show very good performance under moderate operating conditions with temperatures below 90°C and relative humidities (r.h.) around 100%. Unfortunately, the performance drops significantly under the stringent operating conditions for PEFCs requested by industry (T > 100°C, relative humidity smaller than 50%).\textsuperscript{3,18}

Therefore, the desire for not only cost-competitive new materials but also materials matching these aggravated prerequisites is increasing. Among the various methods to prepare proton conducting membranes a very versatile approach is the radiation grafting of commercially available base films. Radiation processing itself is a well-established and economical method for the modification of polymers.\textsuperscript{24} The attractiveness of this method includes that it allows not only the combination of very different types of polymers (hydrophobic backbone vs. hydrophilic side chains) but also the utilization of cost-effective commercially available base films, thereby avoiding the necessity of film casting or other difficulties associated with film formation using sensitive polymers.\textsuperscript{25-28}

In contrast to other methods which allow the combination of two polymers, e.g., blending, irradiation grafting allows the covalent connection of these polymers, which results in a phase separation on a much lower length scale than achievable with blending. The phase separation in such copolymers is driven by the enthalpy associated with the demixing of incompatible segments. Continued separation from microscale to macroscale domains is impeded by chemical bonds between the different segments.\textsuperscript{1} Furthermore, a wide selection of possible monomers or monomer combinations and base films allows the development of specifically tailored membranes in an at the same time industrially applicable process.

Despite the increasing interest in grafted membranes for fuel cell application and the intensive research for high performing, versatile and, most importantly, cost-competitive PEMs,\textsuperscript{3, 20-32} the understanding of the polymer structure and morphology as well as its impact on properties such as proton mobility and conductivity is rather limited.\textsuperscript{33, 34} Model polymeric or oligomeric systems are used to investigate the impact of polymer architecture on the properties of the polymer and have clearly outlined the importance of phase separation and microstructure on the magnitude of proton conductivity.\textsuperscript{18, 35, 36}

However, most of these model systems comprise an elaborate synthesis. Therefore, the next intriguing step is to move from these “lab” model systems to model systems of a method capable of being scaled up to industrial processes. As already indicated, the
radiation grafting of monomers into commercially available base films is such a process. In this thesis concepts of influencing polymer architecture based on radiation grafting will be presented and their impact on fuel cell relevant membrane properties evaluated.

1.2. Proton Exchange Membranes (PEMs)

Proton exchange membranes (PEMs) are polymers with an architecture specially designed to provide a continuous network of ionic channels in which protons can be transported. Acidic groups (e.g. sulfonic acid) are immobilized in the polymer structure and provide charge carriers upon dissociation. To maintain the structural integrity that is essential for their application this hydrophilic phase is often combined with hydrophobic components (ranging from incorporated particles/fibers over substituents to separate polymers).

1.2.1. Polymer Electrolyte Fuel Cells (PEFCs)

One of the key applications for these proton exchange membranes is in the fuel cell (PEFC). With the trend towards the creation of a more sustainable energy scenario fuel cells have attracted special attention due to their potential of clean and efficient power generation (theoretical efficiency of 83% under standard conditions (practical: 50 – 70% at 75°C) compared to an efficiency of 58% at 500°C (practical: ~40%) for combustion engines). Fuel cells are energy conversion devices that convert the chemical energy of a fuel (e.g. hydrogen) and an oxidant (mostly oxygen) into electrical energy. This thesis is focused on the investigation of structure-property correlation in radiation grafted membranes for low temperature PEFCs with typical operating temperatures between 60°C and 100°C. A comprehensive review of all different kinds of fuel cells and applications thereof can be found in the literature. A schematic representation of the working principle of a PEFC is shown in Figure 1.2. Hydrogen and oxygen gas are fed to the membrane electrode assembly (MEA) – the primary electrochemical element – consisting of a PEM placed between two gas diffusion electrodes (GDEs). The electrochemical reactions occur on the surface of the noble metal catalyst in the catalyst layer. For the function of the device it is essential that the PEM effectively separates the reactant gases and acts as an electrical insulator while at the same time mediating the electrochemical reactions by transporting the charged species (in the present case protons).
1. Introduction

Figure 1.2: Schematic principle of a proton exchange membrane fuel cell (PEFC).

These protons and electrons, which travel via an external circuit, react with oxygen at the cathode to form water as the only waste product.

Despite a theoretical efficiency of 83%, the performance of a fuel cell under operating conditions is subjected to substantial losses. For a detailed discussion of fuel cell thermodynamics and voltage loss mechanisms the reader is referred to corresponding literature as this is not the aim of this section. Generally, fuel cell performance is characterized by current-voltage curves, so-called polarization curves, and voltage losses (or overpotentials) can be classified into three types (Figure 1.3): activation or charge transfer losses, ohmic losses and mass transport or concentration losses.

Even in absence of current the theoretical reversible cell potential ($U_{rev}$) is not reached due to, e.g., reactant crossover and the formation of a mixed potential at the cathode side involving side reactions such as the oxidation of Pt catalyst particles or formation of peroxides. The voltage in absence of current is referred to as open circuit voltage ($U_{OCV}$) and ranges usually between 0.9 and 1.1 V.
1. Introduction

**Figure 1.3:** Schematic polarization curve showing different loss contributions.

In an operating fuel cell the magnitude and share of the total loss of the three types of overpotential change with the current density. For low current densities activation losses are the main contribution. The kinetics for hydrogen oxidation at the anode are fast and can be largely neglected in their contribution to activation losses, which are dominated by the slow kinetics of the oxygen reduction reaction at the cathode side.

At very high current densities, on the other hand, when the transport of reactants and product water is hindered mass transport overpotential becomes significant. Mass transport losses comprise not only diffusion losses, such as of the oxygen molecule in the catalyst layer and gas diffusion layer, but also protonic transport losses within the ionomer in the catalyst layer. Before these concentration limitations evolve, ohmic losses – predominantly resulting from the ionic resistance within the PEM – represent an important contribution. For such current densities, e.g. 1.5 A cm\(^{-2}\), the membrane contribution to fuel cell losses (voltage efficiency) can be roughly assessed. For a hydrogen/oxygen fuel cell the membrane causes \(~9\%\) efficiency loss under fully humidified conditions. As the conductivity of PEMs decreases at reduced humidification, the membrane contribution to the total losses increases at lower relative humidity (70\% r.h.: \(~10\%\); 50\% r.h.: \(~12\%)\). Thus, if the conductivity of a membrane at given conditions is increased by a factor of 2, the loss that can be attributed to the PEM is halved.

The advantage of PEFC comprises not only the utilization of a solid electrolyte which eliminates leakage issues and the necessity of handling hot and corrosive liquids but also
enables a variable load profile and intermittent operation with quick startup under different conditions which makes it interesting for automotive applications but also for remote power generation and back-up power systems.\textsuperscript{41, 47} Regarding automotive applications the current target operating conditions defined by the US Department of Energy (DOE) are a high operating temperature of 120°C and relatively low relative humidity (r.h., \(\leq 50\%\)). Under these conditions PEMs are expected to show a conductivity of 100 mS cm\(^{-1}\).\textsuperscript{48, 49}

1.2.2. \textbf{Two Component Design Principle in PEMs}

When investigating the impact and contribution of structure on PEM properties, it can be a useful approach to consider proton exchange membranes as consisting of two phases, of a structural component and a functional one (acid groups and water domain). This generalization also resembles the two major functions a PEM has to fulfill – the one as an electrolyte and as a separator (Figure 1.4).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Attribution of membrane prerequisites to the conceptual approach of considering PEMs as a two phase system. The impact of this approach on the design of the polymeric material is shown in Figure 1.17.}
\end{figure}

The central property of a PEM is surely its proton conductivity – a characteristic which can be attributed to its function as an electrolyte. At the same time it is crucial for the application in electrochemical devices to maintain mechanical and chemical stability and provide electrical insulation – clearly characteristics of a separator. For efficiency, durability and safe operation it is also important to provide a gas barrier and prevent the
mixing of the reactant gases. The corresponding DOE 2020 performance specifications are shown in Table 1.1.\textsuperscript{30}

**Table 1.1:** U.S. DOE 2020 specifications for the target performance of a PEM in a hydrogen/air operated fuel cell.\textsuperscript{30}

<table>
<thead>
<tr>
<th>Specification</th>
<th>Goal for 2020</th>
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<tbody>
<tr>
<td>max. operation temperature</td>
<td>120°C</td>
</tr>
<tr>
<td>cost</td>
<td>&lt; $20 m\textsuperscript{2}</td>
</tr>
<tr>
<td>conductivity\textsuperscript{**} at:</td>
<td></td>
</tr>
<tr>
<td>- 120°C, 20 – 40% r.h.</td>
<td>125 mS cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>- 30°C, 95% r.h.</td>
<td>83 mS cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>max. gas crossover\textsuperscript{**}</td>
<td>2 mA cm\textsuperscript{-2}</td>
</tr>
<tr>
<td>min. electrical resistance\textsuperscript{***}</td>
<td>1 k Ω cm\textsuperscript{2}</td>
</tr>
<tr>
<td>durability:</td>
<td></td>
</tr>
<tr>
<td>- mechanical</td>
<td>20,000 high/low humidity feed gas cycles at 80°C with ≤ 2 mA cm\textsuperscript{-2} gas crossover</td>
</tr>
<tr>
<td>- chemical</td>
<td>500 h with ≤ 2 mA cm\textsuperscript{-2} gas crossover and &lt; 20% decrease in open circuit voltage</td>
</tr>
</tbody>
</table>

\* based on 2010, dollars and costs projected to high-volume production (5 x 10\textsuperscript{5} fuel cell stacks per year
\** calculated for a membrane thickness of 25 μm
\*** in a fuel cell at 1 atm O\textsubscript{2} or H\textsubscript{2}, nominal stack operating temperature, humidified gases at 0.5 V DC
\**** measured in N\textsubscript{2}/N\textsubscript{2} at 0.5 V DC at 80°C

Other properties as for example the extent of water-uptake cannot be that clearly assigned to one of the two phases. A high water-uptake increases the proton conductivity (electrolyte) but also softens the membrane (decrease of mechanical stability) and increases the crossover of reactants, both characteristics that were assigned to the separator function.

The design of a PEM allows the tailoring of membrane properties by the combination of hydrophilic (acid group containing) and hydrophobic constituents whether in the same polymer or by the combination of two or more different polymers. The incompatibility of hydrophilic and hydrophobic domains leads to a phase separation with ionic groups aggregating to form ionic clusters. Depending on the hydration level of the membrane a network of hydrophilic channels forms through which protons are transported, mediated by water molecules that are either strongly associated with the
polymer surface (acid groups) or present as bulk water in the channels.\textsuperscript{1, 19-21} The hydrophobic segments, on the other hand, prevent dissolution of the polymer and maintain mechanical integrity. The resulting morphology is determined by factors such as the extent of dissimilarity between incompatible constituents, the chain length of each block and their volume ratio.\textsuperscript{1, 9, 51} These and other parameters will be discussed in Section 1.4.

1.2.3.  **Classification of Materials used as PEMs**

Membrane materials used and investigated for application in PEFCs can be classified into three main categories – perfluorinated, partially-fluorinated and non-fluorinated materials (Figure 1.5).

![Classification of Membrane Materials](image)

**Figure 1.5:** Classification of PEM materials into perfluorinated, partially fluorinated and non-fluorinated compounds and some representatives of these groups (cf. Appendix, List of Abbreviations).

1.2.3.1.  **Perfluorosulfonic Acid (PFSA) Membranes**

Perfluorinated sulfonic acid (PFSA) membranes have been the subject of intense research ever since DuPont developed Nafion\textsuperscript{®} in the late 1960s - a membrane intended
for chlor-alkali electrolysis but also revolutionizing fuel cell performances with a two-fold increase in conductivity and an extended lifetime ($10^4 - 10^5$ h instead of $10^3 - 10^4$ h) compared to the standard membrane at this time.\cite{7, 9} Even half a century later, Nafion® is still the state-of-the-art in PEFCs, though further improved regarding stability and performance.\cite{41} Asahi Glass, Dow Chemical and 3M developed PFSA membranes with shorter side chains and/or higher ion exchange capacity (IEC, equivalent of sulfonic acid group per gram dry polymer). Chemical structures of different PFSA membranes are shown in Figure 1.6.

These membranes show high proton conductivity with a good utilization of water molecules under reduced humidification\cite{19, 51-55} as well as good chemical and mechanical stability leading to a high durability under fuel cell operating conditions.\cite{56, 57} The chemical structure comprises a PTFE-like hydrophobic backbone with pendant perfluoroether side chains terminated with a sulfonic acid group. This sulfonic acid group is highly acidic due to the electron withdrawing nature of the adjacent perfluoroether chains ($pK_a < -6$).\cite{58} The strong hydrophilicity of this acid group together with the pronounced hydrophobic character of the perfluorinated backbone facilitates a distinct phase separation, which determines the proton conductivity in these membranes.

![Figure 1.6: Chemical structure of the most common perfluorosulfonic acid membranes used as PEM.](image-url)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Structure</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>DuPont (Nafion®)</td>
<td>$m \geq 1$, $n = 2$, $x = 5 - 13.5$, $y = 1000$</td>
<td></td>
</tr>
<tr>
<td>Asahi Kasei (Aciplex®)</td>
<td>$m = 0 - 3$, $n = 2 - 5$, $x = 1.5 - 14$</td>
<td></td>
</tr>
<tr>
<td>Asahi Glass (Flemion®)</td>
<td>$m = 0$, $n = 1 - 5$</td>
<td></td>
</tr>
<tr>
<td>Solvay (Aquivion®)</td>
<td>$m = 0$, $n = 2$, $x = 3 - 10$</td>
<td></td>
</tr>
<tr>
<td>3M®</td>
<td>$m = 0$, $n = 3$</td>
<td></td>
</tr>
</tbody>
</table>
PFSA membranes with short side chains (SSC-PFSA) usually also exhibit a higher IEC which naturally leads to higher proton conductivity compared to e.g. Nafion®. When SSC and long side chain (LSC) PFSA membranes are compared at the same IEC, water and proton transport properties are comparable and also the phase separation (hydrophobic/hydrophilic) as a function of hydration is similar, though this phase separation is slightly less pronounced in short side chain PFSA membranes. An advantage of short side chain PFSA lies in the higher crystallinity of these membranes, which renders them more suitable for application at higher temperature and also allows the incorporation of a larger number of sulfonic acid groups while maintaining similar mechanical stability as long side chain PFSA membranes with a lower IEC.

PFSA membranes such as Nafion® show good performance and durability at hydrated state and operating temperatures up to 90°C, leading to their utilization in most commercial fuel cell, electrolyzer or redox flow systems. However, they also exhibit several critical shortcomings. One of the major disadvantages apart from the high manufacturing costs of PFSA membranes concerns safety risks arising during manufacturing and use. At temperatures above 150°C toxic intermediates and corrosive gasses are released which is an additional danger, e.g., in FC-car accidents, and limits recycling options. Moreover, dehydration issues and the large electro-osmotic drag coefficient of PFSA membranes, which leads to significant water permeation from anode to cathode (anode drying and/or cathode flooding) during fuel cell operation, renders an advanced hydration system necessary, adding to the total costs associated with PFSA membranes. Another serious drawback is the restriction to moderate temperatures and the deterioration of mechanical properties towards higher temperature (softening) and the increasing permeability for reactants leading to parasitic losses and reduction of the FC efficiency.

Though efforts (including blending, reinforcements, incorporation of nanoparticles or heteropolyacids, etc.) are ongoing to eliminate these shortcomings, alternative membranes received great interest and it is regarded as likely that Nafion® will be replaced in the future. It has been proposed that given the reduced costs are commercially realistic, sacrifices regarding material life time might even be acceptable. Therefore, a range of alternative membrane materials has been under intense investigation. Some examples will be discussed in the following sections.
1. Introduction

1.2.3.2. Partially Fluorinated Membranes

Partially fluorinated materials can combine the advantageous stability of perfluorinated compounds with the reduced costs of hydrocarbon based and/or commercially available components. Early work has been based on $\alpha,\beta,\beta$-trifluorostyrene (TFS, Figure 1.7) membranes. In the simplest form sulfonated TFS is used as a homopolymer (“S” membrane) resulting in a membrane with good thermal and chemical stability but unsatisfactory mechanical properties. This drawback was addressed by blending with poly(vinylidene fluoride) (PVDF) using triethyl phosphate as plasticizer or grafting TFS into a fluorocarbon matrix. Ballard Advanced Materials (BAM) developed membranes derived from sulfonated TFS and TFS derivatives known as BAM3G (Figure 1.7). The synthesis comprises emulsion polymerization of substituted and unsubstituted TFS over a period of 48 h and a post-sulfonation procedure allowing for the combination of various monomer ratios and sulfonation levels (and thereby different IECs). Furthermore, it has been reported that BAM3G membranes show better performance than Nafion type membranes at high current densities.

![Figure 1.7: Chemical structures of polystyrene sulfonic acid (PSSA), poly-$\alpha,\beta,\beta$-trifluorostyrene sulfonic acid (PTFSA) and BAM3G.](image)

Another and potentially more cost-effective way to combine fluorinated and non-fluorinated constituents is via polymer blending. In structural analogy to the material discussed above, polystyrene sulfonic acid (PSSA, Figure 1.7) can be mentioned as an example for hydrocarbon based polymers that was used in blending approaches with fluorinated compounds. However, these approaches yielded membranes with unsatisfactory physical properties as the incompatibility between the hydrophilic PSSA and hydrophobic fluorinated polymers had detrimental effects on mechanical integrity.
and led to increased reactant permeation.\textsuperscript{73} To prevent such macroscopic demixing and the associated negative effects on proton conductivity, reactant permeability and physical integrity, the interface compatibility can be improved by the utilization of a third component or block copolymer derivatives.\textsuperscript{73-76}

Apart from PSSA also other hydrocarbon based polyelectrolytes are combined with perfluorinated polymers. In order to improve component compatibility and obtain an optimized combination of high proton conductivity and mechanical stability, polymer blends of sulfonated poly(arylene ether ether ketone) (sPEEK) with varying content of PVDF were investigated (Figure 1.8).\textsuperscript{77-79}

![Figure 1.8: Partially fluorinated polymer blend system consisting of sulfonated poly(arylene ether ether ketone) (sPEEK) and PVDF.](image)

It was reported that the addition of PVDF, especially PVDF with higher molecular weight, improved the mechanical properties (e.g. higher fracture toughness) of the sPEEK while maintaining a proton conductivity that was despite being lower than in pure sPEEK still comparable to Nafion\textsuperscript{®}. Moreover, the blend membranes showed a gas permeability 5 times lower than the perfluorinated standard and a thermal stability up to 250°C.

However, one of the most intriguing strategies to combine thermally and chemically stable fluorinated polymers with hydrophilic non-fluorinated polymers is \textit{via} radiation grafting. This technique allows the modification of otherwise inert base films with a variety of highly functionalized monomers on a covalent level, which results in a phase separation on a much lower length scale than achievable with blending. A continued separation from microscale to macroscale domains, on the other hand, is impeded by chemical bonds between the different segments.\textsuperscript{1} The commercial availability of the fluorinated base film and easy processability render this approach an attractive and cost-competitive alternative that will be presented in more details in Section 1.3.
1. Introduction

1.2.3.3. Non-Fluorinated Hydrocarbon Based Membranes

Another class of alternative PEMs that has received large interest is based on a non-fluorinated hydrocarbon backbone. Apart from being more environmentally friendly as they are not containing any fluorine, they provide other definitive advantages, such as lower costs, potential availability of base polymer/monomer and are thermally stable allowing for operating conditions above 120°C.\(^3,29\)

One of the most studied aliphatic hydrocarbon PEMs is based on sulfonated styrene either as only component, combined with a crosslinking agent or as block copolymer. Polystyrene sulfonic acid (PSSA) membranes are inexpensive and easy to synthesize but show poor chemical and thermal stability. Especially non-crosslinked PSSA membranes show the typical problems associated with polyelectrolytes, they are brittle under dry conditions, lose their mechanical stability at high relative humidity and dissolve in water.\(^80\) The main chain of PSSA membranes degrades readily under fuel cell operating conditions. Reactive peroxyl (HOO∙) and hydroxyl (HO∙) radicals form at the catalyst surface in the presence of hydrogen and oxygen.\(^7,81\) The two dominant degradation mechanism in PSSA based membranes are radical attack at the α-position of the styrene moiety (Scheme 1.1a) and at the aromatic ring itself (Scheme 1.1b) leading to the formation of benzylic radicals which result in a chain scission of the backbone.\(^82,84\)

![Scheme 1.1: Chemical degradation of PSSA membranes. Radical attack at the α-position of the styrene moiety (route a) and radical addition to the aromatic ring (route b) lead to the formation of a benzylic radical and in the follow-up reactions to chain scission.\(^82,84\)](image-url)
Nevertheless, PSSA based membranes were one of the first PEMs and used in the 1960's Gemini space program of the NASA despite the limited durability (~1000 h) and operation temperature of 60°C.\cite{85,86} It could be shown that the stability can be increased by crosslinking strategies or using α-protected derivatives\cite{86,87} and that the proton conductivity can be optimized by choosing the best polymer architecture\cite{88,89} (see also Section 1.4.). The conductivity of crosslinked non-optimized (linear) PSSA, on the other hand, is reported to be slightly lower to comparable to Nafion\textsuperscript{®} despite incorporating a higher number of sulfonic acid groups per gram dry polymer (expressed by the ion exchange capacity, IEC).\cite{85} Another prominent example of this class is based on commercial block copolymers of the styrene-ethylene/butylene-styrene family, e.g. Kraton G 1650, Dais Analytics), which are post-sulfonated. Fully sulfonated derivatives reach proton conductivities of 70 to 100 mS cm\textsuperscript{-1} when fully hydrated and are reported to be cheaper in production compared to Nafion\textsuperscript{®}. Due to the variety of possible combinations regarding the tailoring of the block lengths and composition, Dais membranes offer the possibility of a vast range of phase-separated morphologies.\cite{3,90} But also these type of membrane shows poor oxidative stability and is therefore only suitable for operating temperatures below 60°C.

Despite the poor chemical stability polystyrene based membranes are intensively studied as they represent an excellent model system that allows the systematic design of polymer structure \textit{via} atom transfer radical polymerization (ATRP) or stable free radical polymerization (SFRP) and therefore investigations on correlations between polymer architecture and membrane properties (see also Section 1.4.).

Hydrocarbon based membranes with an aromatic backbone are expected to be a promising alternative to PFSA membranes. They offer the same advantages as discussed for the aliphatic polymers but have a higher thermal and chemical stability compared to e.g. polystyrene based membranes. This can be attributed to the higher C-H bond energy in aromatic rings compared to aliphatic systems.\cite{3} The aromatic ring can be functionalized by electrophilic and nucleophilic substitution and subsequent oxidation of e.g. a poly(phenylene thioether) to poly(phenylene sulfone) further stabilizes the polymer against desulfonation by reducing the electron density of the aromatic moiety.\cite{7}
Figure 1.9: Common chemical structure of different possible poly(arylene) polymers and examples of sulfonated polybenzimidazoles (sPBI) and sulfonated polyimides (sPI).

Poly(arylene ether) materials such as sulfonated poly(phenylene oxide)\(^9\), sulfonated poly(phenylene ether sulfone) (sPSU)\(^92\text{-}95\) sulfonated poly(ether ether ketone) (sPEEK)\(^18, 19, 96\), sulfonated poly(phenylene sulfone) (sPPS)\(^97\text{-}100\) and their derivatives are the center of numerous investigations (Figure 1.9). The introduction of acid groups, usually sulfonic acid, can be strategically designed by the incorporation of sulfonated monomers or building blocks or be of a random kind when a post-modification approach is followed.\(^3\) Another material family that has been well investigated is based on nitrogen containing heterocycles as sulfonated polyimides (sPI)\(^80, 101\) or sulfonated polybenzimidazole (sPBI)\(^3, 102\text{-}104\). The proton conductivity of membranes of the sPEEK family is reported to be similar to that of Nafion® but displays a weaker phase separation with narrower and more strongly branched hydrophilic channels that have more dead ends.\(^18\) The high water-uptake of this kind of membranes reduced the long-term stability in a fuel cell at 80°C and fully humidified gases.\(^96\) This is also a drawback for sPPS and other highly sulfonated polyaromatic membranes that have a high IEC and can therefore be considered as polyelectrolytes.\(^95, 103, 105\)

Polyelectrolyte drawbacks, such as excessive water-uptake and mechanical properties strongly depending on the humidification level of the membrane (ranging from brittle to dissolution), can be eased by the incorporation of hydrophobic constituents, e.g. by copolymerization or blending, and/or crosslinking of the polymer chains. In polymer blends different types of interaction forces between the blend components can ensure good contact and a homogenous morphology ranging from basic van-der-Waals and
dipole-dipole interaction (e.g. in blends from sulfonated and non-functionalized PSU or PEK)\textsuperscript{106, 107} over electrostatic interaction and hydrogen bridges (ionic-crosslinking, e.g. in blends from sPEEK or sPSU with PBI)\textsuperscript{108-110} to the strongest kind in the form of covalent crosslinking.\textsuperscript{108}

![Figure 1.10: Non-fluorinated ionically crosslinked polymer blend system consisting of sulfonated poly(arylene ether ether ketone) (sPEEK) and polybenzimidazole (PBI).](image)

Examples for ionically crosslinked polymer blends (Figure 1.10) include sulfonated (acidic) polymers as sPEEK or sPSU combined with basic polymers as PBI, different aminated polymers (e.g. aminated PSU) or poly(4-vinylpyridine) (P4VP).\textsuperscript{8, 108, 110, 111} This straightforward kind of crosslinking allows for a variety of combinations of acidic and basic polymers and effectively increases the flexibility of the membrane at dry conditions while showing good thermal stability. However, at a temperature above 70 – 90°C the electrostatic crosslinking starts to fail, especially when polymers with lower basicity were used, which caused problems with dimensional stability.\textsuperscript{96}

1.2.4. Proton Transport Mechanisms in PEMs

In order to design a highly conducting PEM, which can at the same time fulfill the requirements regarding mechanical stability, it is essential to understand the different proton transport mechanisms participating in the overall measured conductivity. The phase separation between hydrophobic and hydrophilic domains, which is facilitated by the interaction with water, leads to the formation of hydrophilic channels in which protons are transported.\textsuperscript{1, 19-21} The morphology adopted thereby is determined by factors such as the extent of dissimilarity between incompatible blocks, the chain length of each block and their volume ratio.\textsuperscript{1, 9, 51} An increased content of sulfonic acid groups (expressed by a higher ion exchange capacity, IEC) leads to a higher water content and a
more pronounced dissociation of the acidic group resulting in an increased effective proton mobility and thus higher proton conductivity. The effective proton mobility includes factors such as the tortuosity and the degree of dissociation of the acid.\textsuperscript{112, 113} Therefore, a lower degree of tortuosity, corresponding to a more direct conduction pathway, leads to a higher effective conductivity and, hence, to a lower resistance of the membrane.\textsuperscript{18-21, 35, 114}

Transport of protons in proton exchange membranes proceeds in water-swollen hydrophilic channels according to three different mechanisms or a combination thereof (Figure 1.11), strongly depending on the hydration level of the membrane.

A structural diffusion in close proximity to the “pore wall” referred to as surface mechanism already enables proton transport at very low hydration levels. Even before the solvation shell of the sulfonic acid group is saturated, the acid dissociates to some extent and the “free proton” can migrate between the sulfonic acid groups. For this conductivity a minimum hydration of one to two water molecules per sulfonic acid group is sufficient and close proximity of sulfonic acid groups is favored as it reduces the necessary activation enthalpy.\textsuperscript{115-117} However, transport via the surface mechanism at such low hydration levels has a higher activation enthalpy than the diffusion of protons and water molecules in pure water or in the bulk water within a hydrophilic pore and has to be considered as local conductivity.\textsuperscript{7} For higher humidification the impact of this transport mechanism on the total/macroscopic conductivity is larger and its general rate of proton transport can furthermore be affected by the conformation and flexibility of the polymer.

**Figure 1.11:** Schematic illustration of the different mechanisms of proton transport. In the green highlighted area close to the hydrophilic/hydrophobic domain wall proton “hopping” occurs in the so called surface mechanism via sulfonic acid groups. In a more distant region
protons either diffuse (vehicular mechanism) or are transported via the Grotthus mechanism (see text).

Apart from the structural diffusion along the surface of the pore walls, at higher water content the protons are transported via the vehicle and Grotthus mechanism, with activation enthalpies for water diffusion and proton conductivity approaching the values of pure water at around $\lambda = 6$ and $\lambda = 12$ (measured for a Nafion® membrane).\textsuperscript{7, 100, 118} This is not to be confused with macroscopic diffusion constants being the same as in pure water - they are one order of magnitude smaller – which is caused by the geometrical confinement to the hydrated hydrophilic domain. For $\lambda < 5$ the dominant transport mechanism is assigned to a cooperative diffusion of protons and water molecules (vehicle mechanism) as in this humidification range the conductivity diffusion coefficient equals the water diffusion coefficient.\textsuperscript{19} Towards higher water contents ($\lambda > 5$) another structural diffusion process (Grotthus mechanism) is causing additional conductivity. This mechanism depends on intermolecular proton transfer where the protonic charge carrier is transferred along a hydrogen bond network between a chain of water molecules. The transformation process of the hydrogen bonds ($H_5O_2^+ “Zundel ion” \rightarrow H_9O_4^+ “Eigen ion” \rightarrow H_5O_2^+$) is a rapid process on a sub-picosecond time scale \textsuperscript{119} and is the dominant mechanism for conductivity in “free water”.\textsuperscript{119} However, as a structural diffusion process, the Grotthus mechanism is affected by symmetry reduction (e.g. by confinement or temperature)\textsuperscript{120} and electrostatic or geometrical interactions between water molecules and the polymer matrix which are the stronger the lower the water content of the membrane.

The polymer morphology affects all of the above mentioned transport mechanisms, not only via the tortuosity of the ionic channels and the proximity of acid groups but also regarding structural confinement and electrostatic interactions between water molecules and polymer which increases the activation enthalpy of the different transport mechanism.\textsuperscript{18-21, 35, 114}

\section{1.3. Radiation Grafted Membranes}

\subsection{1.3.1. Radiation Induced Grafting}

Within the various methods to modify polymeric materials, radiation grafting of commercially available base films proved itself as a very versatile technique that can be easily up-scaled to industrial processes. Radiation processing itself is a well-established and economical method for the modification of polymers.\textsuperscript{24} Characteristic material
properties, such as thermal stability, melt flow, chemical resistance and mechanical strength, can be significantly improved applying this method. Moreover, surface properties and the processability of the polymer can be influenced. Therefore, radiation grafting was used in different fields of application such as to enhance biocompatibility, the preparation of substrates for cell tissue growth and the modification of the surface of glass or non-woven fabrics.

The attractiveness of this method includes that it allows not only the combination of very different types of polymers (hydrophobic backbone vs. hydrophilic side chains) but also the utilization of cost-effective commercially available base films, thereby avoiding the necessity of film casting or other difficulties associated with film formation (Figure 1.12). In contrast to other methods which allow the combination of two polymers, e.g., blending, irradiation grafting allows the covalent connection of these polymers, which results in a phase separation on a much lower length scale than achievable with blending. The phase separation in such copolymers is driven by the enthalpy associated with the demixing of incompatible segments. Continued separation from microscale to macroscale domains is impeded by chemical bonds between the different segments. Furthermore, a wide selection of possible monomers or monomer combinations and base films allows the development of specially tailored membranes in a process that is at the same time industrially applicable.

![Principle of radiation grafting.](image)

**Figure 1.12**: Principle of radiation grafting.

In the field of membranes, this technique was used to prepare ion exchange membranes or membranes for chloralkali industry and electrodialysis. Among a widespread
application in the academic research, radiation grafting found its way into the production of commercially available products such as polyethylene-g-acrylic acid, which can be used as separator in batteries, for ion exchange non-woven fabrics for air and water purification and for functional fabrics as well as cell culturing dishes.\textsuperscript{124}

The history of radiation grafting started with Chapiró in the late 1950s and was then adopted by Chen to produce the first cation exchange membrane by grafting styrene and styrene / divinyl benzene into a polyethylene film with subsequent sulfonation as battery separator and for dialysis applications.\textsuperscript{125, 126}

At the Paul Scherrer Institute (PSI) the research of radiation grafted membranes started with G. G. Scherer in the 1990s by grafting FEP with styrene sulfonic acid under $\gamma$-irradiation.\textsuperscript{127, 128} Over the years, the membrane performance could be improved by, amongst other approaches, altering the base film and the irradiation source, adding crosslinking co-monomers and optimization of the sulfonation procedure.\textsuperscript{127, 129-131}

Radiation grafted membranes for PEFCs have to compete with Nafion\textsuperscript{®} membranes – the current state-of-the-art PEMs (cf. Section 1.2.3.1). One of the advantages of radiation grafted membranes in this context comprises the opportunity to use rather cost-effective commercially available base films and an easy processability, whereas the synthesis of Nafion\textsuperscript{®} is a difficult multi-step process resulting in high production costs to which other system associated costs add (e.g. complex water management system due to strong electro-osmotic drag in this type of membrane, cf. Section 1.2.3.1).\textsuperscript{129}

Moreover, the different parameters like thickness and chemical nature of the base film, the irradiation source and dose, the monomers and amount of grafted polymer can be chosen independently, rendering this technique a versatile method to produce optimized and tailored membranes.

Regarding the irradiation grafting, two different types can be distinguished, the simultaneous and the pre-irradiation grafting.

In case of the simultaneous approach, the base film is $\gamma$- or electron irradiated in the presence of the monomer solution. Thereby, the radicals are generated in both, base film and monomer solution, leading not only to a polymerization onto the surface (and later bulk) of the material but also within the solution.\textsuperscript{132} The advantage of this one-step-synthesis is that the radicals in the base film are generated \textit{in situ} and cannot undergo decomposition pathways during storage. Moreover, decomposed radicals are replaced by newly generated ones. The disadvantage lies in the formation of significant amounts of homopolymer in the grafting solution and consequently an ineffective monomer utilization and low level of grafting efficiency in the system. To suppress the polymerization in the grafting solution, inhibitors like Fe\textsuperscript{2+} and Cu\textsuperscript{2+} can be added.\textsuperscript{26}
1. Introduction

Nevertheless, in case of the synthesis of fuel cell membranes, traces of metal ions in the final membrane can lead to severe degradation under fuel cell conditions and should therefore be avoided.\textsuperscript{27, 133} In contrast to the simultaneous grafting technique, the \textit{pre-irradiation grafting} comprises two process steps.\textsuperscript{134} In the first step, the base film is irradiated to generate either trapped radicals (irradiation under vacuum) or alkyl peroxides (irradiation under air) and subsequently stored between -18°C to -80°C, depending on the polymer material used.\textsuperscript{135-137} In the second step, the monomer solution is introduced to the irradiated film and the grafting reaction is initiated either by these trapped radicals or by thermal decomposition of the peroxides. The advantage of this technique regarding an industrial upscaling is the decoupling of the irradiation from the grafting process, thus enabling a fast roll-to-roll irradiation (cost intensive step)\textsuperscript{26} and a subsequent grafting (low costs, time dependent). In case of the simultaneous grafting, the expensive irradiation must be applied during the whole time consuming grafting process. Moreover, the formation of homopolymer in the grafting solution is reduced to a minimum, because the initiators are only located within the base film and are not formed to a large extent in the grafting solution, thereby increasing grafting efficiency and monomer utilization.

1.3.2. Types of Irradiation

To create the active sites that are used for the grafting procedure ionizing irradiation is used. A detailed description of how radiation interacts with the material and which effects radiation has on polymeric materials can be found in textbooks, cf. for instance references \textsuperscript{138-140}. Among the large number of ionizing radiation, three types are mainly used for the activation of polymers: γ-radiation, electron beam and swift heavy ions (SHI).\textsuperscript{141} Important parameters associated with the irradiation process are: i) the absorbed dose, which is defined as the amount of energy deposited in the polymer material and given in Gray (Gy, equivalent to J kg\textsuperscript{-1}); ii) the radical yield (G value), which is defined as the number of free radicals generated for 100 eV energy absorbed per gram of material, and describes how efficiently radicals can be created in the respective polymer material and iii) the linear energy transfer (LET) value describing the energy transfer to the polymer per unit length for a given type of radiation.\textsuperscript{142}

The main difference between γ- and electron radiation and swift heavy ions is the nature of the radiation. γ-rays (photons) are electromagnetic radiation, whereas electrons and swift heavy ions are charged particles and therefore the interaction with the polymer material is different. The majority of photons passes the material without interaction, yet upon one of the comparatively rare interaction events, they lose almost all of their
energy. Electrons and swift heavy ions, on the other hand, lose energy almost continuously on their way through the bulk material by many small energy transfers.\textsuperscript{142}

Nevertheless, intense investigations showed that $\gamma$-radiation as activation source for radiation grafting leads to a higher damage of the base film, compared to electron irradiation, as the dose rate that can be achieved with $\gamma$-radiation is smaller and thus the irradiation time is prolonged. Therefore, at the Paul Scherrer Institute the activation of the polymer films was changed from $\gamma$- to electron radiation over the years.\textsuperscript{143}

Another important feature is the homogeneity of introduced activation. Whereas $\gamma$- and electron irradiation leads to a homogeneous distribution of the activated sites throughout the polymer film (characterized by a low LET value, e.g. around 0.3 keV $\mu$m$^{-1}$)\textsuperscript{141}, the irradiation with swift heavy ions (characterized by a high LET value, e.g. more than 100 keV $\mu$m$^{-1}$)\textsuperscript{141} generates linear local tracks of damaged material and reactive species that can be used for subsequent grafting procedures. The fundamental differences in both approaches and their impact on membrane properties is the focus of Chapter 8.

1.3.3. Base Polymers and Irradiation Effect

Radiation grafted membranes are synthesized by applying ionizing radiation on polymer base films with a subsequent modification. These polymer films are manufactured on an industrial scale for various applications. Unfortunately, radiation grafting is not yet one of the targeted applications, thus making it inevitable to be aware of the requirements needed for an efficient and successful membrane synthesis to select the most suitable commercially available polymer film. One of the most important prerequisites is the ability to yield sufficiently stable active sites upon irradiation which can be used as initiators for the subsequent grafting reaction. In addition, the active sites must be accessible for the monomer meaning that the base film has to allow diffusion of the monomer into the bulk of the material. In special cases, such as in ethylene-$\textit{alt}$-tetrafluoroethylene (ETFE), monomer diffusion is only facilitated upon modification by the ongoing polymerization (cf. Section 1.3.4). The polymer itself should be hydrophobic to trigger the hydrophilic (grafts) – hydrophobic (base film) phase separation, being essential for the efficient formation of hydrophilic channels and thus the proton conductivity of the final membrane. Finally, it should possess a sufficient thermal, mechanical and chemical stability to withstand the conditions generated in the fuel cell.

Among the wide range of available polymeric films, fluorinated polymers are especially suitable for radiation grafting due to their high thermal stability, the pronounced
hydrophobicity that is essential for the phase separation in the later membrane, the chemical resistance, particularly against oxidation and hydrolysis and their low permeability to gases as well as low flammability.\textsuperscript{144, 145}

The pool of possible fluorinated base films contains polytetrafluoroethylene (PTFE), ethylene-\textit{alt}-tetrafluoroethylene (ETFE), fluorinated ethylene propylene (FEP), perfluoroalkoxy alkane (PFA), polyvinyl fluoride (PVF), polyvinylidene fluoride (PVDF) etc., but due to this thesis being focused on the partially fluorinated base film ETFE, the following discussion of base film properties is restricted to the fluorinated or partially fluorinated polymers PTFE\textsuperscript{146-148}, ETFE\textsuperscript{149-152}, FEP\textsuperscript{136, 153-155} and PVDF\textsuperscript{156, 157} most commonly used in radiation grafting. More information on other polymers can be found in recent reviews\textsuperscript{43, 158, 159}.

Upon irradiation of the polymer film numerous reactions take place. Bond scission occurs predominantly homolytically yielding radicals but also to a minor extent heterolytically forming ionic groups.\textsuperscript{160} The polymer chains can undergo several modifications like chain scission, crosslinking or cyclization. Moreover, the release of volatile products or the formation of unsaturated groups such as double bonds can be observed.\textsuperscript{150, 160-162} If the irradiation is conducted in the presence of oxygen, peroxyl radicals and their derivatives, e.g., hydroperoxides are generated, which as mentioned above can be used for the initiation of the grafting reaction. The formation and ratio of these produced “damages” is dependent on the polymer material, additives contained therein, temperature, the type of irradiation and the applied dose.\textsuperscript{142}

Regarding the irradiation of the base film, the yield of radical species is an important parameter. The radicals formed within the bulk material can be measured by EPR or ESR (electron paramagnetic resonance/electron spin resonance).\textsuperscript{163} The availability of radiation data for fluorinated polymers, however, is quite limited and only a small number of studies have been reported as outlined below.

Partially fluorinated substrates show better radiation stability than their perfluorinated counterparts. The response to radiation of PVDF displaying a partially fluorinated polymer and PTFE as a fully fluorinated polymer can be exemplarily compared. The radiation chemical yield (G value) for the formation of radicals in PVDF is much higher (3.3)\textsuperscript{26} compared to that of PTFE with 0.14 – 0.40 \textsuperscript{164-166} and more crosslinking events take place (PVDF: 0.65 – 1.0 crosslinking events per 100 eV of absorbed dose \textsuperscript{167-169}; PTFE: 0.1 – 0.3 \textsuperscript{170}). PTFE is very sensitive towards ionizing radiation, leading to a high number of chain scission events (higher by a factor of ten compared to PVDF; PTFE: 1 – 4 chain scission events per 100 eV of absorbed dose \textsuperscript{164, 171}; PVDF: 0.3 – 0.64 \textsuperscript{167-169}). Another important aspect is the evolution of gaseous decomposition products, which is
not only much higher in case of the partially fluorinated PVDF compared to PTFE (PVDF: 1.7\textsuperscript{172}; PTFE: 0.02 \text{–} 0.3\textsuperscript{141, 171, 172}) but also the products are more toxic. In contrast to PTFE, which yields mainly CO, CO\textsubscript{2} and CF\textsubscript{2}O\textsuperscript{141}, the main gaseous product of PVDF is HF\textsuperscript{173}. With view to industrial upscaling, these byproducts must be considered and suitable safety precautions should be established, especially in case of the highly toxic HF. The formation of the even more hazardous F\textsubscript{2}, however, is unlikely as the probability for a fluorine atom transfer and associated disproportionation reactions leading to F\textsubscript{2} formation in analogy to H\textsubscript{2} formation in polyolefins\textsuperscript{141, 174} are insignificant in case of fluoropolymers due to an increased bond strength. PTFE exhibits a very low stability against irradiation due to the lack of a “pull linkage” as delivered by the C-H bond in partially fluorinated polymers. Taking into account the covalent bond energies present in these polymers (C-C: 345 kJ mol\textsuperscript{-1}; C-H: 416 kJ mol\textsuperscript{-1}; C-F: 489 kJ mol\textsuperscript{-1})\textsuperscript{175}, main chain scission is prevalent in perfluorinated polymers. To give a rough estimation for other fluorinated polymers, the tendencies for crosslinking and degradation are as follows:\textsuperscript{140}

Crosslinking: PVDF > ETFE > FEP > PTFE
Degradation: PTFE > FEP > ETFE > PVDF

These trends show that with higher fluorine content chain scissions are favored, whereas with rising hydrogen content the crosslinking reactions are preferred.

In another work by Mitov et al., the radical yield was measured by ESR and EPR spectroscopy for the partially fluorinated base films ETFE, PVDF and FEP.\textsuperscript{163} ETFE shows the highest radical yield, whereas FEP yields the lowest. The radical yield at low doses can be estimated to be around 2 for PVDF and ETFE and 1.4 for FEP. Approaching higher doses, the radical yield declines due to recombination reactions.\textsuperscript{163} Another event reducing the radical yield is the formation of hydroperoxides when the irradiation of PVDF or ETFE is carried out in air. In FEP base films, however, the irradiation in air increased the radical concentration, which was attributed to a facilitating effect of oxygen on the chain scission mechanism and therefore a higher number of formed radicals.\textsuperscript{163}

Other properties that effect the performance of the later PEM are, e.g., the crystallinity of the base film. On the one hand, grafting only proceeds in the amorphous phase. On the other hand, a higher base film crystallinity increases the mechanical strength of the PEM, the glass transition temperature, which influences the accessibility of active sites.
in the bulk material and the mechanical integrity of the PEM, the melting point (mechanical strength at elevated temperature) and the molecular weight. A comparison of these values for selected fluorinated base films can be found in reference 176.

As already outlined before, the mechanical stability of a PEM is of major interest as the loss of it does not only lead to an operational failure of the fuel cell but also causes safety issues. Therefore, a high mechanical stability of the base film even after irradiation is essential as grafting and functionalization will further decrease this characteristic. The influence of irradiation on the mechanical properties of different base films was analyzed by Chen et al. (Figure 1.13).177 As reasoned above, perfluorinated polymers, i.e., PTFE, FEP and PFA, showed the highest impact of irradiation and a significant decrease in fracture toughness, due to chain scission and other degradation effects. The partially fluorinated polymers, on the other hand, show a much smaller effect of increasing dose. ETFE is reported to show the highest fracture toughness over the whole range of applied doses. PVDF exhibits a much smaller elongation at break value but a good maintenance of mechanical properties upon irradiation.

![Figure 1.13: Mechanical properties of various fluoropolymers, expressed as elongation at break value, as a function of irradiation dose in air.177 Reprinted from J. Membr. Sci., Chen, J.; Asano, M.; Maekawa, Y.; Yoshida, M., Suitability of some fluoropolymers used as base films for preparation of polymer electrolyte fuel cell membranes, 249-257, Copyright 2006, with permission from Elsevier.](image-url)
Grafting and functionalization further reduce the mechanical stability, which can be expressed by the elongation at break value. It could be shown that the irradiation had only an insignificant influence on the elongation at break, whereas the grafting and the subsequent sulfonation reduced the value from \( \sim 300\% \) to \( \sim 100\% \). Furthermore, the comparison with Nafion\textsuperscript{®} proves the ETFE based radiation grafted membrane to possess a higher mechanical stability than the industrial benchmark.\textsuperscript{178}

1.3.4. \textit{“Grafting Front” Mechanism in Radiation Grafting}

The modification of fluorinated base films is often accompanied with problems arising from their insufficient swelling in the reaction solution (solvent, reagents, additives, etc.). This was already described and investigated by Chapiró\textsuperscript{179} who proposed that radiation grafting of base films that show little to no swelling in the grafting solution propagates through the so-called grafting front mechanism (Figure 1.14).\textsuperscript{180-182} The grafting is initiated at the surface of the polymer film and the already grafted areas swell in the monomer solution thereby facilitating further monomer diffusion towards the center of the film. Grafting occurs from both sides of the base film with grafting fronts moving towards the center of the film and eventually coalescing. The shape and extent of these grafting fronts can vary depending on the diffusion coefficient of the monomer into the base film and the polymerization rate, thus leading to a complex reaction-diffusion mechanism.\textsuperscript{183-185} Two simplified examples of grafting fronts propagating into the bulk of the base film are shown in Figure 1.14.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{grafting_front.png}
\caption{Illustration of the grafting front mechanism in radiation grafting (see text).}
\end{figure}
If monomer diffusion is much slower than the polymerization rate, monomers entering the base film are instantly consumed by the polymerization of the grafted chains and the grafts in the surface area basically reach their statistical chain length before propagation towards the inner regions can occur (Figure 1.14 a). This leads to very sharp fronts of highly functionalized base film and non-modified base film regions in the center.

If the diffusion of the monomer into the base film is faster than the polymerization, a fraction of monomer is not consumed by the growing graft chains and enters the bulk of the base film through the “opened-up” structure of the grafted regions. New grafted chains are started in the center of the film, while the polymerization at the outer parts still continues. This leads to a more flat geometry of the grafting fronts and their coalescence at an early stage (Figure 1.14 b).

For the application of proton conducting membranes where protons have to be transported in the through-plane direction, a good connection of functionalized regions is essential. The shape and extent of the grafting fronts can be influenced by parameters such as the reaction temperature, the swelling of the polymer film in the monomer solution, dose rate (simultaneous grafting) / total dose (pre-irradiation grafting), the monomer concentration and polymerization rate as well as the film thickness. Some of these aspects have been investigated in Chapter 6.

1.3.5. Optimized PSI Gen 2 Membrane

As mentioned in Section 1.2.3.3. PSSA based materials show significant degradation under fuel cell operating conditions. This was also the case for the first generation of PSI membranes, FEP-g-PSSA. Under constant current conditions (80°C, H₂/O₂, 1 bar, 100% r.h., 0.5 A cm⁻²) the durability of this type of membrane was limited to around 50 hours.₁³¹ To increase the stability and as a first step towards the optimization of radiation grafted membranes, the degree of crosslinking was found to be an important parameter.₁³₅ The addition of crosslinker, however, forces one to accept a compromise between proton conductivity and stability as the incorporation of crosslinking agents successfully reduces the dimensional change and water-uptake. Though a smaller dimensional change upon swelling is beneficial for the lifetime of a PEM, the reduced water-uptake also entails a decreased proton conductivity. In case of FEP based grafted membranes, the addition of the crosslinking agent divinylbenzene (DVB, Figure 1.15) could reduce the area shrinkage from 29 to 15%.₁⁴³ However, a further increase in crosslinking agent incorporation causes not only a strongly reduced proton conductivity but also deteriorated mechanical properties, leading to brittle and poorly processable membranes.₁⁴⁹ Crosslinked membranes are more dense and show a reduced water-
uptake, which affects the gas crossover during fuel cell operation leading to a lower permeation of reactant gases and therefore less radical formation. Together with the more strongly linked PSSA chains this leads to a significant increase in durability from the above mentioned 50 h to 7900 h under the same test conditions.

![Chemical structures of FEP-g-P(SSA-co-DVB) and FEP-g-P(AMSSA-co-MAN).](image)

**Figure 1.15:** Chemical structures of FEP-g-P(SSA-co-DVB) and FEP-g-P(AMSSA-co-MAN).

During the last decades, intensive research was undertaken on the decomposition pathways and mechanisms of PSSA grafted membranes in the fuel cell. It was found that the α-hydrogen of the styrene moiety represents the weak link and is readily attacked by radical species formed, leading to chain scission and the loss of graft component. Apart from more strongly crosslinked PSSA chains which cannot be washed out after single chain scissions, α-protected derivatives were investigated. TFS is one of these monomers - which was also discussed in Section 1.2.3.2. - that was investigated in this context, but due to slow reaction kinetics, difficulties in sulfonation and the high costs of the monomer, TFS grafted membranes could not be established as a suitable alternative. An evident solution to this problem is the blocking of the α-hydrogen by a methylene group. α-methylstyrene (AMS) was used for grafting reactions but showed only poor radical polymerization kinetics and is therefore hardly usable for grafting reactions. In 2006 Li et al. reported the co-grafting of AMS with styrene and could demonstrate that the kinetics of AMS can be improved by adding suitable co-monomers. Another co-monomer that could significantly improve the grafting kinetics of AMS is acrylonitrile (AN). In order to increase the chemical stability of the co-monomer, AN was exchanged by α-methyl acrylonitrile (MAN) to protect the α-hydrogen of the nitrile moiety (Figure 1.15). This strategy resulted in an increased lifetime of 550 h compared to the original 50 h under the same conditions.

In the next step both strategies – crosslinking and protection of the α-position – were combined to generate a crosslinked membrane with stabilized grafts. This membrane
showed a high durability. However, the lifetime of the so far optimized membrane could not be determined due to failure of the test setting after 1100 h. \textsuperscript{194, 195}

The final step towards optimization comprised a change of the base film from FEP to the more stable ETFE, which also shows a higher radical yield and grafting efficiency, and the incorporation of the optimized crosslinking agent diisopropylene benzene (DIPB). This so-called PSI Gen2 membrane is synthesized with a molar ratio of AMS to MAN of 1:1 and a grafting level of 40 – 45\%.\textsuperscript{37} The chemical structure is given in Figure 1.16.

![Chemical structure of PSI Gen2 and MEA lifetime under dynamic operating conditions (80°C, 50% r.h., 2.5 bar) compared to commercial Nafion membranes.](image)

**Figure 1.16:** Chemical structure of PSI Gen2 and MEA lifetime under dynamic operating conditions (80°C, 50% r.h., 2.5 bar\textsubscript{a}) compared to commercial Nafion membranes.\textsuperscript{37}

The direct comparison of the Gen2 membrane with Nafion NR212 and Nafion\textsuperscript{®} XL-100 could prove its superior properties. The lifetime is increased by about one third compared to the stabilized Nafion\textsuperscript{®} of the XL-100 series while maintaining a fuel cell performance comparable to that of the commercial standard (Figure 1.16).\textsuperscript{37} Table 1.2 shows selected parameters of PSI Gen2 compared to Nafion\textsuperscript{®} 212 and Nafion\textsuperscript{®} XL-100. It could be shown, that radiation grafted membranes represent a versatile and powerful alternative to the existing commercially available membranes like Nafion\textsuperscript{®}. 

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\textsuperscript{194} [Reference]

\textsuperscript{195} [Reference]

\textsuperscript{37} [Reference]
1. Introduction

**Table 1.2:** Characteristic properties of PSI Gen2 membrane compared to commercial Nafion® membranes.\(^3\)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>thickness [µm]</th>
<th>IEC [mmol g(^{-1})]</th>
<th>water-uptake [wt%]</th>
<th>conductivity [mS cm(^{-1})]</th>
<th>H(_2) crossover [mA cm(^{-2})]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in water swollen state at RT</td>
<td>in water swollen state at RT</td>
<td>80°C, 50% r.h., 2.5 bar,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSI Gen2</td>
<td>40 ± 2</td>
<td>1.59 ± 0.03</td>
<td>27 ± 6</td>
<td>73 ± 12</td>
<td>0.82 ± 0.02</td>
</tr>
<tr>
<td>Nafion NR212</td>
<td>64 ± 1</td>
<td>1.10 ± 0.01</td>
<td>42 ± 1</td>
<td>97 ± 15</td>
<td>2.54 ± 0.03</td>
</tr>
<tr>
<td>Nafion XL-100</td>
<td>33 ± 2</td>
<td>0.90 ± 0.01</td>
<td>34 ± 8</td>
<td>56 ± 5</td>
<td>4.09 ± 0.39</td>
</tr>
</tbody>
</table>

### 1.4. Structure-Property Correlations in PEMs

Despite the increasing interest in grafted membranes for fuel cell application and the intensive research for high performing, versatile and, most importantly, cost-competitive PEMs,\(^3, 29-32\) the understanding of the polymer structure and morphology as well as its impact on properties such as proton mobility and conductivity is rather limited.\(^33, 34\) In the last years several overview articles have summarized the restricted pool of investigations on structure-property relations in all classes of PEM materials and highlighted the importance of such studies for the development of high performing PEMs.\(^1, 35, 51, 114, 196\)

As already mentioned in Section 1.2.2., it can be beneficial for the understanding of the impact of structure on PEM properties to consider proton exchange membranes as consisting of two phases – a structural component and a functional one (acid groups and water domain) – and attribute specific properties to a specific domain.\(^51\)

The structure of the final PEM is defined by the characteristics of the two components (Figure 1.17). In case of radiation grafted membranes, such as ETFE-g-PSSA the base film dominates the structural phase and its properties such as crystallinity, extent of hydrophobicity, molecular weight, possible branching and crosslinking are crucial. Important characteristics of the electrolyte constituent (PSSA grafts in the above example), on the other hand, are for example the kind of protogenic group, the flexibility of graft chain and the ionic site density. The interplay between these
components – and how they interact with water – influences the transport properties of protons but also of water and reactants.

In this section several tunable parameters and their impact on PEM properties will be presented. Among these parameters, special attention will be paid on investigations of polymer architecture.

**Figure 1.17:** Schematic representation of the conceptual approach to consider PEMs as a two phase system and attribution of several tunable parameters that influence the final structure and therefore properties of PEMs.

One of the most obvious parameters influencing proton conductivity is the acidic strength of the protogenic group as a higher acidity will result in a higher number of dissociated protons even under reduced humidification. Proton conductivity is strongly depending on the number of available charge carriers, therefore a sufficient acidic strength is essential. The effect of increased acidic strength was for example investigated by the group of Watanabe. They used a poly(arylene ether) membrane type to
compare the properties of a membrane with incorporated superacidic perfluorosulfonic acid groups (pKa < -6) with those bearing sulfonic acid groups directly attached to the aromatic backbone (pKa ~ -1). The membranes with higher acidic strength showed significantly increased proton conductivity, which was attributed not only to the facilitated proton dissociation but also to the enhanced phase separation that was induced by the stronger hydrophilicity. This concept was also followed by the group of Kerres in the development of poly(pentafluorostyrene sulfonic acid) grafted onto ETFE. As mentioned previously, phase separation is driven by the dissimilarity between the hydrophobic and hydrophilic components and is an important factor in high performing PEMs. The impact of a higher dissimilarity was for example shown by the group of Holdcroft. The authors compared PS-g-PSSA membranes with PSSA grafted to poly(acrylonitrile) (PAN) backbone chains. With the PAN backbone being more hydrophilic than the PS backbone this allowed the authors to investigate the effect of backbone hydrophilicity/hydrophobicity on the morphology and membrane properties such as proton conductivity and water-uptake. Though TEM micrographs showed no differences in ionic domain morphology, differences in proton conductivity and water-uptake were rather pronounced. The more hydrophilic PAN did not restrict the water-uptake to the same extent as the PS backbone, which resulted in much larger swelling for equivalent IEC values. However, this higher content of water did not result in a higher proton conductivity. For IEC values above 1.3 mmol g\(^{-1}\) PS-g-PSSA membranes showed a significantly higher conductivity than PAN-g-PSSA membranes suggesting that a large fraction of the water is not situated in the proton conducting channels but associated with the PAN backbone. This was strengthened by the observation that TEM micrographs started to show differences between both types of membrane upon hydration.

The example discussed above shows that despite the general association that a higher water-uptake (or more accurately: a higher number of water molecules per sulfonic acid group; \(\lambda\)) increases the proton conductivity it is not that trivial. A higher water volume fraction is surely beneficial but at the same time the state of the incorporated water and its involvement in proton transport is important. Physical (e.g. geometrical confinement) and chemical (e.g. electrostatic interaction with immobilized ionic groups) influences on the water molecule affect its diffusion coefficient and thermal behavior. These differences can be analyzed via NMR techniques or differential scanning calorimetry (DSC). DSC measurements allow the differentiation of water into three categories (tightly bound, loosely bound and free water) depending on the melting behavior. A comparison between a sulfonated poly(arylene ether sulfone) (BPSH)
membrane and Nafion® shows that in Nafion® the amount of loosely bound and free water, which can participate in proton transport is higher and starts to form at lower values of water-uptake.\textsuperscript{204} The high fraction of more tightly bound water in BPSH is reported to induce lower proton conductivity.

Another very important parameter that affects membrane properties is the processing or history of polymer membranes. Different processing conditions can induce different morphologies and transport properties in chemically identical polymers. Not only the properties of Nafion® were found to be different depending on its thermal history\textsuperscript{118} but also in BPSH the transport properties changed upon thermal treatment.\textsuperscript{205} Kim \textit{et al.}\textsuperscript{205} found that there is an optimum temperature for treatments in liquid water yielding a distinct morphology which facilitates proton conductivity and leads to an increased cell performance. Elabd \textit{et al.}\textsuperscript{206-208} investigated the properties of a triblock copolymer consisting of partially sulfonated polystyrene blocks and polyisobutylene (S-SIBS) and found not only different morphologies ranging from periodic lamellar microdomains to non-periodic co-continuous microdomains depending on the ionic content of the membrane but also increased proton conductivity when tetrahydrofuran was used as a solvent for casting instead of, e.g., chloroform. Furthermore, significant differences have been found between Nafion® membranes in solution cast form or prepared by extrusion. Casting temperature, solvent and counter-ion are investigated on their effects on membrane properties.\textsuperscript{64, 209-211}

A highly interesting work was performed by Park and Balsara on symmetric diblock copolymer films of sulfonated polystyrene and polymethylbutylene.\textsuperscript{212, 213} The authors subjected the polymer to different processing techniques such as solvent casting, pressing of the cast film, orientation in an electric field, or shear alignment and analyzed the impact on morphology and proton conductivity (Figure 1.18). It was reported that pressing isotropic samples, which were obtained by casting, yielded highly anisotropic membranes with a lamellar structure aligned in the plane of the film (perpendicular to the transport direction of protons in a FC) and that this anisotropy was also reflected in a pronounced conductivity difference in both directions (in-plane and through-plane). The application of electric or shear fields on the isotropic samples, on the other hand, resulted in membranes with a lamellar structure aligned perpendicular to the plane of the film. However, the extent of alignment was not as high as in the pressed samples and the increase of through-plane proton conductivity compared to the isotropic sample was less than 20%.
1.4.1. **Copolymer Architecture**

For a deeper understanding of the effects of copolymer architecture on morphology and membrane properties such as proton conductivity and water-uptake model polymeric or oligomeric systems are used to investigate whether, for example, a diblock, multiblock, random or graft ionic copolymer is favorable. A random copolymer is a polymer with a statistical distribution in the monomer sequence whereas alternating copolymers have a strictly alternating repeat unit. Block copolymers are linear polymers comprising two or more homopolymer subunits. They can be further categorized depending on the number of subunits (diblock, triblock, multiblock). Graft copolymers, on the other hand, are non-linear polymers with grafted chains consisting of a different repeating unit than the main chain attached to it. They are often considered as a special type of block copolymers.

In alternating and random copolymers the homopolymer sequence is usually too short to allow phase separation. Therefore, these types of polymers tend to show a single-phase morphology. Block and graft copolymers, however, can be synthesized with a variety of compositions and chain lengths that allows the study of a variety of morphologies. Graft polymers consisting of ionic grafts attached to a hydrophobic backbone allow in principle the design of the size of ionic clusters which would be
determined by the lengths of the grafts and the number of ionic domains being determined by the number density of grafts. The size and number density of ionic clusters is expected to control the percolation threshold in these membranes.

Holdcroft et al. synthesized PS-g-PSSA with a controlled graft length of 32 repeat units and variable graft density. The properties of these graft copolymers were compared with random polymers of styrene and styrene sulfonic acid (PS-r-PSSA) of equal ionic content to investigate the impact of polymer architecture on phase separation and morphology. The random analogue showed no distinct phase separation whereas the graft structure caused a sharp and well-defined nanophase separation together with continuous ionic channels. This structural difference was shown to have a huge impact on water-uptake and proton conductivity. As in the random structure the hydrophobic parts were more distributed and less ordered than in the graft polymer their ability to restrict swelling was not sufficient to prevent excessive water-uptake compared to the graft system. Moreover, the proton conductivity was higher for PS-g-PSSA than for PS-r-PSSA. This can be attributed to the more pronounced phase separation and clustering of ionic domains, which facilitates proton transport in the graft system and a dilution of charge carriers by the excessive water-uptake in the random analogues. For example, at an ion content of 16 mol% the proton conductivity in the graft system was 13 times higher while the water-uptake was only 40% of the water-uptake in the random analogue.

![Graft structure](image1.png) ![Block co-polymer structure](image2.png)

**Figure 1.19:** Schematic representation of graft and block copolymer architecture.

The same group investigated the differences in graft versus diblock copolymer architecture (Figure 1.19) using copolymers containing fluorous and sulfonated styrene units. TEM micrographs of the dry membranes showed that the morphologies of the graft derivative (P(VDF-co-CTFE)-g-PSSA) are characterized by an interconnected network of small ionic clusters of 2 – 3 nm in size, which the authors indicated as similar to the “cluster-network” in Nafion (10 nm ionic clusters interconnected by narrow ionic channels). The diblock membranes (P(VDF-co-HFP)-b-PSSA), on
the other hand, formed well-segregated morphologies of ion-rich, lamellar (or perforated lamellar) structures with a long-range ionic order. Furthermore, they showed an excessive swelling in water, exhibited poor mechanical properties, and an inferior proton conductivity in the through-plane direction. In contrast, the graft polymer tolerated much higher ionic contents without excessive swelling and dissolution, which led to membranes that possessed highly concentrated, isotropically connected ionic domains.

Figure 1.20: Schematic representation of variations in graft length and graft density.

In order to investigate the morphological impact of graft length, graft density and ionic content, Chung et al. used atom transfer radical polymerization (ATRP) to synthesize the model system P(VDF-co-CTFE)-g-PSSA (Figure 1.20). The three described parameters were carefully controlled to obtain on the one hand graft copolymers possessing low graft density (0.3 – 0.8 mol%) and long PSSA graft length (DPstyrene = 70 – 120), which formed a microphase separated morphology with long-range ionic channels (lamellar / cylindrical), embedded in a highly crystalline fluorocarbon matrix. On the other hand, they synthesized graft copolymers with higher graft density (1.4 – 2.4 mol%) and short PSSA graft length (DPstyrene = 10 – 30) that exhibited a disordered cluster network morphology with small cluster size. The latter showed an improved performance under low r.h. conditions and increased conductivity at higher temperatures together with a less pronounced swelling behavior. Apart from this, Chung et al. also reported that the molecular weight ($M_w$) of the P(VDF-co-CTFE) backbone has a significant effect on the water swelling behavior of the membrane and a higher $M_w$ is favorable as it results in smaller ionic channel width and enhanced resistance to excessive water swelling at higher ionic contents.

This work was further intensified by Holdcroft et al. who synthesized a series of P(VDF-co-CTFE)-g-PSSA model systems with a fixed graft density but varying graft
chain length ($\text{DP}_{\text{styrene}} = 35, 88, 154$) and sulfonation levels to evaluate its impact on membrane morphology and membrane properties. Thereby, they could confirm the key role of the graft length for proton conductivity. Membranes synthesized with long graft chains and a low sulfonation level resulted in smaller ionic clusters, which, according to Holdcroft, allowed them to retain more water at low humidity conditions and therefore maintain higher proton conductivity at temperatures above 70°C and over a wide humidity range.

The above mentioned research results have clearly outlined the importance of phase separation and microstructure on the magnitude of proton conductivity. However, most of these studies have been performed on solution cast membranes synthesized by lab-scale techniques such as ATRP. Structure-property correlations in approaches like radiation grafting which can be, on the one hand, easily scaled up and, on the other hand, have the particularity of modifying a preformed film instead of ending with a casting procedure are rare to find. Although the insights gained with the above mentioned studies are to some point of a general nature, it is reasonable to assume that grafting in a preformed matrix will be accompanied by restrictions that are not present when synthesizing a graft polymer in solution and subsequent solution casting. These restrictions will most probably affect the obtained morphology and thus the properties of the final membrane. Therefore, it is essential to extend the investigations on structure-property correlations to this type of membranes.
Chapter 2.  Methods and Experimental Techniques

This chapter comprises a collection of experimental techniques used in the course of this thesis. Most of the information can also be found in the following sections where the experimental techniques used in the respective chapter are described. However, this section is intended to give a compact summary to facilitate accessibility to the reader as well as some extended information.
2. Methods and Experimental Techniques

2.1. Membrane Synthesis

2.1.1. Materials

The base polymer ETFE was purchased from two different suppliers: DuPont (Tefzel® 100LZ, Circleville, USA, 25 μm film) and Saint-Gobain (Norton®, Courbevoie, France, 25 μm film).

The reagents used during membrane synthesis included styrene (98%, Fluka), 1,3-diisopropenyl benzene (DIPB, 97%, Sigma Aldrich), glycidyl methacrylate (GMA, 97%, Sigma Aldrich), 2-propanol (IPA, PROLABO®, VWR), ethanol (PROLABO®, VWR), acetone (PROLABO®, VWR), chlorosulfonic acid (98%, Fluka) and dichloromethane (PROLABO®, VWR). All reagents and the monomer were used as received without removal of inhibitors. In all cases ultra-pure water (18.2 MΩ·cm, ELGA) was used and hydrogen, oxygen and nitrogen (Messer, Lenzburg, Switzerland) of a purity of at least 4.5 were used as received.

2.1.2. General Procedure

Rectangular samples were cut from the base film roll (16 cm in the machining direction, MD, and 14 cm in the transverse direction, TD). The samples were washed in ethanol and dried at 60°C under reduced pressure (~10 mbar) before storing in zip-lock PE bags for the irradiation procedure. In the standard procedure electron irradiation was used to activate the base films, which were subsequently stored at -80°C until used. For the grafting reaction the pre-irradiated films were immersed in a solution containing the monomer(s). Oxygen was removed from the grafting solution by purging with nitrogen before placing the reactors in a thermostatic water bath for the required time. The grafted films were washed with acetone or iso-propanol and extracted with toluene over night before drying under reduced pressure (~10 mbar) and a temperature of 60°C. Subsequent sulfonation was performed as described in Section 1.1.5.

2.1.3. Irradiation

2.1.3.1. Electron Irradiation

For all samples except those described in Chapter 8, electron irradiation was used to activate the base film. The ETFE films were pre-irradiated in an air atmosphere by an electron beam at LEONI Studer AG in Däniken, Switzerland (MeV class accelerator). Figure 2.1 shows a photograph and a schematic representation of
the electron beam facility used. The acceleration voltage was 2.1 MeV with a beam current ranging from 5 to 20 mA. For the different experiments discussed in this thesis deposited doses of 3, 5, 30 and 50 kGy were applied. To protect the samples from backscattering and heating of the aluminum trays, which were used for conveying, cardboard was placed between the aluminum and the samples. The irradiation dose was adjusted by a combination of beam current and the speed of the conveyor and controlled with alanine pellet dosimeters (FarWest Technology Inc.). These dosimeters were placed among the base film samples. After exposure, the irradiated films were immediately placed in dry ice for transportation and stored at -80°C until further processing.

Figure 2.1: Photograph and schematic representation of the electron beam facility at LEONI Studer AG (Däniken, Switzerland).

2.1.3.2. **Swift Heavy Ion (SHI) Irradiation**

The SHI irradiation of the ETFE base films was conducted by Oxyphen AG (Wetzikon, Switzerland). The films were irradiated under vacuum with high-energy ions of Kr ($^{84}$Kr$^{16+}$) at a specific energy of 383 MeV. Four different fluences of the ion-beam were investigated: $100 \times 10^6$ ions cm$^{-2}$, $320 \times 10^6$ ions cm$^{-2}$, $960 \times 10^6$ ions cm$^{-2}$ and $2560 \times 10^6$ ions cm$^{-2}$, which will be abbreviated following the notation $K_{xy}$ (= $xy \times 10^6$ ions cm$^{-2}$). All films were stored at -80°C until used.
2.1.4. **Grafting Reaction**

Grafting reactions were carried out with 7 cm × 7 cm pre-irradiated ETFE films in a standard glass reactor with a capacity of approximately 60 ml (3 cm diameter, 18 cm height). A larger reactor with a capacity of ~600 mL was used if larger amounts of a sample had to be synthesized (e.g. for the QENS measurements, cf Section 2.6.). This reactor and the standard grafting setup are shown in Figure 2.2.

After determination of the mass of the used base film sample the films were immersed in a monomer solution of 20% (v/v) styrene (S) in 70% (v/v) iso-propanol (IPA) and 10% (v/v) ultra-pure water. The grafting solution was degassed with nitrogen for 1 h before placing the vessel in a thermostatic water bath at 55°C for the duration of the reaction. In order to obtain different degrees of grafting, various reaction times were applied, after which the grafted films were rinsed with acetone or iso-propanol and extracted with toluene for 16 h to remove residual monomer and homopolymer not covalently attached to the base film. Finally, the grafted films were dried at 60°C under reduced pressure (~10 mbar) before determining the mass of the grafted film.

Table 2.1 summarizes the different grafting parameters for the various types of samples discussed in this thesis.

![Figure 2.2: Photograph of the setup used for grafting with nitrogen distribution lines, an exemplary reactor (600 mL) and water baths as indicated in the picture.](image-url)
Table 2.1: Parameters for the synthesis of different radiation grafted films.

<table>
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<td>S</td>
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<td>3, 5 kGy</td>
<td>55</td>
<td>IPA/H₂O</td>
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<td>S</td>
<td>-</td>
<td>30, 50 kGy</td>
<td>50, 55</td>
<td>IPA/H₂O</td>
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<td>5, 7, 9</td>
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<tr>
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<td>-</td>
<td>SHI</td>
<td>55</td>
<td>IPA/H₂O</td>
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<tr>
<td>S / DIPB</td>
<td>9/1, 8/2</td>
<td>5 kGy</td>
<td>55</td>
<td>IPA/H₂O</td>
<td>7/1</td>
<td>20</td>
</tr>
<tr>
<td>S / GMA</td>
<td>7/3, 1/1, 4/6</td>
<td>5 kGy</td>
<td>60</td>
<td>IPA</td>
<td>-</td>
<td>25</td>
</tr>
</tbody>
</table>

2.1.5. Sulfonation

The standard sulfonation procedure for radiation grafted films was used. Sulfonation of the grafted films was performed in a 2 L glass reactor using 2% (v/v) chlorosulfonic acid in dichloromethane. The films were separately placed in the solution and possible gas bubbles were carefully removed with a PTFE rod before the reactor was closed and protected against light with a PVC shielding. After stirring for five hours at room temperature the sulfonated films were removed from the reaction mixture and repeatedly rinsed with ultra-pure water. Hydrolysis of the functionalized films to sulfonic acid groups was performed in water at 80°C for 15 h.

2.2. Ex-Situ Characterization

2.2.1. Gravimetric Determination of the Grafting Level

The graft level of each film was gravimetrically determined using the following equation:

\[ GL = \frac{m_g - m_0}{m_g} \cdot 100\% \quad (2.1) \]

where \( m_0 \) and \( m_g \) represent the mass of the sample before and after grafting, respectively.
2.2.2. **Ion Exchange Capacity (IEC) and Water-Uptake Measurements**

*Ex situ* fuel cell relevant properties, such as the ion exchange capacity (IEC), water-uptake and hydration number were determined in fully swollen state at ambient conditions. The IEC is defined as

$$ IEC = \frac{n(H^+)}{m_{dry}} \quad (2.2) $$

where \( n(H^+) \) is the molar number of protons and \( m_{dry} \) is the dry weight of the membrane. The theoretical IEC of a polystyrene grafted membrane at a specific grafting level (GL) can be calculated using the following equation:

$$ IEC_{th} = \frac{GL}{M_{Styrene} + (M_{Styrene} + M_{SO_3}) \cdot GL} \quad (2.3) $$

The experimental IEC was determined at least three times by titration with each sample consisting of two punched discs (diameter of 2 cm in water swollen state). After a proton/potassium exchange (stirring in 1 M KCl for 12 h at room temperature) the free accessible protons were titrated with a 0.05 M KOH solution by means of a SM Titrino 702 instrument (Metrohm, Herisau, Switzerland).

The water-uptake (\( Q \), swelling) of the membrane displays its ability to absorb water and can be calculated according to the following equation:

$$ Q = \frac{m_{wet} - m_{dry}}{m_{dry}} \cdot 100\% \quad (2.4) $$

The hydration number (\( \lambda \)) is the molar ratio between water and sulfonic acid groups and is calculated from the IEC and the water-uptake values according to:

$$ \lambda = \frac{n(H_2O)}{n(SO_3H)} = \frac{Q}{IEC \cdot M_{H_2O}} \quad (2.5) $$

2.2.3. **Dimensional Change upon Grafting**

In order to investigate the effect of base film anisotropy on the grafting procedure the dimensional change upon grafting was measured for both directions – the machining (MD) and the transverse direction (TD).

Therefore, squares of pristine base film with defined dimensions were prepared and grafted to obtain different graft level. To ensure fast (increased processing time has a
detrimental effect on the radical concentration within the base film) and accurate handling a punching tool (5.4 cm × 5.4 cm) was used as depicted in Figure 2.3.

![Figure 2.3](image)

**Figure 2.3:** Photograph of the punching tool used to ensure an accurate starting dimension for the measurement of the dimensional change upon grafting. One side is marked to ensure distinction between machining direction (MD) and transverse direction (TD).

The dimensions of the grafted films were measured and the dimensional change in the two orientations plotted as a function of GL. The results are discussed in Chapter 3.

### 2.2.4. Infrared (IR) Spectroscopy

The determination of the composition of the grafted films was carried out using Fourier transform infrared spectroscopy (FTIR), on a Perkin Elmer FTIR System 2000 spectrometer. The spectra were recorded at room temperature with a 4 cm\(^{-1}\) resolution in a spectral range from 4000 to 400 cm\(^{-1}\) and 32 scans. The interpretation and curve fitting was performed using GRAMS / AI software (version 9.1) from Thermo Fisher Scientific Inc., assuming a mixed Gaussian and Lorentzian shape for the peak fitting.

#### 2.2.4.1. IR calibration curves

Upon grafting, the introduction of the graft polymer induces an expansion of the film in all three dimensions, which leads to a dilution of the corresponding components and therefore to a decreasing band intensity of, e.g., the peaks corresponding to the ETFE base film. The quantification of single film components can therefore not be done directly using the intensity of the FTIR vibrational bands.\(^{25}\)

In the first step, a calibration curve for homopolymer grafted films (e.g. ETFE-\(g\)-PS and ETFE-\(g\)-PGMA) was established to enable quantitative compositional analysis by transmission FTIR spectroscopy. Homopolymer grafted films at different grafting levels
were analyzed and the integrals of bands corresponding to the grafted monomer were normalized to the bands attributable to the ETFE base film according to:

$$\bar{A} = \frac{A_{\text{Monomer}}}{A_{\text{ETFE}}}$$  \hspace{1cm} (2.6)

This methodology yields a linear dependence of the normalized bands on the gravimetrically measured grafting level (Figure 2.4).

**Figure 2.4:** Example for a calibration curve. For this calibration curve for ETFE-g-PS the characteristic vibration of styrene at 1493 cm\(^{-1}\) was normalized to the characteristic ETFE vibration at 1325 cm\(^{-1}\). The obtained slope is \(m = 45.3 \cdot 10^{-4}\).

For the determination of the GMA content the ratios of the vibrations at 1388 cm\(^{-1}\) and 910 cm\(^{-1}\) (characteristic for GMA) versus ETFE characteristic vibrations at 1325 cm\(^{-1}\) and 509 cm\(^{-1}\) were used (\(m_{1388/1325} = 22 \cdot 10^{-4}, m_{905/1325} = 62 \cdot 10^{-4}, m_{1388/509} = 52 \cdot 10^{-4}, m_{905/509} = 101 \cdot 10^{-4}\)).

For the compositional analysis of co-grafted films the normalized characteristic monomer vibrations (\(\bar{A}\)) were formed and the monomer-specific grafting level was calculated according to:

$$GL_{\text{Monomer}} = \frac{\bar{A}}{m}$$  \hspace{1cm} (2.7)
2.2.5. **Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) Spectroscopy**

To analyze the through-plane distribution of the grafted polystyrene chains on the micrometer scale, sulfonated copolymer films were swollen in water for 2 h, subsequently frozen in liquid nitrogen and fractured to obtain a sharp cross-section area without considerable smearing. Sample holders used for surface or cross-sectional analysis are shown in **Figure 2.5**. Scanning electron microscopy (SEM) images were taken with an FE-SEM Ultra 55 (Carl Zeiss, Oberkochen, Germany) and energy dispersive X-ray (EDX) analysis was performed using a compatible accessory (EDAX TSL, AMETEK) and analyzed with EDAX TEAM™ software (version V4.3). The standard gun-to-sample distance was 8.5 mm with a magnification of 1600 and an acceleration voltage of 10 kV. An aperture of 60 µm was used. The images were taken in the secondary electrons mode. For sulfur distribution profiles perpendicular to the plane of the membrane, ImageJ software (National Institutes of Health) was used.

![Figure 2.5: Photographs of sample holders used for SEM and EDX measurements.](image)

**2.3. Proton Conductivity Measurements**

2.3.1. **In-Plane Proton Conductivity**

The in-plane conductivity was measured at room temperature in fully swollen state by means of a four point-probe conductivity cell (Bekktech BT-112) consisting of four Pt-electrode wires (Figure 2.6a). Rectangular samples (3.0 cm × 1.2 cm) of hydrated membranes were cut and mounted into the cell. To ensure membrane hydration, the
conductivity cell was immersed in ultra-pure water during the measurement (Figure 2.6b). Impedance measurements were performed using a Zahner IM6 (Zahner Messtechnik, Kronach, Germany) where impedance and phase angle were measured at 1 kHz with 10 mV amplitude of the AC perturbation signal and the phase shift of the measured impedance at 1 kHz was below 5° to ensure that the measured value is the true ohmic resistance. The thickness of the membranes was measured with a thickness gauge (MT12B, Heidenheim, Germany).

Figure 2.6: Photographs of a Bekktech BT-112 cell used for in-plane conductivity measurements in fully swollen state (a). To ensure humidification the cell was placed in ultra-pure water during the measurement. The photograph b) shows this setup without water.

The conductivity can be calculated according to:

$$\sigma = \frac{d}{R \cdot w \cdot t}$$

(2.8)

With $\sigma$ representing the proton conductivity in $\text{S cm}^{-1}$, $d$ the distance between the two voltage sense probes (inner Pt clamps, 4.2 mm), $R$ the measured resistance in $\text{k}\Omega$, $w$ the width of the sample in cm (1.2 cm in the present case) and $t$ the thickness of the membrane in water swollen state ($\mu\text{m}$).

2.3.2. Through-Plane Proton Conductivity

To characterize the through-plane proton conductivity at different relative humidity values is an important tool to compare different membranes and evaluate the impact of compositional or structural changes on membrane properties.
The through-plane proton conductivity in dependence of the relative humidity (r.h.) was measured in a four point-probe setup with the 740 Membrane Test System from Scribner Associates Inc. (North Carolina, USA) at a temperature of 80°C (Figure 2.7).

![Figure 2.7: Photographs of the membrane test system (MTS-740) used for through-plane conductivity measurements at different relative humidity values and a temperature of 80°C. a: MTS-740 as purchased from Scribner Associates Inc. (North Carolina, USA) and an additional pressurized water vessel at the bottom. b: Cell head with attached distance indicator to adjust a pressure of 19.2 bar. c: Magnification of the part of the cell head that includes the sample and is inserted in the measurement chamber. d: Membrane sample with attached gas diffusion electrodes as used in the measurement setup.]

Each sample was compressed between gas diffusion electrodes from E-TEK DivisionSM (ELAT HT-140E-W) with a pressure of 19.2 bar. This pressure was adjusted via a defined length compression of a spring implemented inside the cell head (Figure 2.7b). To ensure comparability all samples were subjected to the same measurement protocol consisting of 2 h preconditioning at 95% r.h., followed by stepwise decrease of r.h. At each new r.h. the sample was conditioned for 45 min per 15 – 20% r.h. decrease and 30 min per 5 – 10% r.h. decrease. The proton conductivity was measured at relative humidity values of: 95, 90, 80, 55, 50, 35, 30, 10 and 5% r.h.
Electrochemical impedance spectroscopy (EIS) (N4L PSM1735, Newtons4th Ltd, Leicester, UK) was performed after each step for a frequency range between $10^7$ and 1 Hz and with an amplitude of 10 mV at open circuit potential. 5% H$_2$ in N$_2$ gas was fed to the sample chamber at a flow rate of 500 mL min$^{-1}$. The specific conductivities were calculated based on the thicknesses of the fully hydrated membranes, which were measured with a thickness gauge (MT12B, Heidenheim, Germany). The specific conductivity was determined using the following equation:

$$\sigma = \frac{l}{A \cdot R_{ohmic}}$$

(2.9)

where $A$ is the overlapping area of the electrodes (0.5 cm$^2$), $l$ is the membrane thickness and $R_{ohmic}$ is the high frequency intercept of the complex impedance with the real axis.

**Figure 2.8:** Exemplary impedance spectra (Nyquist plot) and applied equivalent circuit model for high relative humidity values (a) and low relative humidity values (b). See text for details.

The ohmic resistance of the membrane ($R_{ohmic}$) was calculated using an equivalent circuit model to fit the obtained data (Figure 2.8). For this the program ZView (version 3.4b, Scribner Associates, Inc.) was used.
For relative humidity values between 95% and 30% r.h. an equivalent circuit model comprising the ohmic resistance of the membrane \( R_{\text{ohmic}} \), two different charge transfer resistances \( R_{\text{CT}} \) and \( R_{\text{ct}} \) and two different constant phase elements (CPE) were used (Figure 2.8, a). For low relative humidity values (10% and 5% r.h.) also bulk capacity effects had to be accounted for \( C_{\text{bulk}} \), Figure 2.8, b).

### 2.4. Small Angle Scattering (SAS) Experiments

Small angle scattering (SAS) experiments were performed in the framework of the CROSS Departmental Initiative and European Soft Matter Infrastructure (ESMI) project (Integrated Infrastructure Initiative Nr. 262348), in collaboration with the laboratory of neutron scattering and imaging (LNS) at PSI, the Adolphe Merkle Institute (AMI) and the Division of Physical Chemistry of the University of Lund.

Small angle scattering of X-rays (SAXS) or neutrons (SANS) are experimental methods applied for the structural characterization of various materials in length-scales ranging from a few nm to hundreds of nm. The fundamentals of both techniques are the same only differing in the used probes and the sensitivity associated with them. X-ray scattering is sensitive to electronic density differences as they may arise not only from different chemical compositions but also for example from the differences between crystalline and amorphous phases in a semi-crystalline polymer film as ETFE. Neutron scattering, on the other hand, is sensitive to differences in the scattering length density of a material. These techniques can provide similar or complementary information as X-rays and neutrons are sensitive to different elements. Therefore, SAXS and SANS are very powerful instruments to study the phase separation and morphology of polymeric systems as discussed in this thesis.22, 223

Figure 2.9 shows a schematic representation of the principle of small angle scattering. A monochromatic X-ray or neutron beam is targeted onto the sample. Only a small fraction of the primary beam is scattered upon interaction with the electron clouds (in case of X-ray) or the nuclei (in case of neutrons). To prevent damage to the detector a beam stop captures the non-scattered X-rays or neutrons before they could hit the detector. The scattered radiation is recorded with a 2D detector in dependence of the diffraction angle \( 2\Theta \) and azimuthal angle. The 2D scattering pattern provides information on the structural orientation within the sample (Figure 2.10). If there is only random orientation as in isotropic materials or crystal powders the scattered radiation hits the detector in circles of equal intensity around the primary beam (Figure 2.10a). In anisotropic samples, e.g. in a lamellar system, on the other hand, the scattering pattern shows semi-circles as in Figure 2.10b.
Figure 2.9: Schematic representation of the small angle scattering principle.

The 2D scattering pattern is converted into a 1D spectrum of intensity versus momentum transfer or scattering vector \( Q \) (nm\(^{-1}\)). This scattering vector is defined as

\[
Q = \frac{4\pi \sin \Theta}{\lambda}
\]  

(2.10)

with \( \lambda \) representing the wavelength of the beam (nm) and \( \Theta \) the half of the scattering angle. The scattering vector can be transformed to the characteristic lengthscale of the observed structural element with following equation:

\[
d = \frac{2\pi}{Q}
\]  

(2.11)

Figure 2.10: Excerpt from Figure 1.18\textsuperscript{212} showing exemplary 2D scattering patterns for a randomly oriented system (a) and an oriented lamellar system (d). Adapted with permission from Park, M. J.; Balsara, N. P. Macromolecules \textbf{2010}, \textit{43}, (1), 292-298. Copyright 2010 American Chemical Society.
Therefore, structural features that are displayed at a small scattering vector correspond to a large lengthscale in real space.

2.4.1.1. X-ray

Small angle X-ray scattering (SAXS) experiments were performed in the framework of the CROSS project in collaboration with the laboratory of neutron scattering and imaging (LNS) at PSI and the Adolphe Merkle Institute (AMI):

Small-angle X-ray scattering (SAXS) spectra of the investigated samples were recorded at room temperature by using a NanoMax-IQ instrument (Rigaku Innovative Technologies, Auburn Hills, MI USA). Raw data were processed according to standard procedures, and the scattering spectra are presented as a function of the momentum transfer \( Q = 4\pi\lambda^{-1}\sin(\theta/2) \), where \( \theta \) is the scattering angle and \( \lambda = 0.1524 \text{ nm} \) is the photon wavelength. The samples were measured under reduced pressure. Some of the SAXS experiments were also performed in collaboration with the Division of Physical Chemistry of the University of Lund in the framework of the European Soft Matter Infrastructure (ESMI) project (Integrated Infrastructure Initiative Nr. 262348):

Small-angle X-ray scattering (SAXS) experiments were performed on a SAXS-lab instrument (JJ X-ray, Skovlunde, Denmark). The instrument has a Genix 3D X-ray source (Xenocs SA, Sassenage, France) providing a photon wavelength \( \lambda = 0.154 \text{ nm} \). Scattering was recorded with a 2D 300 K Pilatus detector (Dectris Ltd., Baden, Switzerland). The three different instrumental setups applied offered a \( Q \)-range coverage of \( 1 – 27.5 \text{ nm}^{-1} \), \( 0.23 – 7.3 \text{ nm}^{-1} \) and \( 0.03 – 2.2 \text{ nm}^{-1} \). Azimuthally averaged scattering curves were obtained from the 2D scattering patterns with the SAXSGUI program. The samples were measured under reduced pressure.

2.4.1.2. Neutrons

Small angle neutron scattering (SANS) experiments were performed in the framework of the CROSS project in collaboration with the laboratory of neutron scattering and imaging (LNS) at PSI.

SANS experiments were performed on the SANS II and SANS I instruments at PSI. However, the SANS II instrument is the standard instrument for SANS measurements in this thesis. On these instruments a quasi-continuous beam is monochromatized by a velocity selector. In the case of SANS II the applied wavelength \( \langle \lambda \rangle \) values were 0.518 and 1.035 nm with a wavelength spread \( (\Delta\lambda/\lambda) \) of \( \sim10\% \). In the case of SANS I the applied wavelength \( \langle \lambda \rangle \) was 0.45 nm with a wavelength spread \( (\Delta\lambda/\lambda) \) of \( \sim10\% \). The
samples were mounted on a conventional temperature controlled sample changer directly (in case of base films) or in 1 mm quartz cuvettes (fully swollen or nominally dry sulfonated membranes). The neutron beam was defined with a $10 \times 7 \text{ mm}^2$ aperture (corners covered with a $d = 10 \text{ mm}$ circular aperture) in front of the sample (SANS II) or with a $10 \times 5 \text{ mm}^2$ aperture (SANS I). Scattered neutrons were detected with position-sensitive $^3\text{He}$ detectors with $128 \times 128$ pixels, with a pixel size of $4.3 \times 4.3 \text{ mm}^2$ (SANS II) or $7.5 \times 7.5 \text{ mm}^2$ (SANS I). The sample to detector distance and collimation were $1.1 \text{ m}$ and $3 \text{ m}$ (at $\lambda = 0.518 \text{ nm}$), $4 \text{ m}$ and $4 \text{ m}$ (at $\lambda = 0.518 \text{ nm}$), and $6 \text{ m}$ and $6 \text{ m}$ (at $\lambda = 1.035 \text{ nm}$) offering a $Q$-range coverage of $0.3 - 2.9 \text{ nm}^{-1}$, $0.093 - 0.8 \text{ nm}^{-1}$ and $0.03 - 0.27 \text{ nm}^{-1}$ on SANS II, while on SANS I a sample to detector distance of $1.6 \text{ m}$ and collimation of $3 \text{ m}$, with an off-centered detector position was offering a $Q$-range coverage of $0.75 - 7.4 \text{ nm}^{-1}$.

In order to follow the influence of different values of relative humidity on the structural features of the membranes SANS experiments were also performed under defined relative humidity conditions. For this, samples were equilibrated for 14 days in a sealed container with a saturated salt solution maintaining a specified r.h. at $25^\circ \text{C}$ ($\text{MgCl}_2$: 33% r.h.; $\text{Mg(NO}_3)_2$: 52.8% r.h.; $\text{NaCl}$: 75% r.h.). For 0% r.h., the samples were dried under reduced pressure at $80^\circ \text{C}$ for $24 \text{ h}$. Afterwards the samples were transferred to specially designed aluminum cells (Figure 2.11) which were sealed using IceCube elastomer (Freudenberg). The windows of the cells were made of Si wafer and used for measurements on SANS II. On SANS I experiments were performed exclusively on nominally dry or $\text{D}_2\text{O}$ swollen membranes.

**Figure 2.11:** Photographs showing the main components of the humidity cell in the sequence of cell assembly. a) Frame of the aluminum cell. b) Ice cube sealing in contact area between the aluminum frame and the Si wafer window. c) Si wafer window (almost transparent for neutrons). d) The thickness of the sample area is defined by the thickness of the Ice cube sealing between the two aluminum frames. d) The cell is closed (0.2 Nm) and airtight.
Data treatment was performed with the “Graphical Reduction and Analysis SANS program” package (GRASP) (developed by C. Dewhurst, ILL). The 2D data was corrected for background and dark counts according to standard procedures, and 1D scattering curves were obtained by azimuthally averaging either in a 360° sector around the direct beam position or in two 90° sectors along the machining and the transverse direction of the sample (SANS II), or in 180° sectors along horizontal direction of the sample (off-centered detector position on SANS I).

2. Methods and Experimental Techniques

2.5. Pulsed-Field-Gradient (PFG) NMR Measurements

Pulsed-field-gradient (PFG) NMR measurements were performed within the framework of the CROSS Departmental Initiative and European Soft Matter Infrastructure (ESMI) project (Integrated Infrastructure Initiative Nr. 262348), in collaboration with the laboratory of neutron scattering and imaging (LNS) at PSI and the University of Lund.

Pulsed-field-gradient (PFG) NMR diffusometry is an effective method to gain insight into the mobility of a species over an adjustable length scale (~100 nm to ~10 μm) by employing magnetic field gradients and the attenuation of the spin-echo signal. This decay is due to the combined translational motion of the spins, which results in a dephasing of the nuclear spins. The spatially well-defined gradient pulses label the spins and couple the detected NMR signal with the average displacement of the observed molecules, thereby allowing the determination of the self-diffusion coefficient \( D \) for this species in the studied material. Applying this method allows to track diffusion over timescales ranging from ~1 ms to 1 s. According to Madsen, this can provide useful information on coupling of structural heterogeneity with transport within materials, since molecular diffusants sample the host matrix and their diffusion reflects structural complexity. In combination with other analytical methods such as small angle scattering this method provides deep insight into morphology, anisotropy and domain structure.

Therefore, PFG-NMR was applied to investigate the diffusion of water molecules within a series of ETFE-\( g \)-PSSA membranes with different grafting levels over a time scale of 20 ms to 40 ms. Furthermore, a set of crosslinked membranes with a fixed grafting level of 25% and a varying crosslinking level (corresponding to 0, 2 and 4 Vol.% of DIPB in the grafting solution) were analyzed. The dependence of the diffusion coefficients on temperature and relative humidity was investigated. The results of these measurements are discussed in Chapter 3.

The samples were prepared in advance by cutting 4 to 5 films of the corresponding grafting level in 1.5 cm × 7 cm stripes. These stripes were tightly rolled into a cigar
shape and transferred into an NMR tube (as depicted in Figure 2.12). The short edge of the stripes is not only parallel to the tube axis but also to the magnetic field applied in the measurements and therefore the analyzed direction in diffusometry. Afterwards, the desired relative humidity was adjusted by storing the open samples together with saturated aqueous salt solutions (52.8 % r.h.: sat. Mg(NO$_3$)$_2$ solution; 93.7 % r.h.: sat. KNO$_3$ solution) in sealed containers at a temperature of 25°C.

![Figure 2.12: Sketch of preparation procedure with exemplarily marked measured direction for samples where the transport properties were measured in machining direction.](image)

PFG stimulated-echo (STE) NMR technique was performed on a Bruker Avance II 200 spectrometer (Bruker, Karslruhe, Germany, $^1$H resonance frequency: 200.13 MHz) with a Bruker DIFF-25 gradient probe. The gradient pulse was 0.5 ms, the time between the gradients was varied between 20 and 40 ms and the gradient strength was linearly ramped from 0 to 9.6 T/m in 16 steps. The dwell time was 20 μs and the pre-scan delay was 50 μs. NMR data was processed in MatLab (www.mathworks.com). Goldman-Shen NMR experiments were performed prior to the PFG STE measurements to rule out cross-relaxation between solid and liquid to ensure that the diffusion coefficients can be used without further corrections.

2.6. Quasi Elastic Neutron Scattering (QENS)

Quasi-elastic neutron scattering (QENS) experiments were performed on FOCUS, the time-of-flight spectrometer for cold neutrons at PSI, in the framework of the CROSS project and in collaboration with the laboratory of neutron scattering and imaging (LNS) at PSI.
In contrast to SAS experiments (Section 2.4.) which are time independent, QENS allows the investigation of dynamic correlations. In this scattering process neutrons exchange some of their energy with the objects of the scattering material thereby picking up or releasing kinetic energy. This energy transfer is directly related to the molecular motion and therefore gives information about water diffusion and the confined surrounding of the moving species if an appropriate model is used.\textsuperscript{22}

The applied wavelength was 0.575 nm. To avoid any correlation between sample orientation and specific momentum-transfer vectors a cylindrical sample holder with an outer radius of 7 mm was used. In this holder typically six layers of membranes were rolled up onto an inner cylinder with an outer radius of 5.75 mm (Figure 2.13). Two layers each were rolled with their machining direction and transverse direction, respectively, parallel to the symmetry axis of the cylinder. The remaining two layers were rotated by 45° in the two possible directions.

In order to achieve an intermediate relative humidity of the samples, the membranes were equilibrated for six days in the presence of a saturated aqueous solution of Mg(NO\textsubscript{3})\textsubscript{2} at a temperature of 25 °C (~53% r.h.)\textsuperscript{233} before placing the six layers into the sample holder (Figure 2.11). After the insertion, the open sample holder was further equilibrated in Mg(NO\textsubscript{3})\textsubscript{2} atmosphere, and 0.3 mL saturated salt solution was injected at the bottom of the sample holder before closure. The inserted solution was shielded from neutrons with cadmium during the QENS measurements.

![Figure 2.13: Photographs of the sample holder used for QENS measurements.](image)

The experimental data were analyzed with the DAVE data reduction software.\textsuperscript{234} Transmission values were estimated from the chemical composition and water content of the sample. A vanadium standard was measured for calculating detector efficiency and determining the instrumental resolution function. For background subtraction,
QENS data from the empty sample holders was collected. The energy transfer range was -0.7 meV to +0.7 meV and the momentum transfer range was 3 nm\(^{-1}\) to 18 nm\(^{-1}\) with steps of \(\Delta Q = 1\) nm\(^{-1}\), resulting in 15 different \(Q\)-groups. The experimental curves were fitted by using the PAN package being part of the DAVE software. The experimental spectra of the dynamic structure factor \(S(Q, \omega)\) were fitted against the linear combination of three terms:

\[
S(Q, \omega) = I_{el}(Q) \cdot R(Q, \omega) \otimes \delta(\omega) + I_{qel} \cdot R(Q, \omega) \otimes L(Q, \omega) + Bg(Q, \omega). \tag{2.12}
\]

The first term indicates elastically scattered neutrons (the Dirac delta function convoluted with the instrumental resolution function \(R(Q, \omega)\)) with intensity \(I_{el}\), the second term is caused by quasi-elastically scattered neutrons (a Lorentzian function \(L(Q, \omega)\) convoluted with \(R(Q, \omega)\), and the last term represents a linear baseline as background. The proton dynamics, in terms of the self-diffusion constant \(D\), are determined via the momentum-transfer-dependent half-width at half maximum (HWHM) of the Lorentzian function: \(\Gamma(Q, \omega)\). It can be shown that irrespective of the details of the diffusion process, at sufficiently low \(Q\) values the broadening of the quasi-elastic spectra is simply proportional to the diffusion coefficient \(D\):

\[
\Gamma(Q) = \frac{h}{2\pi} D Q^2 \tag{2.13}
\]

where \(h\) is the Planck constant.\(^{235}\) Thus, the diffusion coefficients can be determined via a model-free analysis by estimating \(L(\omega)\) and \(\Gamma\) at different momentum transfer values.

### 2.7. Electrochemical Atomic Force Microscopy (EC-AFM)

EC-AFM experiments were performed in collaboration with the University of Applied Sciences Esslingen.

This technique is an extension of the normal AFM measurement setup which provides information on the topography of the surface and, at the same time, on the local proton conductivity. The experimental setup is shown in Figure 2.14. All experiments were performed in an environmental chamber with humidified air on both sides of the cell. A water reservoir was used to ensure constant humidification of the membrane and enable stable measurements. The atmosphere was set to a relative humidity of \(45 \pm 3\)% and voltage was applied to measure a net current. This current is driven by electrochemical reactions on both sides of the membrane. At the anode water reacts at the Pt catalyst layer to form oxygen and protons. These protons are transported through the
hydrophilic channels of the membrane and recombine with the oxygen from the air atmosphere at the Pt coated tip of the AFM probe (cathode side) to form water. Therefore, current is only measured when the conductive AFM-tip is in contact with such a hydrophilic channel or a cluster thereof.

To obtain images with high resolution further measurements were performed without attached water reservoir. The r.h. in the sample chamber was set to $75 \pm 5\%$ in these cases.

![Figure 2.14](image.png)

**Figure 2.14:** Schematic representation of the setup used for EC-AFM measurements. Some of the data discussed in **Chapter 8** was also measured without water reservoir.

### 2.7.1. Sample Preparation

For surface measurements the membranes were taped onto the AFM steel sample holder with conductive carbon adhesive tape, which was previously impregnated with Pt black particles (Sigma Aldrich, $< 50$ nm). Additional measurements with a water
reservoir beneath the conductive adhesive tape were taken to improve humidification. Relative humidity was set to \(45 \pm 3\)%.

For measuring cross-sections, the membranes were embedded with Teroson 6700 2-component Polyurethane glue (Henkel). After curing 24 h at room temperature, the samples were cut by microtome into slices of 150 – 200 µm and fixed on a sample disk similarly to the surface measurements. To ensure sufficient humidification, all cross-section samples were equilibrated at 80% relative humidity for at least 1 h prior to the measurement.

2.7.2. **AFM-Measurements**

AFM-measurements were performed by a Multimode 8 atomic force microscope (Bruker) with a closed loop scanner (nPoint) in PeakForce TUNA™ mode. The current evaluated in tapping mode was averaged with a lock-in amplifier. The contact current is averaged over the tip-sample contact time whereas the TUNA current is averaged over the whole tapping period. Platinum coated OMCL-AC240TM AFM-probes (Olympus) were used. All measurements were executed in a gas tight chamber at 45 ± 3% r.h. for surface measurements with water reservoir and 75 ± 5% r.h. for measurements without a water reservoir. The applied bias was varied between 1.5 and 2.3 V. The exact values for each measurement are noted in the results part. Images were taken with a resolution of 1024 × 1024 pixels and a scan rate of 0.25 Hz.

2.8. **In-Situ Characterization**

2.8.1. **Preparation of Membrane Electrode Assembly (MEA) and Cell Assembly**

![Figure 2.15: Schematic representation of a membrane electrode assembly (MEA).](image-url)
Methods and Experimental Techniques

For *in-situ* single cell tests of the synthesized membranes and the comparison with standard materials such as Nafion® (NR-212) and the unmodified ETFE-g-PSSA (25% GL, low dose electron irradiated) regarding their performance in a fuel cell, membrane electrode assemblies (MEA) were formed in the first step.\(^\text{130}\)

**Figure 2.15** shows a schematic representation of such an MEA whereas **Figure 2.16** displays photographs of the different steps during MEA preparation and cell assembly.

**Figure 2.16:** Photographs of the different steps during MEA preparation and cell assembly. For an explanation of the different steps (photographs) see text.
a) For the accurate assembly a metal frame was used to align the membrane (4.3 cm \( \times \) 5.4 cm), gas diffusion electrodes (from Johnson Matthey Fuel Cells, type ELE 0263-0983, loading: 0.4 mg Pt/cm\(^2\)) and the polyethylene naphtalate (PEN, 25 \( \mu m \)) subgaskets. The subgasket increases the stability of the MEA and FC setup. After the assembly the single components were laminated in a hot-press at defined temperature, load, and duration (110\(^\circ\)C/2.5 MPa/180 s).

b) The photograph in Figure 2.16 b shows an exemplarily laminated MEA. For better visibility a slightly yellowish colored membrane was used (hydrolyzed ETFE-g-P(SSA-\(\omega\)-GMA)).

c) Parallel flow fields with 1 mm channel and land width machined into graphite plates were used.

d) (and e)) The MEA was symmetrically sandwiched between gaskets of FEP (25 \( \mu m \)) and PTFE (100 \( \mu m \)) to ensure gas tightness.

e) The second flow field plate was attached before

f) the current collector plate was laid on top of an insulating film (PTFE, 100 \( \mu m \)).

g) The second endplate was attached and

h) the cell was tightened in steps up to a torque of 3 Nm.

The active area of the above described N1D cell design is 15.8 cm\(^2\).

2.8.2. Cell Tests

The MEAs were operated in a single cell mode at 80\(^\circ\)C and 2.5 bar\(a\) backpressure on both sides with hydrogen and oxygen fed at a flow rate of 600 mL min\(^{-1}\). Figure 2.17 shows a photograph taken of the fuel cell test stand used in this work. After 12 h conditioning at constant current density (0.5 A cm\(^{-2}\)) and 100% relative humidity, the first polarization curve was measured. Polarization curves are, as mentioned in Section 1.2.1., used to characterize fuel cell performance indicating the relationship between cell voltage and current density and giving information about the different overpotentials in a fuel cell. If all other cell and test stand components as well as measurement parameters are kept constant (as in the present work) this allows a comparison of the performance between different membranes. To obtain such a polarization curve the cell voltage is recorded as a function of current density, starting at OCV and stopping at a current density of 2000 mA cm\(^{-2}\). As a safety measure the measurement was stopped when the cell voltage dropped below 0.1 V.

Furthermore, polarization curves were also recorded at reduced relative humidity values (50% and 70% r.h.). For this the cell was conditioned at 70% r.h. for 2 h (gas flow rate:
2. Methods and Experimental Techniques

2000 mL min⁻¹, 0.1 A cm⁻²) before the next polarization curve was taken; the same applies for the measurements at 50% r.h..

Cell voltage and high frequency resistance (HFR at 1 kHz, AC milliohm meter model 3566, Tsuruga, Japan) were continuously monitored over the entire length of the test protocol.

Figure 2.17: Photograph of the fuel cell test setup used for the in-situ characterization of the synthesized membranes.

2.8.2.1. Humidity Cycling

To measure the stability of a certain type of membrane against humidity cycling in a fuel cell, various MEAs were conditioned as described in Section 1.8.2. and subjected to up to 9 cycles of humidity changes as described in the protocol above (1 cycle: 100% r.h.
(→ 70% r.h. → 50% r.h. → 100% r.h.) at the end of each conditioning phase a polarization curve was measured and the performance loss of the membrane calculated. The iR-correction method \(^{236}\) was applied to verify that the observed performance loss can be unambiguously attributed to membrane degradation rather than a degradation of the electrode or other fuel cell components. Thereby, the iR-corrected cell potential was determined according to the following equation: 

\[
E_{\text{IR-free}} = E_{\text{cell}} + iR_{\Omega}
\]

with \(i\): current density, \(E_{\text{IR-free}}\): cell potential after correction for ohmic resistance, \(E_{\text{cell}}\): cell potential without corrections, \(R_{\Omega}\): ohmic resistance or high frequency resistance.

2.8.3. **Hydrogen Permeation Measurements**

Electrochemical hydrogen permeation measurements based on the single cell configuration were conducted to assess the mechanical integrity and gas permeability of the membranes.

After the protocol described in Section 2.8.2., hydrogen crossover through the membrane was measured using an electrochemical method\(^{237, \ 238}\) under the same conditions that were applied for the cell tests at 100% r.h. (80°C and 2.5 bar, backpressure on both sides). Fully humidified gasses with a flowrate of 600 mL min\(^{-1}\) were fed to the anode and cathode. But instead of oxygen nitrogen was supplied at the former cathode side. The difference in hydrogen partial pressure on both sides (cathode (\(N_2\)): low hydrogen partial pressure; anode (\(H_2\)): high hydrogen partial pressure) leads to the formation of a concentration gradient across the membrane. After 1 h the cell is equilibrated and remains at a cell potential of approximately 0.1 V. In the following measurement the cathode (\(N_2\)) serves as working electrode while the anode (\(H_2\)) serves as reference and counter electrode. When voltage is applied a net current can be measured caused by the oxidation of hydrogen at the Pt catalyst. Due to the extremely fast kinetics of the hydrogen oxidation reaction the diffusion limited current is already measured at low potentials (\(~200\) mV) and therefore the measured current should be independent of further increase in voltage. However, an ohmic behavior can be observed with the measured crossover current increasing with increasing voltage. **Figure 2.18** shows an example of such a permeation measurement. To separate the current resulting from hydrogen crossover from the ohmic side current, the potential was cycled once from 200 to 800 mV (in steps of 100 mV and back in steps of 200 mV, with a 60 s equilibration time at each voltage step) and the hydrogen crossover rate was estimated by extrapolating the fitted curve to 0 mV with this value representing the diffusion-limited hydrogen oxidation current density.
Figure 2.18: Example of a hydrogen permeation measurement. Extrapolation of the fitted curve to 0 mV yields the diffusion-limited hydrogen oxidation current density.
Chapter 3. Influence of Base Film Anisotropy

The partially fluorinated ETFE is an excellent candidate for a base film in radiation grafting. Owing to the manufacturing process of extruded ETFE, the microstructure of the base film is inherently anisotropic. Proton mobility and conductivity strongly depend on the structure and orientation of the polymer chains within the PEM. Therefore, this chapter presents detailed investigations on the influence of the inherent anisotropy of the base material. Pulsed field gradient NMR was used to investigate water diffusion at defined temperature and relative humidity values. Furthermore, the effect of base film inherent anisotropy on the proton conductivity and dimensional change of the membrane upon grafting was analyzed. For these studies the model system of polystyrene grafted into ETFE and its sulfonated derivative was used.

The present chapter consists of a reproduction of the following publication:


3. Influence of Base Film Anisotropy

3.1. Abstract

In order to investigate the structure-property correlations of grafted proton conducting membranes, the model system consisting of an ETFE base film grafted with polystyrene and subsequent sulfonation (ETFE-g-PSSA) along with crosslinked derivatives ETFE-g-P(SSA-co-DiPB) were synthesized. The characteristics of the final membranes were characterized by PFG-NMR diffusometry, in-plane conductivity and by investigations of the dimensional changes of the grafted membranes. The collected data were correlated with the inherent anisotropy of the ETFE base film.

3.2. Introduction

Polymer electrolyte fuel cells (PEFCs) are environmentally friendly and efficient electrochemical energy conversion devices and received therefore growing attention in the global research strategies. Regarding PEFCs, the proton exchange membrane (PEM) plays a key role and is therefore the target of extensive investigations to obtain commercially attractive fuel cells. Such a membrane is required to meet several specifications, such as good chemical and mechanical stability and gas barrier properties. Moreover, high proton conductivity along with low electrical conductivity and balanced water transport are prerequisites.\(^1\), \(^3\), \(^16\) One way to prepare these membranes is via radiation grafting, which offers a high degree of design flexibility to develop ion conducting membranes for electrochemical application.\(^{158}\) A commercially available base film (ETFE, poly(ethylene-alt-tetrafluoroethylene)) is irradiated using electron beam technology to produce reactive species in the bulk material, which are reacted with selected monomers to produce well-defined membranes (Scheme 3.1). In analogy to today’s state of the art perfluorosulfonic acid (PFSA) membranes, such as Nafion\(^{\circledR}\) (DuPont), radiation grafted membranes consist of a polymer backbone that provides mechanical integrity and strength as well as functional groups responsible for, e.g., proton conductivity. In contrast to Nafion\(^{\circledR}\), with the radiation grafting technique these two functionalities can be freely combined and adapted.

The partially fluorinated ETFE is an excellent candidate for a base film as it does not show the common disadvantages associated with perfluorinated polymer films (very low stability against irradiation, poor grafting kinetics)\(^{158}\) while at the same time being still resistant against acids or alkalis. Furthermore, its relatively high mechanical, thermal and electrical resistances\(^{24}\) make it especially interesting for final applications as ion exchange membranes.
3. Influence of Base Film Anisotropy

Scheme 3.1: Synthetic pathway for the preparation of proton conducting membranes based on ETFE base film, e.g. ETFE-\text{-g}-polystyrene sulfonic acid (ETFE-\text{-g}-PSSA).

Owing to the manufacturing procedure of extruded ETFE, the microstructure of the base film is inherently anisotropic\(^{239}\) (machining direction (MD) vs. transverse direction (TD)). This anisotropy is still present in the final membranes and is expected to have a strong influence on their performance.\(^{240}\) Despite the increasing interest in grafted membranes for fuel cell application and the intensive research for high performing, versatile and cost-competitive PEMs,\(^{3, 29-32}\) the understanding of the polymer structure and morphology as well as its impact on properties such as proton mobility and conductivity is still rather limited.\(^{33, 34}\) With the discussed properties strongly depending on the structure and orientation of the polymer chains within the PEM, it is crucial to investigate the structure-property relationship in these membranes more closely. Therefore, detailed investigations on the influence of the inherent anisotropy of the base material of these membranes are presented in this paper.

### 3.3. Experimental

#### 3.3.1. Materials

The base polymer ETFE was purchased from DuPont (Tefzel® 100LZ, Circleville, USA, 25 μm film). The reagents used during membrane synthesis included styrene (98%, Fluka), 1,3-diisopropenylbenzene (DiPB, 97%, Sigma Aldrich), chlorosulfonic acid (98%, Fluka), 2-propanol, acetone and dichloromethane (Prolabo®, VWR). All reagents and the monomer were used as received without removal of inhibitors. In all cases ultra-pure water (18.2 MΩ, ELGA) was used.
3.3.2. **Membrane Synthesis**

The membranes used in this study were prepared according to procedures reported in our earlier work.\textsuperscript{178,241} The deposited dose was 5 kGy and the grafting was performed at 55°C.

3.3.3. **Pulsed-Field-Gradient (PFG) NMR and In-Plane Conductivity Measurements**

PFG stimulated-echo (STE) NMR technique was performed\textsuperscript{230} on a Bruker Avance II 200 spectrometer (Bruker, Karlsruhe, Germany, \textsuperscript{1}H resonance frequency: 200.13 MHz) with a Bruker DIFF-25 gradient probe. The gradient pulse was 0.5 ms, the time between the gradients was varied between 20 and 40 ms and the gradient strength was linearly ramped from 0 to 9.6 T/m in 16 steps. The dwell time was 20 μs and the pre-scan delay was 50 μs. NMR data was processed in MatLab (www.mathworks.com). Goldman-Shen NMR experiments were performed prior to the PFG STE measurements to rule out cross-relaxation between solid and liquid to ensure that the diffusion coefficients can be used without further corrections.\textsuperscript{231} The samples were prepared by cutting several stripes of membranes (1.5 cm x 7 cm), rolling them tightly to avoid major air gaps and transferring them into common NMR tubes. The diffusion measurements were carried out in the direction parallel to the axis of the NMR tube. The different relative humidities (r.h.) were adjusted by equilibrating the samples in the tube for 12 days in a sealed container with a saturated salt solution maintaining a specified r.h. at 25°C, (Mg(NO\textsubscript{3})\textsubscript{2}: 52.8% r.h.; KNO\textsubscript{3}: 93.7% r.h.)\textsuperscript{224}. Afterwards the NMR-tubes were sealed and measured at 20 and 80°C.

The in-plane conductivity was measured at room temperature by means of a four point-probe conductivity cell (Bekktech BT-112) consisting of four Pt-electrode wires immersed in liquid water. More details can be found elsewhere.\textsuperscript{149,242}

3.4. **Results and Discussion**

3.4.1. **Diffusion Measurements**

Pulsed-field-gradient (PFG) NMR diffusometry is an effective method to gain insight into the mobility of species over an adjustable length scale (~100 nm to ~10 μm)\textsuperscript{226} by employing magnetic field gradients and the attenuation of the spin echo signal. This allows the determination of the self-diffusion coefficient \(D\) for a species in the studied material.\textsuperscript{226,228} Applying this method allows to track diffusion over timescales ranging
from ~1 ms to 1 s and provides useful information on coupling of structural heterogeneity with the magnitude of diffusion of the observed species.

Therefore, PFG-NMR was applied to investigate the diffusion of water molecules within a series of ETFE-g-PSSA membranes with different grafting levels over a time scale of 20 to 40 ms. Furthermore, a set of crosslinked membranes with a fixed grafting level of 25% and a varying crosslinking level (corresponding to 0, 10 and 20 vol% (wrt. total monomer) of DiPB in the grafting solution) were analyzed.

In this series of samples the dependency of the diffusion coefficient on temperature and r.h. was investigated. A length-scale dependency of the diffusion coefficient could not be observed despite the cluster-channel structure of the hydrophilic phase in grafted membranes of this type. This is caused by the limits of the technique, which does not allow a shorter measurement time than about 1 ms which in the presented system corresponds to a length scale of ~250 nm, whereas the dimension of the hydrophilic clusters in the membrane where almost bulk water diffusion properties can be expected is only a few nm.

The data shown in Figure 3.1a and Table 3.1 reveal only a minor influence of the grafting level on the diffusion coefficient of water ($D_{H_2O}$) for the lower temperature of 20°C, whereas it has a significant impact at 80°C (for comparison $D_{H_2O}$ of pure water: $2.2 \cdot 10^{-9}$ (21°C), $6.0 \cdot 10^{-9}$ m$^2$ cm$^{-1}$ (80°C)). Using the Arrhenius equation, the apparent water diffusion activation energy was determined to range between 18 and 25 kJ/mol.

**Figure 3.1:** Diffusion coefficients of water in the systems a) ETFE-g-PSSA for different GL and b) ETFE-g-P(SSA-co-DiPB) at a fixed GL of 25% and various crosslinking content. *r.h. adjusted at 20°C, cf Section 3.3.3.
In contrast to the grafting level, an increased r.h. already shows its impact at lower temperatures, making the r.h. and the temperature the dominant factors to affect the conductivity, whereas the GL seems to play only a subordinate role.

Despite earlier observations on the impact of the incorporation of a crosslinking agent, the diffusion coefficient showed only a faint decrease with increasing crosslinking content (Figure 3.1b). The influence of the temperature and the r.h., however, lies in a comparable range to the values obtained for the non-crosslinked membrane (Table 3.1).

Table 3.1: Diffusion coefficients of H₂O in TD at different conditions obtained by PFG-NMR measurements.

<table>
<thead>
<tr>
<th>GL / wt%</th>
<th>D(_{H₂O}) / m² s(^{-1})</th>
<th>D(_{H₂O}) / m² s(^{-1})</th>
<th>D(_{H₂O}) / m² s(^{-1})</th>
<th>D(_{H₂O}) / m² s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>53 % r.h. @ 20 °C → 80 °C</td>
<td>94 % r.h. @ 20 °C → 80 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>3.15 \times 10^{-11}</td>
<td>1.36 \times 10^{-10}</td>
<td>1.09 \times 10^{-10}</td>
<td>3.93 \times 10^{-10}</td>
</tr>
<tr>
<td>25</td>
<td>4.10 \times 10^{-11}</td>
<td>1.84 \times 10^{-10}</td>
<td>1.01 \times 10^{-10}</td>
<td>4.20 \times 10^{-10}</td>
</tr>
<tr>
<td>42</td>
<td>4.67 \times 10^{-11}</td>
<td>2.65 \times 10^{-10}</td>
<td>1.30 \times 10^{-10}</td>
<td>5.28 \times 10^{-10}</td>
</tr>
<tr>
<td>25%-10-D₈PB</td>
<td>3.29 \times 10^{-11}</td>
<td>1.83 \times 10^{-10}</td>
<td>9.57 \times 10^{-11}</td>
<td>4.33 \times 10^{-10}</td>
</tr>
<tr>
<td>25%-20-D₈PB</td>
<td>3.00 \times 10^{-11}</td>
<td>1.75 \times 10^{-10}</td>
<td>8.34 \times 10^{-11}</td>
<td>-</td>
</tr>
</tbody>
</table>

In order to investigate the difference in the diffusion coefficient for MD and TD, two different samples for an ETFE-g-P(SSA-co-D₈PB) membrane with a GL of 25% and a crosslinking content of 10 vol% (wrt. total monomer) were prepared and analyzed. The diffusion coefficient in TD appears to be 1.5 times higher than in MD (MD: 1.21 \times 10^{-10} m² s\(^{-1}\); TD: 1.83 \times 10^{-10} m² s\(^{-1}\)). This was the first indication that a transport property (here: water movement) in the membrane is not superior in MD, as one might expect intuitively considering the base polymer chains are preferentially oriented in MD, but in TD.

3.4.2. In-plane Conductivity Measurements

At a length-scale of up to a few hundred μm drastic differences of properties could be observed as a function of the investigated direction (cf. Section 3.4.1.). These structure-property correlations, caused by the anisotropy of the base material, were more closely
investigated at macroscopic length-scales by proton conductivity measurements performed in the MD and TD orientation of the membrane in liquid water swollen state for different GLs.

The analysis of the obtained in-plane proton conductivity data confirms the impact of the anisotropy of the base film and the results of the diffusometry measurements: TD is favored over MD when it comes to properties associated with the grafted polymer. At lower GL the relative difference of these two orientations is up to 30%, whereas this difference slowly decreases with increasing GL (Figure 3.2a). Surprisingly, at a GL as high as 67% the difference is still about 8%, indicating that even such a high content of grafted polymer does not lead to completely uniform H⁺ transport properties. In case of a crosslinked system the observed difference in MD and TD is even more pronounced, reaching nearly 40% instead of 20% difference for an non-crosslinked system with the same GL (Figure 3.2b).

Comparing the results of the PFG-NMR and the in-plane conductivity measurements, it is quite apparent that the impact of a higher GL is much stronger for the latter, whereas the effect seems to be only marginal for the diffusion coefficients at 20°C. This observation can also be extended to the crosslinked system (Figure 3.2b). Although the diffusion coefficients show only a slight decrease for higher crosslinking levels, the conductivity in the same direction drops significantly. Taking this into account, a possible explanation might be that for the conductivity a further factor plays an
important role, which is not accounted for in the diffusion coefficient: the number of transported charge carriers (in this case protons). As the in-plane conductivity is measured in fully swollen state, the water uptake is governed by the volume fraction of hydrophilic domains (determined by the GL) and the extent of crosslinking, which prevents excessive swelling. Therefore, in case of DiPB containing membranes, for example, an increased crosslinking level leads to a reduced ionic cluster size and hydrophilic channel width. This reduced channel width limits the number of transported charge carriers and thus reduces the conductivity.

3.4.3. Dimensional Change

At the macroscopic length scale, beside the investigation of the conductivity, a closer look at the dimensional change of the film upon grafting could provide information about the distribution and preference of the new grown polymer in the base film, as grafting with a new polymer leads to a dilution and “swelling” of the base polymer film and therefore to a dimensional change. Accordingly, squares of pristine base film with defined dimensions were prepared and grafted to obtain different GL. The dimensions of the grafted films were measured and the dimensional change in the two orientations plotted as a function of GL (Figure 3.3). The data suggests two different regimes. For lower GL, the film seems to grow more strongly in MD, whereas the growth in TD is more pronounced at higher GL. Furthermore, the MD growth seems to approach saturation after its strong initial phase. In contrast, growth in TD continues to be more pronounced after the transition.

![Figure 3.3: Dimensional change upon grafting for MD and TD of an ETFE film.](image-url)
3. Influence of Base Film Anisotropy

3.5. Conclusions

In the present study, a closer look at the effect of structural elements of the base material on certain properties associated with the new grafted polymer was taken. The influence of the inherent anisotropy of the base film was investigated with PFG-NMR diffusometry, in-plane conductivity measurements, and the evaluation of the dimensional change upon grafting. These three properties show a higher value in TD. As the structure of the polymer is expected to be similar in through-plane direction and TD due to the extrusion process used for film fabrication, this could be an advantage regarding the function of the membrane in the fuel cell. Different sensitivities towards crosslinking were found to impact the conductivity and diffusion coefficient. More detailed investigations of the microstructure of the base film and the grafted membrane are currently being performed using small-angle neutron scattering.
Chapter 4. Influence of Variations in Base Film Nanostructure

This chapter comprises a continuation of the studies on the impact of the structure of the base film on the final PEM. It will be shown that the performance and stability of radiation grafted PEMs in fuel cells strongly depend on the microstructure of the underlying base polymer and go far beyond anisotropy. Differences in the arrangement of the crystalline phase in the otherwise chemically identical semi-crystalline base films can already affect proton conductivity, water uptake and the stability in a fuel cell. Small-angle scattering was used to investigate the nanoscale structure of the base polymers, grafted films and membranes and correlated with membrane properties.

The present chapter consists of a reproduction of the following publication:


4. Influence of Variations in Base Film Nanostructure

4.1. Abstract

The proton exchange membrane (PEM) is a key element of a polymer electrolyte fuel cell, and radiation-grafting is an attractive option for the synthesis of PEMs. Via a systematic investigation of a well-defined model material, sulfonated polystyrene grafted poly(ethylene-alt-tetrafluoroethylene), ETFE-g-PS(SA), we show that the performance and stability of radiation grafted PEMs in fuel cells strongly depends on the microstructure of the underlying base polymer. The nanoscale structure of the base polymers, grafted films, and membranes is probed by small-angle scattering, and the nanoscale proton dynamics is probed by quasi-elastic neutron scattering. The results of these techniques correlated with fuel cell relevant properties - including proton conductivity, water uptake - and fuel cell performance clearly indicate that differences in the arrangement of the crystalline phase in the otherwise chemically identical semi-crystalline base films can have considerable impact, representing an essential aspect to consider in the development of proton exchange membranes prepared via pre-irradiation grafting.

4.2. Introduction

Electrochemical cells such as fuel cells or batteries are expected to be a key element in the distribution chain of renewable energy.44 The use of hydrogen as an energy ‘vector’, i.e., as a universal energy carrier, is an appealing concept, because it could form the backbone of a decarbonized energy economy.246 Hydrogen can be produced from renewable sources, and it can be converted to electricity in fuel cells in clean and efficient manner for various applications. Notably, the polymer electrolyte fuel cell is particularly attractive for applications with variable load profile and intermittent operation, such as portable electronics, distributed power generation, and electric vehicles. The heart of this type of fuel cell is a polymer electrolyte: the proton exchange membrane (PEM). Starting in 2015, fuel cell electric vehicles have started to be available on the market (e.g., Toyota Mirai)247 and residential micro-CHP systems (ENE FARM) become cost-competitive to competing technologies.248 Nevertheless, it is important to push technology forward and continue research towards better and cheaper materials and components.249, 250

PEMs contain superacid groups, typically sulfonic acid, tethered to the polymer. Upon humidification the acid dissociates, releasing a mobile proton. Proton conductivity is dependent on the water content and on the connectivity of aqueous domains.251 Nanoscale phase segregation, viz., the structure, morphology and characteristic size of
domains, are shown to play an important role in the conductivity of PEMs. The current design paradigm aims at decoupling the principal roles of electrolyte and separator by combining two or more - usually immiscible - polymers, for example via block copolymerization, blending, radiation grafting or via the creation of (semi)-interpenetrating polymer networks. Preserving an intimate and homogeneous mixing of these two principal roles on the nanoscale, resulting in (co-)continuous phases, is desired. This can be promoted by tailoring the length and the incompatibility of the polymer constituents, by which one can also control both the nanoscale morphology and the characteristic size of the phase-segregated domains.

Radiation-grafting is an attractive option for forming copolymers. It offers a potentially low-cost synthesis as well as the possibility of introducing various types of functionalities into diverse polymer substrates. This results from the fact that the synthesis involves commodity materials and processing steps well-established in the polymer industry. Thus, the implementation of a roll-to-roll process and an eventual scale-up is straightforward.

Radiation grafted PEMs can be based on various and chemically different matrix polymers. The nature of the matrix polymer was shown to influence the synthesis and the fuel cell relevant properties of the resulting PEMs, as the structure and morphology of the grafted film and membrane is predefined to a certain extent by those of the base polymer. This is an important aspect when considering that commercially available base polymers show variations in their physical properties - even in the case of otherwise chemically identical products. The existence of variations in film properties between different manufacturers is not unusual. Unfortunately, neither the literature nor the manufacturer reports precise information describing these variations and related uncertainty - other than an estimate of the crystallinity in the case of semi-crystalline polymers. Considering the physical and chemical phenomena underpinning radiation grafting, such variations cannot be excluded from influencing the kinetics as well as the final outcome of radiation grafting. Consequently, an understanding of effects resulting from such variations is valuable.

In our recent work, we have shown that radiation grafted membranes can be optimized in terms of the choice of base polymer, grafting monomers and composition to compare favorably with state-of-the-art commercially available perfluorinated membranes (Nafion® type) regarding fuel cell performance and durability. In these membranes, ETFE film of 25 μm thickness was used as base polymer.

In this article we present a series of systematic investigations revolving around the question of the impact of the morphology of the base polymer film on the properties of...
4. Influence of Variations in Base Film Nanostructure

the obtained final membrane, a topic which so far has received little attention. We chose a model system of styrene grafted onto ETFE base film of 25 μm thickness with similar crystallinity from two different suppliers (DuPont, Saint-Gobain), followed by sulfonation to obtain the proton conducting membrane. It is expected that the insights gained regarding the role of the base polymer are of a generic nature and can be transferred to more complex grafting systems, such as the one mentioned above optimized for fuel cell application. The nano- and microstructure is analyzed by small-angle scattering and elemental analysis via energy dispersive X-ray (EDX) spectroscopy in the scanning electron microscope (SEM), respectively. Small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS) have been proven to be useful for the structural characterization of various polymer electrolyte membranes at various length scales of interest. The nanoscale dynamics of protons, carrying information about self-diffusion on the ps-timescale, is studied by quasi-elastic neutron scattering (QENS). These findings are complemented with ‘macroscopic’ properties of fundamental importance for fuel cell operation.

4.3. Experimental Section

4.3.1. Chemicals

The base polymer matrices, poly(ethylene-alt-tetrafluoroethylene) (ETFE), were purchased from two different suppliers DuPont (Tefzel® 100LZ, Circleville, USA) and Saint-Gobain (Norton®, Courbevoie, France) as films of 25 μm thickness. The reagents used during membrane synthesis included styrene (98%, Fluka), 2-propanol (PROLABO®, VWR), acetone (PROLABO®, VWR), chlorosulfonic acid (98%, Fluka) and dichloromethane (PROLABO®, VWR). The reagents and the monomer were used as received without removal of inhibitor.

4.3.2. Membrane Synthesis

Radiation grafted membranes based on ETFE base films of 25 μm thickness were prepared as previously reported via electron-beam activation using an MeV class accelerator to a dose of 5 kGy, styrene monomer in a mixed isopropanol / water solvent, and 2% (v/v) chlorosulfonic acid in dichloromethane as sulfonating agent. The grafting level of each film was gravimetrically determined according to:

\[ GL = \frac{m_\text{f} - m_\text{o}}{m_\text{o}}, \]

(4.1)
where \( m_0 \) and \( m_g \) represent the weight of the sample before and after grafting, respectively. To obtain different degrees of grafting, various reaction times were applied (Supporting Information, Section 4.6, Figure 4.12). The copolymer membranes - ETFE\textsubscript{DuPont}\textsuperscript{-g}-PS(SA) and ETFE\textsubscript{Saint-Gobain}\textsuperscript{-g}-PS(SA) - will be referred to as DP and SG (PEMs).

Nafion\textsuperscript{®} PFSA membrane (NR-212, solution cast, IEC 0.98±0.04 mmol g\(^{-1}\)) was purchased from DuPont and was used as received.

### 4.3.3. \textbf{Sample Characterization Techniques}

Various techniques were applied to characterize films and membranes: 1. SEM / EDX analysis: for determining the through-plane distribution of the grafted polystyrene chains in the samples; 2. Ex-situ characterization: ion exchange capacity, in-plane and through-plane proton conductivity, water uptake and hydration number; 3. In-situ characterization: fuel cell tests, stability measurements, hydrogen permeation; 4. Small-angle neutron and X-ray scattering (SANS, SAXS). A description of these techniques, the experimental parameters and related results are presented in the Supporting Information, Section 4.6..

**Hermans orientation function.** To quantify the nanoscale anisotropy of the samples, we use the Hermans orientation function \((f)\) in the analysis of the SANS spectra.\textsuperscript{265} This approach has been used to characterize the degree of orientation in polymeric films.\textsuperscript{266} The Hermans function is defined as

\[
f = \frac{3\langle \cos^2 \phi \rangle - 1}{2},
\]

where

\[
\langle \cos^2 \phi \rangle = \frac{\int_0^{\pi/2} I(\phi) \cdot \cos^2 \phi \cdot \sin \phi \cdot d\phi}{\int_0^{\pi/2} I(\phi) \cdot \sin \phi \cdot d\phi},
\]

and \( I(\phi) \) is the neutron scattering intensity integrated across the momentum transfer range of the correlation peak \((0.15 \text{ nm}^{-1} < Q < 0.5 \text{ nm}^{-1})\) and \( \phi \) the azimuthal angle. In the present case \( \phi = 0 \) corresponds to the machining direction. \( f \) takes values of 1, 0 or -0.5 for scattering entities being parallel, randomly oriented or perpendicular, respectively, to the direction of reference, which in the present case is the machining direction.\textsuperscript{266}

**Crystallite size estimation.** Wide-angle X-ray scattering (WAXS) spectra were used for the estimation of crystallite sizes by applying the Scherrer law:\textsuperscript{267}
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\[ L = \frac{\kappa \lambda}{\cos \theta \Delta 2\theta}, \quad (4.4) \]

where \( L \) is the size of the crystallites, \( 2\theta \) is the position of the peak with a full width at half maximum of \( \Delta 2\theta \) corrected for instrumental line broadening, and \( \kappa \) is a positive constant depending on the shape of the crystallites.\(^{268}\) The X-ray scattering spectra were obtained with only one sample orientation, and therefore the obtained information is not representative for all the three dimensions, and we do not consider any possible strain-induced broadening. Since we do not have information about the crystallite shape, we consider that the shape is similar for all studied samples, and we set \( \kappa \) equal to 1. Consequently, we do not necessarily obtain the true crystallite size. We apply the approach to compare relative sizes of the crystallites found in the different samples, by using the following equation:

\[ L = \frac{\lambda}{\cos \theta \Delta 2\theta} = \frac{2\pi}{4\pi^2 \kappa \cos \theta \Delta 2\theta} = \frac{2\pi}{\Delta Q} \quad (4.5) \]

where \( \Delta Q \) is the full width at half maximum (FWHM) of the WAXS peak. To quantify \( \Delta Q \), scattering curves were fitted in the 1.1 nm\(^{-1}\) – 28.9 nm\(^{-1}\) range. This \( Q \)-range fitted best against the phenomenological mathematical model expressed by the linear combination of linear, power, Gaussian and a Lorentzian functions.

**Quasi-Elastic Neutron Scattering.** Quasi-elastic neutron scattering (QENS) experiments were performed on FOCUS, the time-of-flight spectrometer for cold neutrons at the PSI.\(^{232}\) The applied wavelength was 0.575 nm. We were aiming to avoid any correlation between sample orientation and specific momentum-transfer vectors, and therefore, a cylindrical sample holder with an outer radius of 7 mm was used. In this holder typically six layers of membranes were rolled up onto an inner cylinder with an outer radius of 5.75 mm. Two layers each were rolled with their machining direction and transverse direction, respectively, parallel to the symmetry axis of the cylinder. The remaining two layers were rotated by 45° in the two possible directions.

In order to achieve an intermediate relative humidity of the samples, the membranes were equilibrated for six days in the presence of saturated aqueous solution of Mg(NO\(_3\))\(_2\) at a temperature of 25 °C (\( \sim 53\% \) r.h.)\(^{233}\) before placing the six layers into the sample holder (Supporting Information, **Section 4.6, Figure 4.13**). After the insertion, the open sample holder was further equilibrated in Mg(NO\(_3\))\(_2\) atmosphere, and 0.3 mL saturated salt solution was injected at the bottom of the sample holder before closure. The inserted solution was shielded from neutrons with cadmium during the QENS measurements. The experimental data were analyzed with the DAVE data reduction software.\(^{234}\) Transmission values were estimated from the chemical composition and
water content of the sample. A vanadium standard was measured for calculating detector efficiency and determining the instrumental resolution function. For background subtraction we also collected QENS data from the empty sample holders. The energy transfer range was -0.7 meV to +0.7 meV and the momentum transfer range was 3 nm\(^{-1}\) to 18 nm\(^{-1}\) with steps of \(\Delta Q = 1\) nm\(^{-1}\), resulting in 15 different \(Q\)-groups. The experimental curves were fitted by using the PAN package being part of the DAVE software. The experimental spectra of the dynamic structure factor \(S(Q, \omega)\) were fitted against the linear combination of three terms:

\[
S(Q, \omega) = I_{el}(Q) \cdot R(Q, \omega) \otimes \delta(\omega) + I_{qel} \cdot R(Q, \omega) \otimes L(Q, \omega) + Bg(Q, \omega). \tag{4.6}
\]

The first term indicates elastically scattered neutrons (the Dirac delta function convoluted with the instrumental resolution function \(R(Q, \omega)\)) with intensity \(I_{el}\), the second term is caused by quasi-elastically scattered neutrons (a Lorentzian function \(L(Q, \omega)\) convoluted with \(R(Q, \omega)\)), and the last term represents a linear baseline as background. The proton dynamics, in terms of the self-diffusion constant \(D\), is determined via the momentum-transfer-dependent half-width at half maximum (HWHM) of the Lorentzian function: \(\Gamma(Q, \omega)\). It can be shown that irrespective of the details of the diffusion process, at sufficiently low \(Q\) values the broadening of the quasi-elastic spectra is simply proportional to the diffusion coefficient \(D\):

\[
\Gamma(Q) = \frac{h}{2\pi} D Q^2 \tag{4.7}
\]

where \(h\) is the Planck constant.\(^{235}\) Thus, the diffusion coefficients can be determined via a model-free analysis by estimating \(L(\omega)\) and \(\Gamma\) at different momentum transfer values.

### 4.4. Results and Discussion

#### 4.4.1. Base polymer films

As our primary goal here is to elucidate the influence of variations in the base film nanostructure on the final membrane properties, we first quantify these variations. It has been reported that the nanoscale structure of the ETFE matrix (extruded films) is anisotropic.\(^{240}\) This anisotropy originates from the manufacturing process and defines two directions being perpendicular to each other: machining (MD) and transverse direction (TD). MD corresponds to the direction of extrusion and is therefore perpendicular to the axis of the film roll. Scattering contrast between the amorphous and crystalline ETFE phases results in a characteristic small-angle scattering pattern, and the anisotropy clearly reflects in the small-angle scattering spectrum (Figure 4.1 and
Supporting Information, Section 4.6, Figures 4.14 and 4.15). Though very similar in features, the anisotropy of the Saint-Gobain and the DuPont base film is not identical. The azimuthally averaged spectra show that both spectra are characterized by a rather broad correlation peak and an intensity upturn at low angles. The center of the correlation peak \( Q_c \) is indicative of a characteristic distance defined by the amorphous and crystallite ETFE phases. This distance, \( \sim 2\pi/Q_c \), is slightly larger for the DuPont film (\( \sim 25.5 \) nm) than the Saint-Gobain film (\( \sim 21.5 \) nm). The correlation peak is more pronounced in the MD direction than in TD, and to determine the anisotropy based on the small-angle scattering measurements, we use the Hermans orientation function \( f \).

![Figure 4.1: Top: SANS pattern of the two ETFE base matrices (logarithm of the intensity is displayed). The MD and TD direction is parallel with the \( Q_y \) and \( Q_x \) axis, respectively. Bottom: Azimuthally averaged SAXS/WAXS and SANS spectra of the two ETFE base matrices.](image)

The degree of overall alignment in the nanostructure is indeed larger for DP (\( f = 0.209 \pm 0.014 \)) than for SG (\( f = 0.103 \pm 0.015 \)). Alternatively we also calculated the order parameter \( P_2 \) (based on a theory developed for the case of scattering from liquid
crystals and applied earlier for grafted copolymer films of perfluorinated poly(ethylene propylene) samples for quantifying the anisotropy of the base films. These calculations also revealed higher degree of alignment in DP than for SG. For further details see Appendix 1 (Section 4.7).

The qualitative comparison of the scattering curves in the WAXS range, containing information about the crystalline phase on the sub-nanometer scale, does not indicate notable differences between the two matrices. This is in agreement with calorimetry measurements highlighting that the crystallinity of the DuPont base polymer is only slightly higher (~36%) than that of the Saint-Gobain base polymer (~33.5%). Also, IR spectroscopy did not reveal any chemical difference between the two base polymers (see Supporting Information, Section 4.6, Figure 4.16). While the internal structure of these domains is not relevant from the point of view of grafting – since these domains remain non-grafted – both the crystallite size and the alignment of the crystallites may influence the grafting process. Small-angle scattering indicates that the typical crystallite size is larger in the DP base polymer: If the crystallites were of identical size in both base polymers, the difference in crystallinity would mean a higher number density of the crystallites in DP as compared to SG. A higher number density would certainly result in smaller distances between neighboring crystallite domains, which would consequently result in a correlation peak at a higher $Q$ value. This is not observed in SANS and SAXS, as DP, despite its slightly higher crystallinity, presents a lower peak center position in the scattering spectra. Therefore, we argue that the DP base film contains larger crystallites. This hypothesis is confirmed by the WAXS data (Supporting Information, Section 4.6, Figure 4.17). A sharp peak - arising from crystallites and centered at ~13 nm$^{-1}$ - can be observed for both base films. By analyzing the width of this peak, we estimate an average crystallite size of (13.1 ± 0.2) nm for the DP base film and (10.6 ± 0.1) nm for the SG base film.

4.4.2. **Graft copolymer films and membranes**

The small variations in the typical crystallite size and their orientation may influence the grafting kinetics, which is described by the evolution of the grafting level as a function of the grafting time. Concerning reaction time, (Supporting Information, Section 4.6, Figure 4.12), only minor differences were found between the SG and DP base polymers for grafting levels below ~60%. It is however evident that grafting is slightly more time-efficient in the case of the DP base polymer than in the case of SG, especially for higher GL. This indicates that the rate of attaching and growing the styrene chains onto the ETFE backbone is affected. This, in principal, may affect the spatial distribution of the ‘styrene anchors’ as well as the degree of polymerization. This
is because at the processing temperature of 55°C the overall number of active radicals decreases with time due to termination reactions even if polymer grafting does not happen. Furthermore, graft copolymerization starts at the surface of the base polymer and this ‘front’ moves gradually inwards, including the diffusion and subsequent polymerization of styrene as well as the expansion of the ETFE polymer. This may have an impact on the homogeneity of the grafted polystyrene through the film thickness. Indeed, there is an inhomogeneity as witnessed by SEM micrographs and the corresponding EDX analysis (Supporting Information, Section 4.6, Figure 4.18). While the overall target graft level was 25%, the local graft level systematically and symmetrically changes within the film: The maximum value is near the surface and close to 40%, while the graft level gradually decreases and reaches a minimum (15%) in the center of the film.

The grafted film is composed of at least two phases (crystalline and amorphous), and PS and ETFE are immiscible in the amorphous phase. The overall crystallinity is expected to decrease with increasing graft level. On the one hand, this is due to the ‘dilution’ of the base polymer, resulting from the incorporation of amorphous PS domains.142 On the other hand, the intrinsic crystallinity of the base polymer also decreases, owing to the partial disruption and ‘erosion’ of the crystallites due to both grafting and sulfonation.270 Indeed, our WAXS analysis (Supporting Information, Section 4.6, Figure 4.17) confirms that the crystallites become smaller with increasing graft level, and shrink further upon subsequent sulfonation (Figure 4.2).

![Figure 4.2](image-url): Estimated crystallite size before and after sulfonation as a function of grafting level obtained from the analysis of the WAXS region (cf. Supporting Information, Section 4.6, Figure 4.17).
Small-angle scattering spectra recorded at grafting levels of 12%, 25%, 42% and 67% suggest that apart from the impact on crystallites, sulfonation does not induce additional significant changes in the polymer morphology on the length scale of tens of nanometers. In fact, sulfonation has a clear influence on the scattering curves on the $4 - 7 \text{ nm}^{-1}$ momentum transfer range, which corresponds to structural features found on the length scale of a few nanometers (ionomer peak, Section 4.6.2, Figures 4.19 and 4.20). Upon grafting, the structural differences between the two types of base polymer are preserved (Supporting Information, Section 4.6, Figure 4.19): In the grafted copolymers and membranes the characteristic peak appears at a lower $Q$ value in case of DP, still indicating a higher characteristic distance as compared to SG. Additionally, with increasing grafting level, the flattening and broadening of the characteristic peak at $\sim 0.2 \text{ nm}^{-1}$ is observed, which is in agreement with findings reported on similar materials. This can be understood by considering that polymer swelling perturbs the arrangement of crystallites in the amorphous matrix as present in the base film, resulting in a broader distribution of characteristic distances between crystallite domains in the amorphous polymer network. Additionally, since the local graft level is not uniform (SEM/EDX), the polymer swelling is not homogeneous either, which also contributes to the broadening of the characteristic peak in the small angle scattering signal. We point out that small-angle scattering provides information about the whole of the copolymer and does not distinguish between ‘layers’ of different local graft level. Nonetheless, a higher graft level is equivalent with a generally higher degree of polymerization, larger PS domains, and consequently a higher degree of the swelling of the amorphous ETFE phase. This reduces the relative intensity of the characteristic scattering features associated with the base polymer. From the point of view of scattering contrast, the contrast between PS and ETFE is considerably larger than the one found between the amorphous and crystalline domains of ETFE, which explains why the overall scattering intensity increases with increasing graft level. The impact of polymer swelling on the scattering spectra is even more evident in the case of hydrated membranes.

The hydrophilicity of the copolymer is provided by the sulfonic acid groups, whose overall content is quantified by the ion exchange capacity ($IEC$). The $IEC$ is increasing with graft level, and no significant difference between DP and SG membranes is found (Supporting Information, Section 4.6., Equation 4.9, Figure 4.21). However, the water uptake – although it increases with graft level in similar manner – shows more pronounced differences between DP and SG, especially at higher GL (Supporting Information, Section 4.6, Figure 4.22).
In line with what was mentioned above, polymer swelling is expected to reduce the anisotropy parameter, on the one hand, and shift and dampen the correlation peak, on the other hand. Indeed, both tendencies are observed in the SANS spectra of DP and SG membranes being in the dry state and then swollen with D$_2$O (Figure 4.3). The observed difference between the two types of base polymer remains apparent for the dry membranes (at grafting levels of 12%, 25%, 42% and 67%) and is also observed in the SAXS experiments. For the water-swollen membranes, the differences between DP and SG are reduced, and at 67% grafting level the two spectra look very similar.

**Figure 4.3:** Azimuthally averaged scattering curves along the machining direction (MD) of dry and water-swollen (D$_2$O) membranes.

The anisotropy decreases both upon grafting and upon swelling with water (see Supporting Information, Section 4.6, Figures 4.23 and 4.24) as shown by the values of the Hermans function (Figure 4.4) – yet the original difference stemming from the base polymer is rather well preserved. The anisotropy difference between dry and swollen membrane appears larger in DP than in SG, despite the observation that water uptake
follows a quite similar trend, and SG has an even higher water uptake at high graft levels.

**Figure 4.4:** The Hermans functions determined from the SANS spectra. To calculate the values of $f$, the scattering intensity was integrated across the momentum transfer range of the correlation peak ($0.15 \text{ nm}^{-1} < Q < 0.5 \text{ nm}^{-1}$ in the case of base films, $0.1 \text{ nm}^{-1} < Q < 0.4 \text{ nm}^{-1}$ in the case of grafted films and membranes).

Considering these tendencies and variations in the nanoscale structure, one anticipates that these can have an impact on membrane conductivity. As we showed that the ion concentration varies in through-plane direction it is not appropriate to investigate the impact of anisotropy by comparing in-plane and through-plane conductivity. The only approach is by comparing the two in-plane directions – machining and transverse direction – in which the ion concentration is the same (compare Supporting Information, **Section 4.6, Figure 4.18** and the basically identical sulfur distribution profiles for SG and DP). Indeed, as shown in Supporting Information, **Section 4.6, Figure 4.25**, the conductivity differs for MD and TD. First, conductivity measured in the TD is always higher than the one measured in the MD. The origin of this anisotropy in conductivity may be understood by considering certain fundamental properties of diffusive transport (see **Section 4.6.3** for in-plane proton conductivities in perpendicular directions). Second, DP exhibits a tendency for higher conductivity over SG, and the difference between the MD and TD conductivity values is larger in the case of SG membranes. A possible explanation is that although their water uptake is higher (Supporting Information, **Section 4.6, Figures 4.22 and 4.25**), the structural swelling upon humidification, indicated by the decrease of the anisotropy, is smaller for SG membranes (**Figure 4.4**). This is in agreement with earlier results showing that although overall water uptake is an important factor governing proton conductivity of proton conducting membranes, so is the influence of the nano-scale morphology of the
polymer, i.e. the structure and connectivity of the aqueous phase.\textsuperscript{34, 217} Third, it is remarkable that at high water uptake the difference between the MD and TD conductivity values (Supporting Information, Section 4.6, Figure 4.25) is considerably larger for the SG membrane than for the DP membrane. That is, the anisotropy in conductivity is higher for the SG membranes even though the absolute value of the structural anisotropy is smaller. This contradiction may relax when we consider that the relative changes in structural anisotropy upon water swelling are in fact considerably larger in the DP membrane compared to the SG membrane. For example, at a grafting level of 42\% the water uptake of the DP and SG membrane is 60\% and 80\%, respectively (Supporting Information, Section 4.6, Figure 4.25). The corresponding relative structural anisotropy change, quantified as $(f_{\text{swollen}} - f_{\text{dry}})/f_{\text{dry}}$ is 33\% and 17\%, respectively (Figure 4.4). It is a significant difference and a possible cause of anisotropy in conductivity.

The Nernst-Einstein equation is often used to compare ion transport on the macroscopic scale to the diffusivity of tracer species, such as water, in the membrane.\textsuperscript{7, 19, 274} The equation connects the microscale with the macroscopic scale, by stating that, at a given temperature, conductivity is proportional to the free charge-carrier concentration and their diffusion coefficients. It can be shown that the volumetric concentration of these charge-carrier protons $[H^+]$, defined as the number of protons per unit volume of water, is proportional to the IEC and is inversely proportional to water uptake, $[H^+] \propto \text{IEC}/W$, given that the mass density of water in the membrane is that of the bulk value and all the protons of the acidic groups are dissociated.\textsuperscript{33} To decouple this potentially strong dependence as well as the possible influence of proton concentration on the estimation of proton dynamics, QENS is used to directly probe the diffusion of protons and water. It is expected that the proton and water diffusion coefficient reflects predominantly on the nanoscale structure and morphology of the aqueous phase, defining the percolation and the extent of connectivity of the hydrophilic domains.\textsuperscript{244}

As in the through-plane conductivity measurements, we probed membranes of 25\% graft level at a relative humidity value of 53\%. Figure 4.5 shows two representative QENS spectra corresponding to the DP and SG membranes, and Figure 4.6 shows the determined diffusion coefficients. Equation 4.6 was used to interpret the experimental data, and the overall fit (solid blue line in Figure 4.5) is composed of a linear background (dotted red line), a Dirac delta function convoluted with the instrumental resolution function (dashed red line), and a Lorentzian convoluted with the instrumental resolution function (solid red line).
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Figure 4.5: Quasi-elastic neutron scattering spectra from DP (a) and SG (b) membranes at 53% r.h. recorded at 25°C and $Q = 7.4$ nm$^{-1}$.

The half-width at half maximum (HWHM) of the Lorentzian function quantifies proton dynamics, in terms of the self-diffusion coefficient $D$ (Equation 4.7).

Figure 4.6: The quasi-elastic broadening of the Lorentzian function determined at different $Q$ values and the best fits against Equation 4.7 (solid lines).

This approach yields $D = (0.92 \pm 0.03) \times 10^{-5}$ cm$^2$s$^{-1}$ for the DP and $(1.07 \pm 0.01) \times 10^{-5}$ cm$^2$s$^{-1}$ for the SG membrane, this time slightly higher (~15%) for SG. For Nafion®, at similar hydration level and at room temperature (22°C) a higher value, $D = 1.06 \times 10^{-5}$ cm$^2$s$^{-1}$, is reported. One probable origin of this could be the morphology. Several different morphological models have been proposed for the nanostructure of Nafion®. Based on the percolation threshold, it was suggested that the hydrophilic domains in Nafion® grow from a lamellar morphology. Another appealing model is that of cylindrical water-filled nano-channels packed randomly but
aligned in parallel manner. However, while this model naturally indicates a good through-plane conductivity, it somewhat falls behind when it comes to in-plane conductivity: we have measured the conductivity of Nafion® both in-plane and through-plane in fully swollen state, and found similar values of 80 – 85 mS cm$^{-1}$. Recent studies suggest that the model of a seemingly random yet interconnected channel-type network appears to be more appropriate. No matter which model considered, the common characteristic feature of the different Nafion® models is the good connectivity of the hydrophilic phase even at low water content, the tortuosity of the aqueous phase is expected to have a less pronounced dependence on the water volume fraction. In radiation-grafted copolymer membranes – similar to the ones investigated in this article – a strong increase of the tortuosity at low values of water volume fraction was found due to the disordered aqueous phase. Regarding the QENS studies reported here, the lowest $Q$ value accessed is $\sim 3$ nm$^{-1}$, and thus the proton dynamics are probed over a maximum distance of approximately 2.1 nm, that is, we do not probe long-range ‘macroscopic’ dynamics. While the slight difference between the diffusion coefficients determined for the DP and SG membrane may be attributed to the uncertainties in the water sorption and corresponding hydration level during the experiment, the nanoscale QENS and macroscale conductivity measurement are in good agreement regarding their order of magnitude, and the proton dynamics of Nafion® outperform both DP and SG membranes. For a more detailed explanation of this effect, a closer look at the morphology needs to be taken. In case of these DP and SG membranes, one expects to find a rather disordered structure of the aqueous phase, which is partially responsible for providing a quite tortuous aqueous phase for proton diffusion. Given the synthesis, this comes as no surprise: the distribution of the active sites in the base polymer created by irradiation is random. The copolymerization of the pendant chains is governed by a stochastic process and, therefore, both the graft length and the graft density are likely to follow a rather broad distribution. Apart from the ‘templating influence’ of the base polymer structure, the aspects mentioned above are likely to result in arbitrary hydrophilic domains distributed randomly, which swell into a disordered aqueous phase upon hydration. EDX analysis of both membrane types show a systematic decrease of the local degree of grafted polystyrene when moving toward the interior of the copolymer (Supporting Information, Section 4.6, Figure 4.18). This inhomogeneity results in systematically changing local graft level and IEC and, accordingly, a heterogeneous swelling and hydration. Additionally, due to the semi-crystalline microstructure of the base polymer matrix, even within a microscale domain, certain domains are rich in hydrophilic clusters, while other domains are devoid of them. Therefore, heterogeneity is found on two length scales: the one on the macroscale (tracked via EDX) is systematic but the one on the micro-scale is disordered.
However, this through-plane inhomogeneity and the less functionalized center of the membrane (DP and SG) cannot be regarded as the reason for the lower conductivity at decreased r.h. of radiation grafted membranes compared to Nafion® type ones (Figure 4.7). Earlier investigations clearly showed the same trend even for in-plane conductivity measurements\textsuperscript{280} where at high r.h. values their conductivity is as high as that of Nafion® but a serious gap of conductivity values opens at low r.h. The lower conductivity, as compared to Nafion®, is most probably the result of the microscopic heterogeneity of the system. Another reason might be the fundamental difference in the distribution of sulfonic groups along the pendent chains. While the pendent chains of PFSA membranes are hydrophobic, they are terminated with a sulfonic group, which imparts hydrophilicity. In our membranes, each unit of the side chains carries a sulfonic group; hence the entire length of the chain is hydrophilic. In the case of PFSA membranes, water does not favor side chains, and the sulfonic groups tend to be found at the interface of hydrophilic-hydrophobic domains. In the case of sulfonated polystyrene, it is energetically more favorable for the side chain to be located in water. Therefore, the aqueous phase might not be as homogeneous as in the case of Nafion®. The consequence of this difference might be crucial, for the presence of sidechains in the aqueous phase might hinder the diffusion of protons.

![Figure 4.7](image.png)

**Figure 4.7:** Through-plane conductivity measured at 80°C and different relative humidity values (a). Graft level is 25%. The panel b shows the conductivity ratio DP/SG.

**4.4.3. Characterization of membranes in the fuel cell**

The two types of grafted membrane and Nafion® NR-212 were assembled in single cells and characterized under different humidity conditions (50%, 70% and 100% r.h.). The
performance of the cells follows the trend of the conductivity values obtained for the three membranes (Figure 4.8): Under fully humidified conditions the performance of the cell with the DP membrane is close to that of the cell with NR-212, whereas the cell with the SG membrane shows somewhat inferior performance. At reduced r.h., the performance of the DP and SG membranes is below that of NR-212 (for detailed information on measured polarization curves as well as the corresponding HFR and iR-correction see Supporting Information, Section 4.6, Figure 4.26 and Tables 4.1 – 6).

Figure 4.8: Representative polarization curves of DP and SG membranes graft level of 25% and Nafion® NR-212 at different relative humidity values (80°C, 2.5bar, backpressure on both sides, H₂/O₂, flow rates: 100% r.h. – 600 mL min⁻¹, 70% and 50% - 2000 mL min⁻¹).

For further information on the different fuel cell performance characteristics of radiation grafted membranes compared to PFSA membranes (e.g. NR-212) the reader is referred to earlier work²⁸¹-²⁸³, as the focus of this article lies on the comparison of SG and DP membranes. To investigate the stability of DP and SG membranes and
whether the base film influences the stability under fuel cell test conditions, several r.h. cycles (100% → 70% → 50% → 100% r.h.) were performed. At the end of each equilibration phase (for each r.h. setpoint) a polarization curve was recorded and the performance loss of the cell with respect to the initial performance calculated. For both membranes, a decrease in performance with increasing cycle number is observed, yet the performance loss was more pronounced in case of the SG membrane (Figure 4.9).

Figure 4.9: Exemplary polarization curves of nine consecutive cycles for DP (a) and SG (b). One full cycle corresponds to: r.h. = 100% → 70% → 50% → 100% and the measurements were made at 100%.

The comparison of the performance loss after 9 cycles is given in Figure 4.10 for the characteristic current density of 1 A·cm⁻². For all investigated r.h. values, the performance loss of SG is significantly higher than the loss of DP (up to 35% in case of 50% r.h. compared to 19%). The iR-correction method was applied to verify that the observed performance loss was not caused by a degradation of the electrode or other fuel cell components but can be solely assigned to the membrane (for more information on fuel cell data and performance loss see Supporting Information, Section 4.6, Figure 4.26 and Tables 4.1 – 6). Also, the pronounced voltage decrease at high current densities (increasing with cycle number, Figure 4.9) is not caused by mass transport losses but by an increasing ohmic resistance of the membrane with current density.
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Figure 4.10: Performance losses (voltage losses) quantified at a current density of 1 A cm$^{-2}$ after nine relative humidity cycles.

Generally, degradation of sulfonated styrene grafted membranes is triggered by the attack of radical species formed in the fuel cell as intermediates.$^{281, 283}$ Since the DP and SG membranes are chemically identical, the difference found in stability is surprising. One tentative explanation for the different rate of degradation of the two grafted membranes might be that the structural differences of the two base polymers affect the rate of gas crossover that results in the formation of hydroxyl radicals.$^{81}$ This hypothesis was tested by measuring electrochemical hydrogen permeation. The crossover of hydrogen gas is proportional to the oxygen crossover,$^{285}$ and therefore was used to compare gas permeation properties of the two types of membrane. The results, however, disproved the hypothesis, as the hydrogen crossover was measured to be approximately the same ($\sim10$ NμL min$^{-1}$ cm$^{-2}$). Therefore, the different behavior must be related to the dissimilar morphology of the two membranes and the underlying base polymer. The tentative explanation we offer relates to the phenomenon of “swelling-induced detachment of grafts” put forward by Enomoto et al.$^{286}$, according to which the swelling of a membrane with PSSA grafts can lead to rupture of the grafted chains at the interface between crystallites and the amorphous phase. Since the critical location in this case is the polymer regions close to the surface of the crystallites, translated to our DP and SG membranes this would mean that in case of SG, owing to the smaller crystallites in the SG base film (cf. above), there would be a higher volume fraction of this interphase region susceptible to swelling-induced detachment of grafts (Figure 4.11).
Consequently, a higher rate of degradation upon r.h. cycling is expected for SG, which is indeed what is observed. Repeated changes in the hydration state of the membrane thus trigger the detachment of grafts and loss thereof, which leads to a gradual increase of membrane resistance, concomitant with a decrease in fuel cell performance.

In a running fuel cell, particularly if operated in a dynamic and intermittent manner, load changes and start-ups / shut-downs are frequent, which induces changes in the hydration state of the ionomer membrane. A higher resistance of the membrane against swelling/drying-induced detachment of polyelectrolyte grafts is essential for future developments. Therefore, in this respect DuPont ETFE base film shows a clear advantage over ETFE base film from Saint-Gobain. Furthermore, it is conceivable to attempt adjusting the degree of crystallinity and size, possibly also orientation of the crystallites in case they are not of a spherical shape, which provides another handle to the experimenter to design the membrane structure for specific target applications.

The majority of studies performed thus far on radiation grafted ion-conducting membranes have been concerned with the choice of the graft component, whereas the tailoring of the base polymer has been given little attention. The results shown in this study highlight the influence of base film properties and characteristics on the final properties of the membrane. The insights gained call for a dedicated approach to design polymer materials optimized towards the use as a base film material and matrix for ion-conducting membranes prepared by radiation grafting. This will be the subject of forthcoming studies.
4. **Summary and Conclusions**

The systematic investigation of a representative (model) system of pre-irradiation grafted copolymer membranes was aimed at identifying the influence of the morphology of the underlying base polymer film on the structural and functional properties of the resulting grafted films and membranes. Although scattering results and fuel cell relevant properties follow largely similar trends in graft copolymers prepared from the two different ETFE base films from DuPont (DP) and Saint-Gobain (SG), some significant differences are observed. DuPont based membranes exhibited a better proton conductivity, in particular at low relative humidity. Furthermore, the DuPont based membrane was significantly more stable against degradation in the fuel cell subjected to relative humidity cycling. These phenomena could be attributed to differences in the morphology of the base film, such as smaller crystallites in the case of ETFE from Saint-Gobain. Thus, it becomes essential - for the development of new proton exchange membranes prepared via pre-irradiation grafting - not only to investigate the chemical composition of the grafted membrane but also include microstructural analysis starting from the base film. Small-angle scattering experiments proved that nominally identical base films obtained from two main suppliers differ in their microstructure and such differences are to a certain extent preserved in the grafted films and membranes. The differences in the various properties cannot be attributed but to microstructure and indicate that the selection of the base film is important. Moreover, this leads us to the conclusion that a careful design of base polymer material and its morphological features provides an important and essential degree of freedom to optimize properties, performance and stability characteristics of the final ion-conducting membrane.

4.6. **Supporting Information**

The Supporting Information contains additional information about the experiments, and presents reaction kinetics data, SANS, SAXS and WAXS spectra, IR spectra, electron micrographs, EDX images, ion exchange capacity data, water uptake data, in-plane conductivity data, polarization curves, and data summarizing the results of cell stability measurements.

4.6.1. **Experimental Section**

4.6.1.1. **SEM / EDX Analysis**

To analyze the through-plane distribution of the grafted polystyrene chains on the micrometer scale, sulfonated copolymer films were swollen in water for 2 h,
subsequently frozen in liquid nitrogen and fractured to obtain a sharp cross-section area without considerable smearing. Scanning electron microscopy (SEM) images were taken with a FESEM Ultra 55 (Carl Zeiss, Oberkochen, Germany) and energy dispersive X-ray (EDX) analysis was performed using a compatible accessory (EDAX TSL, AMETEK).

**4.6.1.2. Ex-Situ Characterization**

The ion exchange capacity (IEC), proton conductivity, water uptake and hydration number were determined in fully swollen state at ambient conditions. The IEC is defined as

\[
\text{IEC} = \frac{n(\text{H}^+)}{m_{\text{dry}}} \tag{4.8}
\]

where \(n(\text{H}^+)\) is the molar number of acid protons and \(m_{\text{dry}}\) is the dry weight of the membrane. After a proton/potassium exchange (stirring in 1 M KCl for 12 h at room temperature) the free accessible protons were titrated with a 0.05 M KOH solution by means of a SM Titrino 702 instrument (Metrohm, Herisau, Switzerland). The theoretical IEC can be calculated using the following equation, assuming that all styrene units carry one sulfonic acid group:

\[
\text{IEC}_{\text{th}} = \frac{G_L}{M_S + M_{\text{SSA}} G_L} \tag{4.9}
\]

where \(M_S\) and \(M_{\text{SSA}}\) denote the molar masses of styrene (104 g/mol) and styrene sulfonic acid (184 g/mol), respectively. The water uptake (Q) of the membrane, representing the ability to absorb water, is determined by gravimetric means using the following equation:

\[
Q = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \tag{4.10}
\]

The hydration number (\(\lambda\)), defined as the molar ratio between water and sulfonic acid groups, was estimated from the IEC and the water uptake values according to:

\[
\lambda = \frac{n(\text{H}_2\text{O})}{n(\text{SO}_3\text{H})} = \frac{Q}{\text{IEC} \cdot M_{\text{H}_2\text{O}}} \tag{4.11}
\]

The in-plane conductivity was measured at room temperature in fully swollen state by means of a four point-probe conductivity cell (Bekktech BT-112) consisting of four Pt-electrode wires. Rectangular samples (30 mm x 12 mm) of hydrated membranes were cut and mounted into the cell. To ensure membrane hydration, the conductivity cell was immersed in ultra-pure water during the measurement. Impedance measurements were
performed using a Zahner IM6 (Zahner Messtechnik, Kronach, Germany) where impedance and phase angle were measured at 1 kHz with 10 mV amplitude of the AC perturbation signal and the phase shift of the measured impedance at 1 Hz was below 5° to ensure that the measured value is the true Ohmic resistance. The thickness of the membranes was measured with a thickness gauge (MT12B, Heidenheim, Germany).

The through-plane conductivity at different relative humidity values (r.h.) was measured with a 740 Membrane Test System from Scribner Associates Inc. (North Carolina, USA) at a temperature of 80°C, using gas diffusion electrodes from E-TEK DivisionSM (ELAT HT-140E-W).

4.6.1.3. **In-Situ Characterization**

Fuel cell tests were performed with membranes of a grafting level of ~25%. Nafion® (NR-212) was measured as reference. To form a membrane electrode assembly (MEA), membranes were laminated with gas diffusion electrodes from Johnson Matthey Fuel Cells (type ELE 0263-0983, loading: 0.4 mg Pt/cm²) in a hot-press at defined temperature, load, and duration (110°C/2.5 MPa/180 s). Subsequently, the MEAs were assembled into a single cell with a graphite flow field and an active area of 15.8 cm². Further details regarding the cell design can be found elsewhere. The MEAs were operated in a single cell mode at 80°C and 2.5 bar, backpressure on both sides with hydrogen and oxygen fed at a flow rate of 600 mL min⁻¹. After 12 h conditioning at constant current density (0.5 A cm⁻²) and 100% relative humidity, the first polarization curve was measured. Cell voltage and high frequency resistance (HFR at 1 kHz, AC milliohm meter model 3566, Tsuruga, Japan) were continuously monitored over the entire length of the test protocol. The cell was conditioned at 70% r.h. for 2 h (gas flow rate: 2000 mL min⁻¹, 0.1 A cm⁻²) before the next polarization curve was taken; the same applies for the measurements at 50% r.h..

For stability measurements various MEAs with SG and DP PEMs were conditioned as described and subjected to 9 cycles of humidity changes as described above (1 cycle: 100% r.h. → 70% r.h. → 50% r.h. → 100% r.h.) at the end of each conditioning phase a polarization curve was measured and the performance loss of the membrane calculated. The iR-correction method was applied to verify that the observed performance loss was not caused by a degradation of the electrode or other fuel cell components. Thereby, the iR-corrected cell potential was determined according to the following equation: \[ E_{iR-free} = E_{cell} + i R_Ω \] with \( i \): current density, \( E_{iR-free} \): cell potential after correction for ohmic resistance, \( E_{cell} \): cell potential without corrections, \( R_Ω \): ohmic resistance or high frequency resistance.
Electrochemical hydrogen permeation measurements based on the single cell configuration were conducted to assess the mechanical integrity and gas permeability of the membranes. After the usual conditioning period (cf. above) hydrogen crossover through the membrane was measured by an electrochemical method under fully humidified conditions at 80°C and 2.5 bar backpressure on both sides. Fully humidified gases (H₂ and N₂, flowrate 600 mL min⁻¹) were fed to the anode and cathode, respectively. After 2 h the hydrogen permeation was evaluated as a diffusion-limited hydrogen oxidation current density in the range of 200-800 mV.

4.6.1.4. Small-Angle Neutron Scattering

Small-angle neutron scattering (SANS) experiments were performed on the SANS-II instrument at the Paul Scherrer Institute (PSI). On this instrument, a quasi-continuous beam is monochromatized by a velocity selector with a wavelength spread (Δλ/λ) of ~10%. The base film samples were directly mounted onto a conventional temperature controlled sample changer, while hydrated and dry membranes were placed in 1 mm quartz cuvettes for mounting. The illuminated area of the sample was defined by a 10 mm × 7 mm aperture with corners covered with a d = 10 mm circular aperture in front of the sample. Neutrons scattered from the samples were detected with a position-sensitive ³He detector having 128 × 128 pixels with a pixel size of 4.3 × 4.3 mm². Three settings of the instrument were used to cover the Q-range of interest, 0.03 – 2.9 nm⁻¹: The sample-to-detector distances, collimations, and wave lengths were 1.1 m, 3 m, and λ = 0.518 nm, 4 m, 4 m, and λ = 0.518 nm, and 6 m, 6 m, and λ = 1.035 nm, respectively. Data treatment was performed with the “Graphical Reduction and Analysis SANS program” package (GRASP, developed by C. Dewhurst, ILL). The 2D data were corrected for background due to dark counts and scattering from the sample environment according to standard procedures, and 1D scattering curves were obtained by azimuthally averaging either the full detector image (360°) around the direct beam position or in two 90° sectors along the machining and the transverse direction of the sample.

4.6.1.5. Small-Angle X-ray Scattering

Small-angle X-ray scattering (SAXS) experiments were performed on a SAXSlab instrument (JJ X-ray, Skovlunde, Denmark). The instrument has a Genix 3D X-ray source (Xenocs SA, Sassenage, France) providing a photon wavelength λ = 0.154 nm. Scattering was recorded with a 2D 300 K Pilatus detector (Dectris Ltd., Baden, Switzerland). The three different instrumental setups applied offered a Q-range coverage of 1 – 27.5 nm⁻¹, 0.23 – 7.3 nm⁻¹ and 0.03 – 2.2 nm⁻¹. Azimuthally averaged
scattering curves were obtained from the 2D scattering patterns with the SAXSGUI program.

![Graph showing reaction kinetics for grafting of styrene into ETFE films (thickness: 25 µm) of the suppliers DuPont and Saint-Gobain. Reaction parameters: 5 kGy, 55°C, 20% (v/v) monomer. Minor differences were found between the SG and DP base polymers for lower grafting times (< 60% GL). At higher grafting times the differences in grafting level is up to 25% (e.g. after 4 h). The error bars represent the (sample) standard deviation of the mean derived from four samples.]

**Figure 4.12:** Reaction kinetics for grafting of styrene into ETFE films (thickness: 25 µm) of the suppliers DuPont and Saint-Gobain. Reaction parameters: 5 kGy, 55°C, 20% (v/v) monomer. Minor differences were found between the SG and DP base polymers for lower grafting times (< 60% GL). At higher grafting times the differences in grafting level is up to 25% (e.g. after 4 h). The error bars represent the (sample) standard deviation of the mean derived from four samples.

![Sample holder for the QENS experiments. The membrane is not in contact with the solution due to the design of the sample holder. The sample holder consists of two tubes. The membranes were attached on the outside of the inner hollow tube and fixed at the top position. The membranes were not covering the full height of the tube, and left some space at the bottom of the sample holder for the Mg(NO₃)₂ solution. To avoid liquid drops on the sample, the inner tube (with the attached membranes) was inserted into the larger tube before slowly injecting the liquid through the cavity of the inner tube.]

**Figure 4.13:** Sample holder for the QENS experiments. The membrane is not in contact with the solution due to the design of the sample holder. The sample holder consists of two tubes. The membranes were attached on the outside of the inner hollow tube and fixed at the top position. The membranes were not covering the full height of the tube, and left some space at the bottom of the sample holder for the Mg(NO₃)₂ solution. To avoid liquid drops on the sample, the inner tube (with the attached membranes) was inserted into the larger tube before slowly injecting the liquid through the cavity of the inner tube.
4. Influence of Variations in Base Film Nanostructure

Figure 4.14: Anisotropy of the DuPont (a) and Saint-Gobain (b) base films as revealed by SANS experiments. The azimuthally averaged scattering curves of the two-dimensional SANS signal along the machining direction (MD) and the transverse direction (TD) are very different. The anisotropy is clearly higher for DP than for SG.

Figure 4.15: SAXS signal (logarithm of the intensity is displayed) of DP (left) and SG (right) films (~12% GL).
4. Influence of Variations in Base Film Nanostructure

Figure 4.16: IR spectra of ETFE base films purchased from DuPont and Saint-Gobain. The measurement does not reveal any chemical difference between the two base polymers. Panel b) shows a magnification of the spectrum.

Figure 4.17: Interpretation of the WAXS spectra to estimate crystallite size through the Scherrer law, and contributions from the different components of the fit in case of the DP base film (a), and the DP grafted film at 67% GL (b).
4. Influence of Variations in Base Film Nanostructure

Figure 4.18: Scanning electron micrographs of SG and DP cross sections (~25% GL) and EDX sulfur mappings thereof (top). Overlaid sulfur distribution profiles (through-plane) of SG and DP membranes (~25% GL) (middle). The intensity loss at the right edge of the SG graph is caused by artifacts due to a different topography of the surface, which is also reflected in the carbon mapping. At the upper edge of the cross-section (towards the surface of the film) there are some “shadows” (regions were less EDX signal can be detected) visible in the carbon mapping (red, bottom)). As the carbon content does not differ in the “shadow” area from the carbon content in the adjacent “not-shadow” area, this suggests that the decreased intensity in the sulfur profile is also not generated by a decreased sulfur concentration but by the topography of the sample.
4. Influence of Variations in Base Film Nanostructure

Figure 4.19: Azimuthally averaged SAXS curves of grafted films at 12\% (top) and 67\% (bottom) grafting level based on ETFE from DP and SG, before (left) and after (right) sulfonation. Structural differences between the two types of base polymer are mostly preserved upon grafting and sulfonation.

4.6.2. **Ionomer Peak**

In the case of membranes, the scattering peak centered at $\sim 4 \text{ nm}^{-1}$ is the so-called ionomer peak, which has been analyzed in detail on several occasions for similar systems containing sulfonated PS.\textsuperscript{243,257,288} However, in the case of grafted films, we are uncertain about the origin of the small yet evident scattering peak visible near $\sim 7 \text{ nm}^{-1}$. This scattering feature is absent in the case of any of the base films, and thus, it must originate from the grafting reaction. We have never observed this feature previously, and at the moment we can neither discard nor provide any evidence for the hypothesis that there is a common origin of these distinct scattering features. Nonetheless, it is a fact that these two peaks were not observed simultaneously: Upon sulfonating the grafted film, the peak observed at $\sim 7 \text{ nm}^{-1}$ disappears, and the ionomer peak emerges.
As a tentative explanation, we refer to a sub-nanometer-scale heterogeneity in the amorphous region of the graft copolymer, which relates to a coexistence of styrene-rich and styrene-depleted domains. Consequently, the formation of ion-rich domains, now densely packed with sulfonic groups, might be easier within the styrene rich domains. Given the PS-related origin, the fact that this peak is quite independent from the base film material is not unexpected, because the size range corresponding to the peak is significantly smaller than the size and separation distance of the crystallites. The features of this scattering peak can be interpreted well by the linear combination of a linear, a power, and a Lorentzian function (not shown). From this phenomenological mathematical model, the amplitude and center position of the Lorentzian function is determined (Figure 4.20). The amplitude is found to be proportional to the graft level, while the value of the center position first slightly decreases/increases (grafted film/membrane) and then remains constant near ~7 nm\(^{-1}\) (grafted film) and ~4 nm\(^{-1}\) (membrane) with further increasing graft level.

**Figure 4.20:** The center position (a) and amplitude (b) of the Lorentzian function interpreting the ionomer peak (Figure 4.19).
4. Influence of Variations in Base Film Nanostructure

**Figure 4.21:** The ion exchange capacity of SG and DP membranes, shown as a function of grafting level.

**Figure 4.22:** Water uptake at room temperature, shown as a function of grafting level.
4. Influence of Variations in Base Film Nanostructure

Figure 4.23: SANS patterns (logarithm of the intensity is displayed) of DP (left) and SG (right) dry membranes with increasing (top to bottom) grafting levels of 12%, 25%, 42% and 67% (66% in case of SG). Machining direction is vertical, transverse direction is horizontal.
Figure 4.24: SANS patterns (logarithm of the intensity is displayed) of DP (left) and SG (right) membranes swollen in D$_2$O with increasing (top to bottom) grafting levels of 12%, 25%, 42% and 67% (66% in case of SG). Machining direction is vertical, transverse direction is horizontal.
4.6.3. **In-Plane Proton Conductivities in Perpendicular Directions**

The Nernst-Einstein equation connects the microscale with the macroscopic scale, by stating that at a given temperature conductivity is proportional to the free charge-carrier concentration and their diffusion coefficients. As presented before in the case of similar membranes, a random walk is a particularly useful model to explore and capture the essence of correlations between proton conductivity and nanoscale structure. In this model, similar to Brownian motion, proton transport is represented by the sum of discrete and uncorrelated steps performed in a given time. The mean square displacement defines the effective diffusion coefficient via the equation $\langle r^2(t) \rangle = 2 \cdot n \cdot D(t) \cdot t$, where $D$ is the diffusion coefficient and $n$ is the space dimension. The left side of this equation can be expanded as $\langle r^2(t) \rangle = \langle x^2(t) \rangle + \langle y^2(t) \rangle + \langle z^2(t) \rangle$, which indicates that each term (i.e., each dimension) is associated with its own diffusion coefficient: $\langle x^2(t) \rangle + \langle y^2(t) \rangle + \langle z^2(t) \rangle = (2 D_x + 2 D_y + 2 D_z) \cdot t$. In case of isotropic diffusion, where the length of steps are independent of the direction, $D_x = D_y = D_z$. However, if the diffusion is anisotropic $D_x \neq D_y \neq D_z$. To demonstrate this, let us consider the lamellar morphology, which is the most obvious representation of orientation and anisotropy. In such structures, the long-range diffusion is certainly anisotropic: it is more effective along the lamellae (in this simplified model representing the TD direction) than perpendicular to the lamellae. This is simply because the confinement (which in our case is given by the presence of the impenetrable non-grafted hydrophobic ETFE phase) in the two perpendicular directions are different.

![Figure 4.25](image_url): The in-plane proton conductivity at room temperature as a function of water uptake of membranes fully swollen with water. The corresponding graft levels are indicated. MD: machining direction, TD: transverse direction.
4. Influence of Variations in Base Film Nanostructure

![Figure 4.26](image-url)

**Figure 4.26:** Exemplary Polarization curves and corresponding HFR data for DP and SG membranes. Polarization curves of SG and DP membranes at a fixed GL ~25% (NR212 is given as a reference) for different relative humidity values (50%, 70% and 100% r.h.) (a). Corresponding high frequency resistance (HFR) measurements (b).

### Table 4.1: Initial performance loss (%) due to a decrease in r.h. (100% → 70% r.h.; 100% → 50% r.h.).

<table>
<thead>
<tr>
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<th>DP based membranes</th>
<th>SG based membranes</th>
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<tbody>
<tr>
<td></td>
<td>100% → 70%</td>
<td>100% → 50%</td>
</tr>
<tr>
<td><strong>mean</strong></td>
<td>6.6</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>dev.</strong></td>
<td>6.1</td>
<td>0.9</td>
</tr>
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</table>

### Table 4.2: Cycle stability for each relative humidity (100%, 70% and 50% r.h.). Performance loss (PL) is given in %.

<table>
<thead>
<tr>
<th></th>
<th>DP-ETFE-g-PSSA</th>
<th>SG-ETFE-g-PSSA</th>
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<tr>
<td></td>
<td>A cm⁻²</td>
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</table>
Influence of Variations in Base Film Nanostructure

Table 4.3: Exemplary data for iR-correction for DP based membrane (GL ~25%) cells. a: Uncorrected cell voltage ($E_{cell}$). b: Corresponding HFR-table ($R_{ul}$).

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<th>mV</th>
<th>rel. performance loss [%]</th>
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### 4. Influence of Variations in Base Film Nanostructure

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b)

<table>
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<tr>
<th></th>
<th>mΩ cm²</th>
<th>rel. increase in resistance [%]</th>
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<td>69.0</td>
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<td>71.5</td>
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</table>

| 2nd   | 0.5    | 69.1    | 115   | 196   | 0.16   | 7.84   | 11.1   |
|       | 1      | 71.7    | 93.8  | 137   | 0.29   | 5.00   | 10.1   |

| 3rd   | 0.5    | 71.3    | 122   | 209   | 3.45   | 14.6   | 18.4   |
|       | 1      | 74.4    | 101   | 147   | 4.01   | 13.5   | 18.2   |

| 4th   | 0.5    | 74.3    | 130   | 231   | 7.67   | 22.2   | 30.7   |
|       | 1      | 77.9    | 112   | 162   | 8.85   | 25.3   | 30.3   |

| 5th   | 0.5    | 77.5    | 130   | 250   | 12.33  | 22.1   | 41.5   |
|       | 1      | 81.9    | 118   | 179   | 14.55  | 32.6   | 43.8   |

| 6th   | 0.5    | 80.5    | 146   | 257   | 16.7   | 37.5   | 45.7   |
|       | 1      | 86.1    | 130   | 199   | 20.3   | 45.3   | 59.9   |

| 7th   | 0.5    | 83.7    | 159   | 287   | 21.4   | 48.9   | 62.2   |
|       | 1      | 90.6    | 138   | 212   | 26.6   | 54.7   | 70.5   |

| 8th   | 0.5    | 87.2    | 162   | 308   | 26.4   | 51.9   | 74.2   |
|       | 1      | 95.9    | 148   | 234   | 34.0   | 65.6   | 87.7   |

| 9th   | 0.5    | 91.0    | 185   | 329   | 31.9   | 73.9   | 86.4   |
|       | 1      | 101     | 164   | 254   | 41.4   | 83.7   | 103    |
### Table 4.4: Exemplary data for iR-correction for DP based membrane (GL ~25%) cells. iR-corrected cell voltage and corresponding losses per cycle ($E_{iR-free} = E_{cell} + iR$):

<table>
<thead>
<tr>
<th></th>
<th>100% RH</th>
<th>70% RH</th>
<th>50% RH</th>
<th>100% RH</th>
<th>70% RH</th>
<th>50% RH</th>
</tr>
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<tbody>
<tr>
<td><strong>mV</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>1st</td>
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<td>783</td>
<td>767</td>
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<td>803</td>
<td>769</td>
<td>757</td>
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<td>5.65</td>
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<td>781</td>
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<td>765</td>
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<td>762</td>
<td>1.18</td>
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<td>819</td>
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<td>782</td>
<td>0.62</td>
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<td>1.28</td>
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<td>782</td>
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<td>-1.34</td>
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<td>768</td>
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### Table 4.5: Exemplary data for iR-correction for SG based membrane (GL ~25%) cells. a: Uncorrected cell voltage ($E_{cell}$). b: Corresponding HFR-table ($R_{H}$).

<table>
<thead>
<tr>
<th></th>
<th>100% RH</th>
<th>70% RH</th>
<th>50% RH</th>
<th>100% RH</th>
<th>70% RH</th>
<th>50% RH</th>
</tr>
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<tr>
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<td></td>
<td></td>
<td></td>
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<td></td>
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<td>738</td>
<td>683</td>
<td>6.94</td>
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129
### 4. Influence of Variations in Base Film Nanostructure

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<td>404</td>
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</table>

b) |   | mΩ cm² | rel. increase in resistance [%] |
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A cm²</td>
<td>100% RH</td>
</tr>
<tr>
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<td>0.5</td>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>79.8</td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
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<td>0.5</td>
<td>84.6</td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
<td>5th</td>
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</tr>
</tbody>
</table>
4. Influence of Variations in Base Film Nanostructure

Table 4.6: Exemplary data for iR-correction for SG based membrane (GL ~25%) cells, iR-corrected cell voltage and corresponding losses per cycle ($E_{iR-free} = E_{cell} + iR_\Omega$):

<table>
<thead>
<tr>
<th>cycle</th>
<th>mV</th>
<th>rel. performance loss [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>100% RH</td>
</tr>
<tr>
<td>1st</td>
<td>830</td>
<td>797</td>
</tr>
<tr>
<td>2nd</td>
<td>825</td>
<td>798</td>
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<td>3rd</td>
<td>802</td>
<td>784</td>
</tr>
<tr>
<td>4th</td>
<td>825</td>
<td>801</td>
</tr>
<tr>
<td>5th</td>
<td>800</td>
<td>782</td>
</tr>
<tr>
<td>6th</td>
<td>825</td>
<td>801</td>
</tr>
<tr>
<td>7th</td>
<td>800</td>
<td>784</td>
</tr>
<tr>
<td>8th</td>
<td>824</td>
<td>812</td>
</tr>
</tbody>
</table>
After $iR$-correction (that means after removal of the membrane contribution to the cell potential) the corrected cell potential shows only $\leq 2.6\%$ deviation throughout the different cycles. As this is in the range of normal fluctuations and/or measurement inaccuracies, this clearly proves that the observed performance loss was not caused by a degradation of the electrode or other fuel cell components but can be solely assigned to the different membranes. The “higher” performance loss due to a decreasing relative humidity (100\% to 70\% r.h. (<5\%) and from 100\% to 50\% r.h. (<7\%)) is caused by the ionomer coating of the gas diffusion electrodes. The interface properties and ionic conductivity of this ionomer changes with decreasing r.h. and results in this small non-membrane contribution of the observed performance loss.

### 4.7. Appendix 1

In order to quantify the anisotropy of the different samples from the small-angle scattering measurements apart from the Hermans orientation function, we use the method earlier applied for grafted copolymer films of perfluorinated poly(ethylene propylene) samples\textsuperscript{261}. We calculate the order parameter $P_2$ based on a theory applied for scattering from liquid crystals\textsuperscript{269} according to:

$$P_2 = 1 - \frac{3}{2N} \int_0^{\pi/2} I(\phi) \left\{\sin^2 \phi + \sin \phi \cdot \cos^2 \phi \cdot \ln \left[\frac{1 + \sin \phi}{\cos \phi}\right]\right\} d\phi \quad (4.12)$$

where

$$N = \int_0^{\pi/2} I(\phi) d\phi \quad (4.13)$$

$I(\phi)$ is the scattering intensity integrated across the momentum transfer range of the correlation peak discussed above (0.015 Å\(^{-1}\) $< Q < 0.05$ Å\(^{-1}\) in the case of base films, 0.01 Å\(^{-1}\) $< Q < 0.04$ Å\(^{-1}\) in the case of grafted films and membranes), $\phi$ is the azimuthal angle.

Results obtained from SANS data of DP and SG membranes with different grafting levels confirm the higher anisotropy of membranes based on the DP film, furthermore the gradually decreasing anisotropy upon increasing the graft level (Figure 4.27).
Figure 4.27: Order parameter $P_{2\pi}$ derived from the SANS 2D scattering signal for membranes, dry and swollen in D$_2$O at different grafting level. The data points at GL=0 correspond to the base films.
Chapter 5. Incorporation of Glycidyl Methacrylate (GMA)

In Section 1.4, it was shown that the water uptake and even more the capability of a membrane to retain water at reduced relative humidity is essential for maintaining a high conductivity. A certain amount of incorporated water is needed to form a well-connected network of hydrophilic proton conducting channels. The conductivity of radiation grafted and most non-perfluorinated membranes, however, is known to be very sensitive towards relative humidity. In this chapter an approach to increase the water uptake and capability to retain water via the incorporation of a comonomer that is known for its hygroscopic properties is presented. Different amounts of incorporated hydrolyzed glycidyl methacrylate (GMA) and their influence on the properties of sulfonated polystyrene based proton exchange membranes (PEM) such as water uptake and proton conductivity were investigated.

The present chapter consists of a reproduction of a manuscript prepared for submission to the following journal:

5. Incorporation of Glycidyl Methacrylate (GMA)

5.1. Abstract

The aim of this work was to investigate how hygroscopic moieties like hydrolyzed glycidyl methacrylate (GMA) influence the properties of sulfonated polystyrene based proton exchange membranes (PEM). Therefore, several membranes were synthesized by electron beam treatment of the ETFE (ethylene-alt-tetrafluoroethylene) base film with a subsequent grafting of styrene and GMA at different ratios. The obtained membranes were sulfonated to introduce proton conducting groups and the epoxide moiety of the GMA unit was hydrolyzed for a better water absorption. The PEM was investigated regarding its structural composition, water uptake and through-plane conductivity. It could be shown that the density of sulfonic acid groups has a higher influence on the proton conductivity of the PEM than an increased water uptake.

5.2. Introduction

Radiation grafted membranes are an alternative to the state-of-the-art perfluorosulfonic acid membranes, such as Nafion® (DuPont), in polymer electrolyte fuel cells (PEFCs) and other electrochemical applications. Apart from offering a potentially significantly less expensive fabrication method, this versatile technique provides a high flexibility in membrane design, as a wide range of commercially available monomers and thereby possible functionalities can be readily combined with various base films. The partially fluorinated ETFE (ethylene-alt-tetrafluoroethylene) is an excellent candidate for such a base film for fuel cell applications. Drawbacks regarding lower proton conductivity at reduced relative humidity (r.h.) may be overcome by incorporating an adequate combination of monomers. One approach in this context is to enhance the water uptake / retention properties of the radiation grafted membrane by combining / copolymerizing styrene (S) monomers with glycidyl methacrylate (GMA, Scheme 5.1). The hydrolyzed version of this monomer is used in contact lens materials due to its ability to absorb large amounts of water as well as in other biomedical applications incorporating hydrogels.

![Scheme 5.1: Experimental scheme for the copolymerization of styrene and glycidyl methacrylate (GMA) onto an ETFE base film and subsequent functionalization.](image)
5. Incorporation of Glycidyl Methacrylate (GMA)

5.3. Experimental Section

5.3.1. Chemicals

The base polymer poly(ethylene-alt-tetrafluoroethylene) (ETFE) was purchased from DuPont (Tefzel® 100LZ, Circleville, USA) as film of 25 μm thickness. The reagents used during membrane synthesis included styrene (98%, Fluka), GMA (97%, Sigma Aldrich), 2-propanol (PROLABO®, VWR), acetone (PROLABO®, VWR), chlorosulfonic acid (98%, Fluka) and dichloromethane (PROLABO®, VWR). All reagents and the monomer were used as received without removal of inhibitors.

5.3.2. Membrane synthesis

The membrane synthesis was conducted similar to what has been reported in our earlier work (deposited dose 5 kGy, reaction temperature 60°C, monomer concentration 25 vol%). Three different ratios of S and GMA were used in the grafting solution (equivalent to styrene mole fractions of $X_S = 0.7$, $0.5$ and $0.4$) to obtain different ratios in the final membrane. The reaction time was varied to study grafting kinetics. All films and membranes were analyzed gravimetrically and using FTIR spectroscopy. For quantitative compositional analysis by transmission FTIR spectroscopy calibration curves using films containing both individually grafted monomers (ETFE-g-PS and ETFE-g-PGMA) were utilized (cf. Supporting Information, Section 5.6). The through-plane proton conductivity in dependency of the r.h. was measured with the 740 Membrane Test System from Scribner Associates Inc. (North Carolina, USA) at a temperature of 80°C. Further details are reported elsewhere.

5.4. Results and Discussion

A key parameter for the performance of PEMs is their ion exchange capacity (IEC; number of sulfonic acid groups per mass of dry polymer). This parameter is in the present case defined by the amount of polystyrene incorporated into the base film, which means that for higher amounts of incorporated styrene already lower grafting levels (wt%), mass increase caused by the graft component) yield IECs in the range of 1.6 mmol g$^{-1}$ while films with a higher content of GMA need higher grafting levels to reach this IEC. Membranes of an IEC of around 1.6 mmol g$^{-1}$ have shown to yield practical and balanced properties (conductivity, mechanical robustness and chemical stability) for fuel cell application, therefore, this is also the range of IEC that was aimed for in this study. To evaluate the impact of the incorporation of GMA, ex-situ properties of membranes with different incorporated monomer ratios are compared at similar IEC.
5. Incorporation of Glycidyl Methacrylate (GMA)

For the synthesis of fuel cell membranes with defined target grafting level, it is essential to know the grafting kinetics under the chosen reaction conditions and monomer ratios. Therefore, we investigated the influence of the different styrene / GMA molar ratios ($X_S = 0.7, 0.5$ and $0.4$) in the grafting mixture to be able to synthesize membranes with desired composition for comparison. The grafting kinetics are given in Figure 5.5 and reveal only a slight influence of the different compositions of the grafting mixture.

More important than the composition of the grafting mixture is the composition of the grafts in the obtained film (Figure 5.1). In order to investigate the mole fraction of styrene and GMA incorporated in the film, transmission FTIR spectroscopy was used. The amount of S and GMA was determined using calibration curves obtained for the respective individual monomers grafted onto ETFE. Based on the reactivity ratios of the two monomers ($r_S = \sim 0.45$, $r_{GMA} = \sim 0.53$) a higher content of GMA was expected in the film compared to the grafting mixture. IR analysis could not confirm this expectation but showed the incorporation of a high degree of styrene units. With increasing grafting level the fraction of S in the grafts decreased while more GMA was incorporated. This can be explained by the fact that reactivity ratios reported in the literature for the copolymerization of S and GMA were determined in solution. In the present study, however, the polymerization takes place as a diffusion controlled process within the structure of a solid base film. Therefore, differences in reactivity are not surprising. Present results suggest that S diffuses more easily into the ETFE base film than GMA, which results in a higher degree of incorporation of styrene in the early stage of polymerization. After “opening” the base film structure, the diffusion of GMA is facilitated and the fraction of the latter in the grafts rises.

**Figure 5.1:** Styrene mole fraction $X_S$ ($X_{GMA} = 1 - X_S$) incorporated in the grafted film (determined by transmission FTIR spectroscopy) versus grafting level. The initial mole fraction in the grafting mixture is denoted in the legend.
5. Incorporation of Glycidyl Methacrylate (GMA)

The final synthesis step to obtain proton exchange membranes is the functionalization of the grafts, where the proton conducting moiety is introduced (Scheme 5.1). In the present case the functionalization step comprises not only the sulfonation of the S unit but also a ring opening of the epoxide of the GMA. The efficiency of the epoxide hydrolysis was verified by IR spectroscopy (Figure 5.6).

The proton conductivity in a radiation grafted membrane is strongly related to the amount of water in the hydrophilic phase. GMA was introduced to increase this water uptake and thus the proton conductivity of the final membrane, especially under reduced relative humidity (r.h.) conditions. Ex-situ water uptake measurements proved the approach of GMA incorporation to be successful and showed, for membranes of the same IEC, a strongly increased water uptake with higher GMA content (Figure 5.2).

![Figure 5.2: Water uptake (from liquid water) versus experimental ion exchange capacity (IEC) for grafted membranes with varying content of hydrolyzed GMA (given mole fractions correspond to the feed).](image)

Proton conductivity measurements in dependence of r.h., however, showed no enhanced performance due to the increased water uptake (Figure 5.3). Proton exchange membranes with the same IEC are expected to have the same conductivity. Differences in conductivity have to be either attributed to a different proton donating group (higher or lower acidity), which is in the present case not applicable, or to the effect of the comonomer. While under fully humidified conditions there is only a small difference between the co-grafted membranes, which might be caused by minor IEC differences, the behavior with decreasing r.h. strongly deviates. The higher the fraction of comonomer (GMA) in the grafts, the more pronounced the conductivity drop at lower r.h. compared to the pure styrene grafted membrane. Even at higher IEC ($X_S = 0.7, 1.9$)
5. Incorporation of Glycidyl Methacrylate (GMA)

mmol g\(^{-1}\)) the conductivity at lower r.h. falls below that of the styrene only system. A negative effect of the incorporation of other comonomers, e.g. acrylonitrile, on in-plane conductivity was already seen in previous work.\(^{280}\) The fact that also the incorporation of a hygroscopic comonomer that strongly increases the water uptake of the membrane in water does not lead to a better performance emphasizes that the amount of water present in the membrane is not the dominating factor – or at least not the only dominating factor – for proton conductivity.

![Figure 5.3: Through-plane proton conductivity in dependence of r.h. at 80°C for various grafted membranes. IEC values in mmol g\(^{-1}\). If not stated otherwise the IEC is ~1.6 mmol g\(^{-1}\). The data for Nafion NR 212 is given as a reference.](image)

A possible reason for a reduced proton conductivity towards lower relative humidities might be the formation of sulfonic acid esters. Three different outcomes of a condensation reaction seem to be possible, which are depicted in Scheme 5.2. In all cases the sulfonic acid group reacts either with the hydroxyl or carboxylic moiety to form the sulfonic acid ester. This reaction would lead to a decrease of the free sulfonic acid groups participating in the proton conductivity and therefore reduce the latter. In case of the insoluble ETFE based membranes FTIR spectroscopy is a reliable and effective method to investigate transformations of IR sensitive moieties. Therefore, membranes with \(X_S = 0.5\) were chosen as those candidates expected to show the highest amount of possible condensate. Figure 5.7 shows IR spectra of hydrolyzed ETFE-g-P(SSA-co-GMA) under ambient conditions, dried under reduced pressure and dried at elevated temperature (80°C) under reduced pressure (3 h), leading to a stepwise
reduction of the water content in the membrane and therefore increasing the probability of ester formation.

**Scheme 5.2:** Possible condensation products of a sulfonated styrene and hydrolyzed GMA moiety in hydrolyzed ETFE-\(g\)-P(SSA-\(o\)-GMA) membranes.

The most prominent change in the IR spectra was found around 910 cm\(^{-1}\) (Figure 5.7). After intensive drying a signal arises in this region, which disappears upon rehydration. This signal is characteristic for the S-O stretching vibration of anhydrous sulfonic acids, which vanishes in the hydrated state.\(^{296}\) No clear evidence for the formation of sulfonic acid esters can be found in the obtained IR spectra. Therefore, it is proposed that under these conditions no ester formation occurs and we only see the regular dehydration of sulfonic acid hydrates.

Taking these results into account, it has to be presumed that it is the density of sulfonic acid groups in the graft component that has a high influence on the proton conducting behavior of the membrane and the incorporation of GMA seems to have a “diluting effect” that hinders this conductivity despite the increased water uptake. Therefore, a strategy to overcome this diluting effect may consist of combing hygroscopic and acid bearing moieties in one monomer in order to take advantage of the higher water uptake without impairing proton conductivity.

### 5.5. Conclusion

Hydrolyzed glycidyl methacrylate (GMA) was incorporated into a styrene sulfonic acid based radiation grafted proton exchange membrane to investigate the effect of increased water uptake on the proton conductivity, especially under reduced relative humidities.
The comparison of different ratios of GMA and sulfonated styrene in the membrane confirmed the increase of water uptake with increasing GMA content. This, however, did not translate into an improved proton conductivity. An increasing GMA content even impaired the conductivity at reduced relative humidities compared to the pure sulfonated styrene grafted membrane, highlighting that the density of sulfonic groups in the grafts has a higher influence on the proton conductivity than the water content within the membrane.

5.6. Supporting Information

5.6.1. IR Calibration Curves

The determination of the composition of the grafted films was carried out using Fourier transform infrared spectroscopy (FTIR), on a Perkin Elmer FTIR System 2000 spectrometer. The spectra were recorded at room temperature with a 4 cm\(^{-1}\) resolution in a spectral range from 4000 to 400 cm\(^{-1}\) and 32 scans. The interpretation and curve fitting was performed using GRAMS / AI software (version 9.1) from Thermo Fisher Scientific Inc., assuming a mixed Gaussian and Lorentzian shape for the peak fitting.

Upon grafting, the introduction of the graft polymer induces an expansion of the film in all three dimensions, which leads to a dilution of the corresponding components and therefore to a decreasing band intensity of, e.g., the peaks corresponding to the ETFE base film. The quantification of single film components can therefore not be done directly using the intensity of the FTIR vibrational bands.\(^{25}\)

In the first step, a calibration curve for both homopolymer grafted films (ETFE-g-PS and ETFE-g-PGMA) was established to enable quantitative compositional analysis by transmission FTIR spectroscopy. ETFE-g-PS and ETFE-g-PGMA films at different grafting levels were analyzed and the integrals of bands corresponding to the grafted monomer were normalized to the bands attributable to the ETFE base film according to Equation 5.1.

\[
\bar{A} = \frac{A_{\text{Monomer}}}{A_{\text{ETFE}}} \quad (5.1)
\]

This methodology yields a linear dependency of the normalized bands on the gravimetrically measured grafting level (Figure 5.4).
5. Incorporation of Glycidyl Methacrylate (GMA)

**Figure 5.4:** Example for a calibration curve. For this calibration curve for ETFE-g-PS the characteristic vibration of styrene at 1493 cm\(^{-1}\) was normalized to the characteristic ETFE vibration at 1325 cm\(^{-1}\). The obtained slope is \( m = 45.3 \cdot 10^{-4}\).

For the determination of the GMA content the ratios of the vibrations at 1388 cm\(^{-1}\) and 910 cm\(^{-1}\) (characteristic for GMA) versus ETFE characteristic vibrations at 1325 cm\(^{-1}\) and 509 cm\(^{-1}\) were used (\( n_{1388/1325} = 22 \cdot 10^{-4}\), \( n_{905/1325} = 62 \cdot 10^{-4}\), \( m_{1388/509} = 52 \cdot 10^{-4}\), \( m_{905/509} = 101 \cdot 10^{-4}\)).\(^{220}\)

For the compositional analysis of co-grafted films the normalized characteristic monomer vibrations (\( \tilde{A} \)) were formed and the monomer-specific grafting level was calculated according to **Equation 5.2**.

\[
GL_{Monomer} = \frac{\tilde{A}}{m}
\]  

**Figure 5.5:** Grafting kinetics of ETFE-g-P(S-co-GMA) with different styrene mole fractions \( X_S \) in the grafting mixture. As IEC values of under 2.0 mmol g\(^{-1}\) were of interest in this
investigation the grafting time of films with a high content of styrene ($X_S = 0.7$) was kept shorter than of films with lower contents of styrene.

**Figure 5.6:** After the functionalization step, the epoxide vibration at $\sim 910$ cm$^{-1}$ vanishes and the two separated styrene vibrations at $\sim 703$ cm$^{-1}$ and $\sim 667$ cm$^{-1}$ transform into the characteristic signature of a para-substituted aromatic group.

**Figure 5.7:** FTIR spectra of hydrolyzed ETFE-$g$-P(SSA-$co$-GMA) membranes ($X_S = 0.5$) under ambient conditions as well as after drying under reduced pressure and at 80°C under reduced pressure. Figure b) shows an enlargement of the region between 1000 – 800 cm$^{-1}$ where the signal of anhydrous sulfonic acid is found.
Chapter 6.  Grafting Design: A Synthetic Approach

The number density and chain lengths of the graft component influence as outlined in Section 1.4. the morphology adopted by the PEM and therefore also membrane properties such as proton conductivity and mechanical stability. These results were obtained on defined “lab-scale” model systems. Radiation grafted membranes, however, do not allow an exact design regarding the number of repeat units in a graft chain or the number of base film repeat units between grafts. Nonetheless, this chapter presents a synthetic approach to prepare two model compounds – one comprising long graft chains and a low number density, the other having shorter grafts with a higher number density of grafts. The influence of the synthesis parameters, such as applied irradiation dose, reaction temperature and monomer concentration were investigated for their impact on graft distribution. Finally, the optimized systems were compared regarding water uptake and proton conductivity at different relative humidity values.

The present chapter consists of a reproduction of the following publication:


6.1. Abstract

The polymer design concept of short versus long side chains was successfully adapted to radiation grafted membranes, an easy and up-scalable process. This concept was investigated by the generation of two model membranes based on polystyrene sulfonic acid grafted ethylene-\textit{alt-}tetrafluoroethylene, ETFE-\textit{g}-PSSA, prepared by a low versus high irradiation dose. It could be shown that it is essential to adjust the grafting parameters of both systems to obtain two membranes with similar composition in through-plane direction. Especially the high-dose system showed pronounced grafting fronts. A structure-property correlation regarding the influence of the graft lengths on the performance characteristics of electron beam grafted ETFE based proton exchange membranes (PEMs) was shown, e.g. the membrane type (associated with a higher number density of short grafted chains) showed a higher water sorption behavior as well as an increased proton conductivity, especially in the lower relative humidity (r.h.) range.

6.2. Introduction

During the last decades polymer electrolyte membranes attracted more and more interest due to their wide range of potential applications in electrochemical devices, including batteries, chemical sensors, supercapacitors and polymer electrolyte fuel cells (PEFC).\textsuperscript{1-6} Regarding PEFCs, the proton exchange membrane (PEM) plays a key role and is therefore the target of extensive investigations in order to obtain commercially attractive fuel cells. Beside other requirements, high proton conductivity along with low electrical conductivity and balanced water management are of high importance in the design of improved PEM materials.\textsuperscript{1, 3, 236}

Among the various methods to prepare proton conducting membranes (for detailed information compare, e.g., the reviews of Savadogo\textsuperscript{17} and Kerres\textsuperscript{96}) a versatile approach is the radiation grafting of commercially available base films (Scheme 6.1).

\textbf{Scheme 6.1}: Exemplary grafting procedure for PEM materials. The first step is the electron beam irradiation to generate radicals and the subsequent grafting with monomers like styrene. Afterwards the grafts can be functionalized to meet the targeted requirements, e.g. by sulfonation. For more information also see the review of Nasef.\textsuperscript{159}
In the present case, electron beam irradiation was used to generate radicals in the bulk of an ETFE (ethylene-alt-tetrafluoroethylene) film that could undergo a subsequent polymerization reaction with monomers like styrene. This process renders even insoluble and chemical “inert” materials like ETFE accessible for chemical modifications.\textsuperscript{158} Radiation processing itself is a well-established and economical method for the modification of polymers.\textsuperscript{24} Characteristic material properties, such as thermal stability, melt flow, chemical resistance and mechanical properties, can be significantly improved applying this method.\textsuperscript{121} The attractiveness of this method includes that it allows not only the combination of very different types of polymers (hydrophobic backbone vs. hydrophilic side chains) but also the utilization of commercially available base films, thereby avoiding the necessity of film casting or other difficulties associated with film formation.\textsuperscript{25-28} In contrast to other methods which enable the combination of two polymers, e.g., blending, irradiation grafting allows the covalent connection of these polymers, which results in a phase separation on a much lower length scale than achievable with blending. Furthermore, a wide selection of possible monomers or monomer combinations and base films allows the development of specially tailored membranes in an industrially applicable process.

Despite the increasing interest in grafted membranes for fuel cell application and the intensive research for high performing, versatile and, most importantly, cost-competitive PEMs,\textsuperscript{3, 29-32} the understanding of the polymer structure and morphology as well as its impact on properties such as proton mobility and conductivity is rather limited.\textsuperscript{33, 34} Model polymeric or oligomeric systems are used to investigate whether a diblock, multiblock, random or graft ionic copolymer has favorable impact on the proton conducting properties of the polymer.\textsuperscript{18, 35, 36} Zhang et al.\textsuperscript{216} used the model system P(VDF-co-CTFE)-\textit{g}-SPS (SPS = sulfonated polystyrene refers to the abbreviation used by Zhang and means the same as PSSA (polystyrene sulfonic acid) which is used by many others including this work) to investigate the morphological impact of graft chain length, graft density and ionic content. The disordered network morphology of small clusters (graft copolymers with higher graft density and short SPS chains) showed an improved performance under low relative humidity (r.h.) conditions and increased conductivity at higher temperatures together with a less pronounced swelling behavior than the long-range ionic channels which were formed by copolymers with long grafts and low graft density. This work was further intensified by Holdcroft et al.\textsuperscript{217}, who could confirm the key role of the graft chain length for proton conductivity. These studies have clearly highlighted the importance of phase separation and microstructure on the magnitude of proton conductivity.
All of the above mentioned model systems, used to investigate the chemical structure – morphology dependence and the effect of morphology and molecular order on proton conductivity, have been synthesized via atom transfer radical polymerization (ATRP) which is a versatile tool to design block or graft copolymers. But excessive synthetic procedures, macroinitiators, catalysts and ligands render this method a non-competitive approach to replace expensive state-of-the-art PFSA membranes (PFSA = perfluorosulfonic acid based membrane type, e.g. Nafion). Furthermore, the ATRP procedure furnishes only polymeric bulk material that has to be cast into films in an additional subsequent process step.

Therefore, the above mentioned concept of short versus long grafted chain length is adapted to radiation grafted membranes, a system that can be up-scaled in easy and cost effective manner. During the investigations two model systems are distinguished, type A having a long graft chain length but a low graft density and type B exhibiting a high graft density with short chain lengths (Figure 6.1). To ensure that the different morphology is the dominant factor for the performance of the membrane, the overall grafted mass is kept constant as well as the sulfonation level (same IEC for both types of membrane), resulting in the same ratio of hydrophilic to hydrophobic polymer constituents. In contrast to the mentioned ATRP studies, the magnitude of compared numbers of repeating units is most likely not in the range of 10 to 120 but can be assumed to be in a higher range due to the nature of the radiation grafting approach. Unfortunately, it is not possible to determine the exact chain lengths due to the insolubility of the resulting polymer membrane (ethylene-alt-tetrafluoroethylene grafted with sulfonated polystyrene, ETFE-g-PSSA). Nevertheless, an estimation of the graft length of type A and B membranes was made based on dose dependent radical concentrations and the grafting level of the membranes. Type A is synthesized using a low irradiation dose (3 kGy) and is expected to adopt a more lamella kind of structure, whereas type B is associated with a high dose irradiation (30 – 50 kGy) and should adopt a more statistic percolation with a disordered cluster network morphology.

Figure 6.1: Sketch of the graft distribution in membranes illustrating type A (left) and B (right) polymer architecture.
Nevertheless, increasing the irradiation dose by at least an order of magnitude will also lead to a change of the grafting behavior of the irradiated film regarding the kinetics and homogeneity of graft distribution. Therefore, the aim of this work was to synthesize a type B membrane which shows the same homogeneity that can be found in type A and to analyze the difference between both types of membranes. Polystyrene based PEMs were chosen as a model system for this approach and the gained knowledge can be implemented in future membrane design.

### 6.3. Experimental Section

#### 6.3.1. Chemicals

The base polymer poly(ethylene-alt-tetrafluoroethylene) (ETFE) was purchased from DuPont (Tefzel® 100LZ, Circleville, USA as a film of 25 μm thickness. The reagents used during membrane synthesis included styrene (98%, Fluka), 2-propanol (PROLABO®, VWR), acetone (PROLABO®, VWR), chlorosulfonic acid (98%, Fluka) and dichloromethane (PROLABO®, VWR). All reagents and the monomer were used as received without removal of inhibitor.

#### 6.3.2. Membrane Synthesis

The ETFE base films were pre-irradiated in air by an electron beam with different deposited doses (3, 30 and 50 kGy, MeV class accelerator, Leoni-Studer AG, Däniken, Switzerland). After exposure, the irradiated films were stored at −80 °C until further processing. All grafting reactions were carried out with 7 cm × 7 cm pre-irradiated ETFE films in glass reactors (3 cm diameter, 18 cm height, 60 ml capacity) under nitrogen atmosphere. A degassed mixture (50 mL) of 20% (v/v) styrene, 70% (v/v) iso-propanol and 10% (v/v) ultra-pure water served as standard grafting solution. The vessel was placed in a thermostatic water bath at 55 °C for the duration of the reaction. In order to obtain different degrees of grafting, various reaction times were applied, after which the grafted films were extracted with toluene (600 mL) for 16 h to remove residual monomer and homopolymer not covalently attached to the base film, then dried at 80°C under reduced pressure and weighed.

The graft level (GL) of each film was gravimetrically determined using the following equation:

\[
GL = \frac{m_s - m_o}{m_o} \cdot 100\%
\]  

(6.1)
where \( m_0 \) and \( m_g \) represent the weight of the sample before and after grafting, respectively.

Subsequent sulfonation was performed in a 2 L glass reactor using 2\% (v/v) chlorosulfonic acid in dichloromethane (1.5 L). The films were separately placed in the solution and possible gas bubbles were carefully removed with a PTFE rod before the reactor was closed and protected against light with a PVC shielding. After stirring for five hours at room temperature the sulfonated films were removed from the reaction mixture and repeatedly washed with ultra-pure water (3 x 800 mL). Hydrolysis of the functionalized films to sulfonic acid groups was performed in ultra-pure water (800 mL) at 80 °C for 15 h. More information can be found elsewhere. 178, 219, 240, 270, 283, 297-299

6.3.3. **Ex-Situ Characterization**

Ex-situ fuel cell relevant properties, such as the *ion exchange capacity* (IEC), water uptake and hydration number were determined in fully swollen state at ambient conditions. The IEC is defined as

\[
IEC = \frac{n(H^+)}{m_{dry}} \quad (6.2)
\]

where \( n(H^+) \) is the molar number of protons and \( m_{dry} \) is the dry weight of the membrane. After a proton/potassium exchange (stirring in 1 M KCl for 12 h at room temperature) the free accessible protons were titrated with a 0.05 M KOH solution by means of a SM Titrino 702 instrument (Metrohm, Herisau, Switzerland). The swelling (\( Q \), water uptake) of the membrane displays its ability to absorb water and can be calculated according to the following equation:

\[
Q = \frac{m_{wet} - m_{dry}}{m_{dry}} \cdot 100\% \quad (6.3)
\]

The *hydration number* (\( \lambda \)) is the molar ratio between water and sulfonic acid groups and is calculated from the IEC and the water uptake values according to:

\[
\lambda = \frac{n(H_2O)}{n(SO_3H)} = \frac{Q}{IEC \cdot M_{H_2O}} \quad (6.4)
\]

The *through-plane conductivity* in dependency of the relative humidity (r.h.) was measured with the 740 Membrane Test System from Scribner Associates Inc. (North Carolina, USA) at a temperature of 80°C using gas diffusion electrodes from E-TEK DivisionSM (ELAT HT-140E-W).222 Each sample was compressed between the electrodes with 19.2 bar and subjected to the typical protocol of 2 h preconditioning at 95\% r.h., followed by stepwise decrease of r.h.. At each new r.h. the sample was conditioned for
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30 min per 10% r.h. decrease. Electrochemical impedance spectroscopy (EIS) (N4L PSM1735, Newtons4th Ltd, Leicester, UK) was performed after each step. The specific conductivities were calculated based on the thicknesses of the fully hydrated membranes, which were measured with a thickness gauge (MT12B, Heidenheim, Germany). The specific conductivity was determined by the following equation

\[ \sigma = \frac{l}{A \cdot R_{HF}} \]  \hspace{1cm} (6.5)

where \( A \) is the overlapping area of the electrodes (0.5 cm\(^2\)), \( l \) is the membrane thickness and \( R_{HF} \) is the high frequency intercept of the complex impedance with the real axis.

6.3.4. SEM and EDX Analysis

In order to analyze the through-plane distribution of the grafted chains, sulfonated films were swollen in water for 2 h, subsequently frozen in liquid nitrogen and fractured to obtain a sharp cross-section area without smearing. SEM pictures were taken with a FESEM Ultra 55 (Carl Zeiss, Oberkochen, Germany) and energy dispersive X-ray analysis was performed using a compatible accessory (EDAX TSL, AMETEK). For sulfur distribution profiles perpendicular to the plane of the membrane ImageJ software (National Institute of Health)\(^{221}\) was used and the 2D data file was corrected for the orientation of the sample with respect to the EDX detector before analysis.

6.4. Results and Discussion

Membranes of type A were synthesized and thoroughly investigated at the Paul Scherrer Institute over the last decade.\(^{178, 219, 240, 270, 283, 297, 298}\) The optimized reaction conditions for styrene grafting were found to be a mixture of 70 vol% \( \text{iso} \)-propanol, 10 vol% ultra-pure water and 20 vol% styrene monomer at temperatures between 55 and 60°C.\(^{299}\) However, using these conditions for a high dose system bears the danger of grafting fronts leading to an inhomogeneous distribution of grafts in through-plane direction. Especially styrene is known to cause pronounced grafting fronts even at moderate doses. In case of grafting fronts two models are discussed. In the first model the grafting front propagates from the surface area towards the inner regions, while the grafts in the surface region continue to grow (Figure 6.2a).\(^{300}\) In the second scenario, the radical polymerization occurs so fast that the grafts in the surface area basically reach their statistical chain length before the propagation towards the inner regions can occur (Figure 6.2b).
Figure 6.2: Illustration of the grafting front propagation in through-plane direction. [Adapted from F. Wallasch et al., J. Appl. Polym. Sci. 125 (2012), 3500]

Therefore, it is essential to investigate how the system parameters can be manipulated to influence the grafting front mechanism in a way to obtain a homogenous through-plane graft distribution despite the high irradiation doses and unfavorable grafting characteristics of the styrene monomer. In the first step, the extent of the front problem and the resulting inhomogeneity of the membrane were examined using the standard parameters for low dose irradiated films (3/55/20) in a high dose system (50/55/20). The notation x/y/z corresponds to x: dose (kGy), y: reaction temperature (°C) and z: monomer concentration (vol%).

A higher dose leads to a larger number of active sites in the base film and, therefore, to a faster increase in graft level. After 1 h, for example, the GL of a film irradiated with 3 kGy is 12%, whereas the corresponding 50 kGy film already shows a GL of 68%. The grafting kinetics for the 3/55/20 and 50/55/20 parameter systems are shown in Figure 6.3.

Figure 6.3: Reaction kinetics for grafting of styrene into ETFE films (3/55/20 and 50/55/20 parameter systems).
Figure 6.4: EDX mappings of the sulfur Kα signal as well as the corresponding sulfur distribution profiles in through-plane direction and representative SEM images for membranes with different GL (a: 10%, b: 25%, c: 46%, d: 67%) of the 50/55/20 parameter system. Below the double line the corresponding data is given for the 3/55/20 parameter system at a GL of ~25% (e).

The transversal concentration profile was analyzed via EDX spectroscopy using a sulfur mapping as graft propagation tracer. To determine the graft distribution several other techniques have also been used, such as vibrational spectroscopy or confocal laser scanning microscopy. For the sulfur microprobing approach membranes with a grafting level of 10, 25, 46 and 67% were swollen in water and subsequently broken under liquid nitrogen to obtain a clean cross-section of the membranes. Due to the different mechanical properties of pure ETFE and PSSA grafted ETFE, especially when swollen in water, the two domains (hydrophobic / hydrophilic) show different fracture profiles, which can be distinguished even visually with SEM. As shown in Figure 6.4 the sulfur mapping corroborates the visual distinction of grafted and non-grafted regions.
The analysis of the obtained sulfur profiles clearly shows the pronounced grafting fronts even at a grafting level as high as 67%. Comparing the experimental data with the theoretical models highlighted in Figure 6.2, the truth lies in between these two models. At first, a faster increase in GL\textsubscript{local} than grafting front propagation in through-plane direction can be observed, followed by a phase where a saturation of the graft level near the surface seems to be reached and a more pronounced propagation of grafting into the film than increase of GL\textsubscript{local} occurs. The comparison of the values of the 50 kGy system (25% GL) with the profile of the corresponding 3 kGy membrane further illustrates the enhanced grafting front behavior. To describe differences in through-plane homogeneity for different membranes, a suitable value can be the intensity ratio of the sulfur signal obtained, e.g., at the center of the film (\(x = 0.5\)) and the surface (\(x = 0, 1\)), equaling 1 for perfectly homogenous membranes. Applying this to the two mentioned systems, 3/55/20 shows a bulk grafting in the center region (\(x = 0.5; \text{BG}_c = \frac{I_{x=0.5}}{(I_{x=0} + I_{x=1})/2}\)) of 0.59 compared to 0.07 for the 50/55/20 system of the same GL (~25%). A closer look at the sulfur distribution profile of the 3/55/20 system reveals a smooth gradient of graft concentration along the membrane thickness, resulting in visually indistinguishable fracture surface in the SE micrograph instead of the sharp edges of the 50/55/20 system (SEM and EDX). This emphasizes the need for modified reaction conditions in high dose systems. Illustrated by the x/y/z notation, the three most self-evident parameters to be manipulated are the dose itself, reaction temperature and monomer concentration.

Following this approach, the irradiation dose was reduced by 40% to 30 kGy, still offering a tenfold intensity (the dose is assumed to be approximately proportional to the number of generated active centers\textsuperscript{163}) compared to the 3 kGy standard system. For a grafting level of ~25% this results in an increased \(\text{BG}_c\) value of 0.10 compared to 0.07 in case of the 50/55/20 system. A further increase in graft level to ~46% leads to an even higher difference in bulk grafting and \(\text{BG}_c\) values of 0.18 (30/55/20) and 0.09 (50/55/20), which shows that the 50 kGy system does not even reach the bulk grafting of the 30 kGy system when having twice the amount of grafts (for an overview of \(\text{BG}_c\) values see also Figure 6.7). Despite the weak increase in bulk grafting, the analysis of the sulfur distribution profiles reveals still strongly pronounced grafting fronts for the 30 kGy system with no significant flattening of the “sharp edges” between highly grafted areas and nearly non-grafted regions. Therefore, the reaction temperature was reduced by 5°C. This seemingly small difference in temperature already has a major impact on the grafting kinetics. To illustrate this, the grafting kinetics of various systems with different doses and reaction temperatures but fixed monomer concentration of 20 vol% are displayed in Figure 6.5.
A temperature reduction of 5°C results in strongly decelerated reaction kinetics of up to 75% for the 30 kGy system (51 vs. 13% GL after 1 h reaction time) and a similar slowdown in the 50 kGy system (68 vs. 23% GL after 1 h reaction time).

The concept of this reduction in temperature was to decrease the reaction kinetics to a greater extent than the diffusion of the styrene monomer throughout the film thickness. Styrene is not soluble in ETFE and enters the base film predominantly by starting polymerization, which opens the ETFE structure through the incorporation of polystyrene, which allows further propagation of the monomer (and solvent molecules) into the film. With a reaction rate much higher than the rate of monomer diffusion in through-plane direction, the monomer entering the film is largely consumed by the growing polymer chains, which impedes further propagation in through-plane direction. If the polymerization is slowed down, it was expected that a higher monomer concentration can overcome this reaction front and diffuse further into the film to start new polymer chains with radicals located in the bulk ETFE region. However, the impact on the through-plane homogeneity was much less pronounced than the grafting kinetics would have suggested. For the 50/1/20 system the BGc value changed only from 0.07 to 0.09 (~25% GL) and in case of 30 kGy the effect was even less (0.10 compared to 0.11 BGc, ~25% GL), indicating that the temperature decrease has also a major impact on the diffusion of the styrene monomer itself. Similar to the effect of the decrease of the dose, the “sharp edges” between highly grafted areas and nearly non-grafted regions were further softened but not removed, showing, nonetheless, a beneficial influence of the reduced temperature on the graft distribution.

**Figure 6.5:** Kinetics of various grafting systems with different doses and reaction temperatures, but a fixed styrene concentration of 20 vol%.
It is common knowledge that a reaction temperature of 50°C represents the lower limit for a practical pre-irradiation grafting rate (for materials which have been irradiated under air),\textsuperscript{304} due to a tremendous decrease of the reaction kinetics (see e.g. Figure 6.5) and an instability of the grafting process itself. A further reduction of the irradiation dose would render the advantages of a high dose system obsolete and might result in too small differences between type A and type B membranes.

With dose and temperature decrease being not sufficient in smoothing the grafting fronts to obtain a homogenous distribution, the monomer concentration was reduced stepwise (20 → 13, 9, 7 and 5 vol%). In case of the monomer concentration of 13 vol% the 50/55/z and 30/50/z grafting systems were tested to estimate the maximum optimization effect possible. A monomer reduction to 13 vol% has only a minor impact on the BG\textsubscript{c} value of the 50/55/z system (0.07 to 0.08, ~25% GL). The 30/50/z parameter set, however, shows a more pronounced response with an increasing BG\textsubscript{c} value of 0.11 to 0.16 for ~25% GL. In order to test the limits for the reduction of the monomer concentration, the system 50/55/5 was investigated. The obtained BG\textsubscript{c} value of 0.57 for a GL of 22% nearly reached the target homogeneity of the type A membrane (0.59). Nevertheless, the reaction time was more than 24 h and only one of the synthesized films reached this GL while the others showed a range of much lower grafting levels with the same reaction time. Moreover, the obtained films showed inhomogeneous in-plane grafting, recognizable as areas with different extent of tarnishing next to each other. Due to this system instability no further systems were tested with 5 vol% monomer concentration, as a reduction of temperature etc. would only increase this instability. Instead, the monomer concentration was raised again to 9 vol%. As the 30 kGy membranes always show a higher through-plane homogeneity compared to the 50 kGy membranes (e.g., 50/55/9: BG\textsubscript{c} = 0.11; 30/55/9: BG\textsubscript{c} = 0.26; ~15% GL), further tests for optimization were conducted with 30/y/z systems only. Despite the more weakly pronounced homogeneity of the 55°C systems, they offer improved kinetics, which would be beneficial in future applications and were therefore not excluded. The analysis of the 30/55/9 and the 30/50/9 systems (~25% GL) gave BG\textsubscript{c} values of 0.35 and 0.42, respectively. This trend could be further pursued by an additional decrease to a monomer concentration of 7 vol%. The resulting BG\textsubscript{c} values of the corresponding membranes were 0.41 and 0.46. In addition to the increased through-plane distribution, the profiles were similarly shaped as the ones of the 3/55/20 system (Figure 6.6) and no longer showing the sharp edges that dominated the distribution profiles of the initial high dose systems.
In the last step, a further change in temperature and its effect on the system was investigated. Taking the obtained results into account – the fact that the temperature did also affect the monomer diffusion to a great extent as well as the increasing system instability with increasing monomer dilution – the reaction temperature was raised to 60°C for highly diluted systems (9 and 7 vol% monomer concentration). The membranes obtained in this way (GL ~25%) showed BGc values of 0.14 (50/60/9), 0.25 (30/60/9) and 0.38 (30/60/7). Despite a decreased reaction time, the negative effects on through-plane homogeneity were considered more important. Therefore, the 30/50/7 parameter system was chosen to be the best candidate for further comparison with the type A membrane system (3/55/20).

Unfortunately, it is not possible to determine the length of the grafts in ETFE-g-PS(SA) in a straightforward manner as ETFE renders the films and membranes insoluble and thereby precludes the use of most analytical methods. For a rough estimation of chain length the dose dependent spin concentration measurements of Mitov et al.\textsuperscript{163} were used. ETFE shows a radical concentration of roughly $0.6 \times 10^{-6}$ mol g\textsuperscript{-1} after irradiation with 3 kGy and $5.7 \times 10^{-6}$ mol g\textsuperscript{-1} for 30 kGy, respectively, in inert gas atmosphere (Ar). When irradiated in air this concentration is lower by a factor ~0.65. At a grafting level of ~25% this corresponds to grafts consisting of roughly 6’200 monomer units per chain in case of type A (3/55/20) and about 650 monomer units in case of type B (30/50/7) membranes. Nevertheless, this is merely a crude estimate and only intended to illustrate the ratio of short to long grafted chains in more qualitative than quantitative terms.
Figure 6.7: Obtained $BG_c$ (bulk grafting in the center region) values for membranes (~25% GL) obtained with different grafting parameters. ($x/y/z$ corresponds to $x$: dose (kGy), $y$: reaction temperature (°C) and $z$: monomer concentration (vol%))

An important parameter to compare the two systems is their water sorption behavior. These properties are expressed in terms of water content (wt% of water in a wet membrane) and the hydration number ($\lambda$, molar ratio of water to sulfonic acid). As already mentioned before, the number of sulfonic acid groups dominates the water sorption behavior of similar materials. Therefore, the degree of grafting and sulfonation level of both types was kept constant (IEC for both types of membrane ~1.6 mmol/g) to ensure that only differences induced by the different applied radiation dose and grafting parameters were investigated. The comparison of both systems shows that the swelling of the 3/55/20 membrane (45.1 ± 2.3%) is less pronounced than the water uptake of the corresponding 30/50/7 system (52.9 ± 1.7%). As a consequence, the hydration number is higher for the high dose system (15.5 ± 0.5 compared to 13.0 ± 0.6). These results stand in contrast to the data published by Zhang et al.\textsuperscript{216}, who found an increased swelling behavior for membranes with long grafted chains and low graft density. An explanation can be given based on several facts. The different base film used might contribute to these differences. PVDF, which was used by Zhang et al., has a much lower glass transition temperature compared to ETFE ($T_g$(PVDF): -40 °C; $T_g$(ETFE): 110°C)\textsuperscript{158}. The grafting procedure as well as the swelling take place at temperatures where PVDF is already in the rubbery state and therefore much more flexible. In contrast to that, ETFE is much more rigid at these temperatures. In case of the soft PVDF, the bulk regions between the hydrophilic domains could be distorted more easily than in the case of the more rigid ETFE. Therefore, the homogeneous structure of probably more smaller hydrophilic domains is favored for the water uptake in case of
the ETFE, whereas the pronounced hydrophilic regions (usually created by larger graft lengths)\textsuperscript{216} are more beneficial for PVDF swelling.

Apart from this, Zhang et al. also reported that the molecular weight of the P(VDF-\textit{co}-CTFE) backbone has a significant effect on the water swelling behavior of the membrane and a higher $M_w$ is favorable as it results in smaller ionic channel width and enhanced resistance to excessive water uptake at higher ionic contents.\textsuperscript{216} As the ETFE in the 30/50/7 system was exposed to a higher dose, which might have led to a higher number of chain scissions compared to the 3 kGy system, this might have also contributed to this result. However, ETFE is known to be a material that is very stable against irradiation, its mechanical properties are not markedly affected until doses of above 50 kGy.\textsuperscript{178}

The most important property regarding a future application in polymer electrolyte fuel cells is the proton conductivity of the grafted membranes, especially in dependence of different relative humidities. As both membranes are chemically identical and show the same acid concentration, differences in conductivity can only be assigned to structural differences. Figure 6.8 shows the through-plane proton conductivity of both types of membrane with varying r.h..

\textbf{Figure 6.8}: Through-plane proton conductivity at 80°C of membranes of type A and type B (GL $\sim$25\%) in dependence of r.h.
It can be clearly seen that type B offers improved conductivity over the entire r.h. range with increasing trend towards lower r.h. (from 18% at 100% r.h. to 38% at 30% r.h., cf. inset Figure 6.8). This trend was expected when one assumes a more random distribution of smaller ionic domains for type B membranes and, therefore, a higher percolation of the hydrophilic phase at reduced water contents compared to larger and less homogeneously distributed domains in a type A membrane, which would need higher amounts of water for a sufficient connection of these domains.

6.5. **Conclusion**

In this work, the concept of short (type B membranes) versus long grafted chains (type A membranes) was successfully adapted to radiation grafted membranes. Despite the high irradiation dose and the proneness of the styrene monomer to form pronounced grafting fronts, a similar through-plane distribution profile as observed in low dose systems was achieved for type B membranes by manipulating the grafting parameters. These two structurally different but chemically identical types of membrane show different swelling behavior and proton conductivity, especially in the low r.h. range. Increasing the through-plane conductivity at low r.h. (e.g. 30% r.h.) over 35%, type B membranes reveal their superior morphology regarding more stringent fuel cell applications. The investigated model system improves our understanding of structure-property correlations and helps to find synthetic strategies for optimized high-performance membranes based on the versatile electron beam grafting technology.
Chapter 7.   Grafting Design: Structural Investigation

This chapter represents a continuation of Chapter 6. The theoretical concept behind the approach of tailoring the length and number density of grafts in radiation grafted membranes is presented and the influence of both parameters on the phase segregated structure of the model system ETFE-g-PS(SA) investigated. For this small-angle scattering was used.

The present chapter consists of a reproduction of a manuscript prepared for submission to the following journal:

7.1. Abstract

Irradiation is generally perceived as unsuitable to design the building blocks of graft copolymers. We show that this limitation can be eased, and both the graft density and molecular weight of the grafted chains can be scaled in specific manner via two basic parameters: graft level and irradiation dose. This approach adds a novel degree of freedom to the design of irradiation grafted copolymers. Here we focus on synthesizing and characterizing polymer electrolytes, where the copolymer architecture is known to influence both the phase segregation as well as ion transport. The influence of graft density and molecular weight of the grafts on the structural features is probed by small-angle neutron and X-ray scattering.

7.2. Introduction

Irradiation grafting is a versatile method for combining various monomers and base polymers, and provides access to a number of possibilities for specifying overall functionalization and characteristics.\(^{305}\) It is an equally important aspect that the potential for up-scaling is promising.\(^{306, 307}\) Given the inherent advantages, such as having a defect-free thin matrix with a uniform thickness already formed before starting the copolymerization reaction, radiation grafting is particularly well-suited for the synthesis of ion exchange membranes.\(^{308}\) Copolymers dedicated to proton exchange membranes (PEMs) are comprised of ionic, hydrophilic graft side-chains attached to the usually hydrophobic backbone via covalent bonds. Due to the chemical dissimilarity, the side-chains and the matrix are generally not miscible, and segregate spontaneously. The resulting morphology also defines the morphology of the aqueous phase, which is determinant of a good electrolyte, controls the water uptake,\(^{309}\) the ion conductivity,\(^{310}\) the percolation threshold,\(^{243, 276}\) and the tortuosity.\(^{311}\) The ability of tailoring the lengths of the incompatible polymer sub-components is an asset for the optimization of the polymer architecture. Yet when it comes to irradiation grafting based on free radical polymerization, it is generally believed that copolymerization enables adjusting only the overall amount of grafted component, and scaling the dimensions of the polymer constituents is not possible. We show here that this limitation can be eased, and both the molecular weight of the grafts and the graft density can be scaled independently via the two most basic parameters: graft level and irradiation dose. Although it is not the only possible choice, here we concentrate on sulfonated polystyrene grafted poly(ethylene-alt-tetrafluoroethylene), ETFE-\(g\)-PS(SA) (Supporting Information, Section 7.6.1.).
7.3. Theoretical Approach

We use ETFE-g-PS(SA) here as a model system that allows to explore relationships between copolymer architecture, morphology, and conductivity. Our scaling approach has two foundations: First, according to the definition, the graft level \((GL)\) is the ratio of the total mass of polystyrene chains \((m_S)\) grafted onto the ETFE backbone and the total mass of ETFE before grafting \((m_{ETFE})\):

\[
GL \equiv \frac{m_1 - m_0}{m_0} = \frac{m_{PS}}{m_{ETFE}} = \frac{M_S \times \langle n_S \rangle}{M_{ETFE} \times \langle n_{ETFE} \rangle}, \tag{7.1}
\]

where \(m_0\) and \(m_1\) are the mass of the polymer before and after grafting, and \(n_i\) and \(M_i (I = S \text{ or } ETFE)\) are the total number and the molar mass of the given monomer contained in the graft copolymer, respectively \((M_S = 104 \text{ g/mol}, M_{ETFE} = 64 \text{ g/mol})\). In the case of polystyrene (PS) grafted onto ETFE, \(\langle n_S \rangle\) is equal to the average degree of polymerization of PS and \(\langle n_{ETFE} \rangle\) is the average number of base polymer monomer units between neighboring polystyrene grafts. The graft copolymer can be described by the degree of polymerization of the grafted side-chain \((P)\) and graft density \((d \equiv 1/n_{ETFE})\). Given that \(P\) and \(d\) are statistically independent, and \(\chi\) is the crystallinity of the base film material, it can be shown that:

\[
\langle P \rangle \times \langle d \rangle = GL \cdot \frac{M_{ETFE}}{M_S} \frac{1}{1 - \chi}. \tag{7.2}
\]

Second, there is a relationship between the irradiation dose \((\gamma)\) and the number of radicals \((N_r)\) created in the base polymer. In the case of ETFE irradiated by an electron beam under ambient conditions in air, this relationship can be accurately described by the following phenomenological model (Equation 7.3):

\[
N_r(\gamma) = A \times (1 - e^{-B \gamma}), \tag{7.3}
\]

where \(A = 9.15 \cdot 10^{-6} \text{ mol g}^{-1}\) is the saturation value and \(B = 16.78 \cdot 10^{-6} \text{ Gy}^{-1}\) is related to the volume in which the energy is dissipated. The average graft density is proportional to the number of radicals, assuming that chain transfer from the growing PS chains to ETFE is negligible (Equation 7.4):

\[
\langle d \rangle = N_r \times M_{ETFE}. \tag{7.4}
\]

Given that only the amorphous phase is grafted in a semi-crystalline base polymer (Equation 7.5):

\[
\langle P \rangle = \frac{1}{\langle d \rangle} GL \cdot \frac{M_{ETFE}}{M_S} \frac{1}{1 - \chi}. \tag{7.5}
\]
where \( \chi \) is the crystallinity (36 wt\% for our ETFE base film).\(^{313}\) Grafting styrene onto ETFE proceeds via free radical polymerization, which is governed by four steps: initiation, propagation, termination, and transfer. For the sake of simplicity, we have neglected the possible influence of termination and chain transfer on \( \langle d \rangle \) and \( \langle P \rangle \) during this theoretical description. We emphasize that this simplification is not an inherent requirement, and the availability of quantitative information about the rate constants would enable the formulation of a more detailed model. To demonstrate the possibility of adjusting the copolymer architecture of ETFE-g-PS(SA), we irradiated two identical base films with a total dose of 3 and 30 kGy, respectively, using 2.1 MeV electrons. The base films were used for synthesizing grafted films and PEMs at a grafting level of 25\% (Supporting Information, Section 7.6.1.). The synthesis conditions for the high-dose system were adjusted in a manner to obtain the same through-plane homogeneity as in the low-dose system (Supporting Information, Section 7.6.4.).\(^{314}\) We will refer to these copolymers as H (High-dose) and L (Low-dose). As it follows from Equation 7.1 – 5, with these parameters we expect to obtain considerably different graft copolymers, while their ion exchange capacities were kept nearly identical (Supporting Information, Section 7.6.2.). X-ray and neutron scattering were used to explore the influence of graft density and molecular weight on the structural features. These copolymers were probed in the dry, partially hydrated and water-saturated state. To complement small-angle scattering, the proton conductivity was investigated.

7.4. Results and Discussion

Given the immiscibility of the grafts and the backbone, there is no tendency for the PS(SA) and ETFE chains to form a homogeneous phase. Instead, the PS(SA) is expected to segregate into separate domains within the amorphous part of the ETFE matrix. The wide-angle region of X-ray scattering (WAXS)—carrying information about the crystallites of the ETFE base film—does not indicate differences in the dry state between the two systems (Supporting Information, Section 7.6., Figure 7.7). At this graft level, the overall crystallite content was found to be approx. 15 wt\%\(^{243}\) with an average crystallite size of approx. 9 nm.\(^{315}\) To enhance scattering from the ionic groups located exclusively in the grafted domains, the membranes were converted into the Cs-salt form. For both membranes, nearly identical isotropic correlation peaks were observed in the mid-angle region of the X-ray spectra (1 nm\(^{-1} \) < \( Q < 10 \) nm\(^{-1} \), Supporting Information, Section 7.6., Figure 7.7 and 7.8). This so-called ionomer peak is centered at \( Q \sim 4 \) nm\(^{-1} \) and is attributed to the presence of ionic groups aggregating into compact clusters, which follow a liquid-like short-range order. The strong similarity between the two membranes is in agreement with the observation that even very short
PS(SA) graft chains, made up of as few as five monomer units, already show this feature,\textsuperscript{257} while the membranes discussed here are both expected to have much longer pendant chains. The Kinning-Thomas model\textsuperscript{316} describes these ion-rich clusters as spheres with a diameter of approx. 1 nm and an average center-to-center distance of approx. 1.5 nm (Supporting Information, \textbf{Section 7.6.}, \textbf{Figure 7.8}). It is worth mentioning that the ionomer peak can be well interpreted with another structural model, where both the morphology and size of the ion-rich clusters are irregular and random,\textsuperscript{33} and the presence of such structural features was indeed observed in studies using molecular coarse-grained dynamics simulations.\textsuperscript{317} Regarding SANS, the ionomer peak is evident only in water-swollen membranes and centers at $Q \approx 2.5 \text{ nm}^{-1}$ (Supporting Information, \textbf{Section 7.6.}, \textbf{Figure 7.9}). This correlation peak indicates an average center-to-center distance of approx. 2.5 nm, which is larger compared to the value obtained from SAXS measurements with dry membranes. This is the result of swelling of the membrane through water uptake. Therefore, on the corresponding length-scale, neither the shape nor the amplitude indicates differences between the two membranes, confirming that the internal structure of the polystyrene-rich domains is identical in L and H type graft copolymers. Scattering at smaller angles shows three distinct features: a) scattering anisotropy, b) a characteristic peak at $Q \approx 0.2 – 0.3 \text{ nm}^{-1}$, and c) an upturn region where the scattering intensity increases rapidly (\textbf{Figure 7.1}).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.1.png}
\caption{SANS curves of dry grafted films before sulfonation ($GL = 25\%$). The scattering spectra correspond to the machining (MD; left) and transverse (TD; right) directions, which are defined by the orientation of the base film drawn when being produced. For comparison, the corresponding curves of the base film are also shown. The sectorial averaging is explained in \textbf{Section 7.6.}, \textbf{Figure 7.10}.}
\end{figure}

Each of these features is present already in the semi-crystalline ETFE base film.\textsuperscript{33, 288} Two-dimensional scattering patterns clearly show the presence of orientation
(Supporting Information, Section 7.6., Figure 7.10) originating from the production of the ETFE base film. The lack of higher order scattering maxima on the azimuthally averaged scattering curves suggests a distorted lamellar morphology, and the corresponding characteristic distances are quite similar for the low- and high-dose systems, reflecting mostly the graft level.\textsuperscript{315, 318} This distance is however slightly larger for the low-dose system (approx. 34 and 32 nm for L and H, respectively; for comparison, the characteristic distance is approx. 25 nm in the base film).\textsuperscript{315}

The most dominant differences between L and H in the small-angle scattering spectra of the two PEMs appear at the intensity upturn: the scattering intensity is always higher for the L type membrane. The importance of this can be understood by considering the so-called structure factor, carrying information about the arrangement of the amorphous, crystalline, and grafted domains. The structure factor of the grafted domains must reflect the partial crystallinity of the base film, since the grafted domains are present only in the amorphous regions. The distribution of the grafted domains in the amorphous region however can be considered random. This is because a) the distribution of the radicals due to the irradiation of the base film is random, and b) several grafted domains may be present between neighboring crystallites (Supporting Information, Section 7.6.10.). Therefore we expect that the structure factor, dominated by the crystalline-amorphous structure inherited from the base film, is comparable for type L and H samples—apart from a slightly different characteristic distance. Given this and the fact that the volume fraction of the polystyrene is the same for both PEMs (approx. 0.29, Supporting Information, Section 7.6.9.), the higher scattering intensity at low angles in the type L system indicates that this sample has larger and fewer polystyrene domains, while type H has smaller but more numerous polystyrene domains. As we anticipated, this originates most likely from the differences in graft length and graft density. Upon hydration, the PS(SA) domains swell with water and increase in volume, and the shape of the SANS curve is expected to change accordingly. Indeed, depending on the degree of hydration set by the humidity level, the characteristic distance describing the separation of the hydrophilic and hydrophobic domains increases and follows a very similar trend for both PEMs (Figure 7.2 and Section 7.6., Figure 7.11).

The differences between the intensity upturns are preserved (a representative situation—scattering curves for the case of 75% r.h.—is shown in the Supporting Information, Section 7.6., Figure 7.12). It is important to note that the through-plane homogeneity of the local grafting level at a given GL has also an influence on the position of the characteristic peak, related to the amorphous crystalline separation (Supporting Information, Section 7.6.12.).
Figure 7.2: Characteristic distances obtained by analyzing the SANS scattering peak at various relative humidity levels.

Immersed into water, the water uptake (mass of water taken up per mass of dry membrane) of type H is higher than that of type L ($W_L = 0.45 \pm 0.02$, $W_H = 0.53 \pm 0.02$) (Supporting Information, Section 7.6., Figure 7.13). Consequently, the water uptake corresponding to the hydrophilic domains can be easily calculated:

$$\frac{m_{\text{Water}}}{m_{\text{SSA}}} = 1 + \frac{GL \cdot M_{\text{SSA}}}{M_S} \times W = 3.25 \times W,$$

(7.6)

when a GL of 25% is considered. Using Equation 7.6, we calculate a water content of $1.46 \pm 0.07$ and $1.72 \pm 0.07$ for the type L and H membranes, respectively. The corresponding hydration numbers $\lambda$, giving the number of water molecules per sulfonate site, are $\lambda = 12.95 \pm 0.61$ and $\lambda = 15.5 \pm 0.63$ Therefore, while the ion exchange capacities of type H and type L are nearly identical, the hydrophilic phase of type H is able to absorb more water compared to type L. This is relevant when considering that proton conductivity is strongly dependent on water content. Indeed, the positive outcome of this feature could be observed in through-plane proton conductivity measurements performed in partially hydrated states: membrane H systematically outperforms membrane L in terms of proton conductivity (Figure 7.3). While the difference is found to be a function of the relative humidity, it is statistically significant for r.h. values of 10% and higher (Supporting Information, Section 7.6.11.).
Figure 7.3: Through-plane proton conductivity as a function of relative humidity (80°C). The inset shows the ratio between the conductivity of L and H type membranes for r.h. values where the differences are statistically significant (Supporting Information, Section 7.6.11). The dashed line is a guide to the eye. These results are based on data shown earlier, and have been extended with additional measurements.

Given that the total volume of PS(SA) domains is kept the same, the average center-to-center distance between nearest-neighbor PS(SA) domains decreases as the overall number of domains, \( n \), increases: \( \propto \frac{1}{\sqrt[3]{n}} \), and thus, PS(SA) domains are closer to each other in type H compared to type L (Figure 7.4). Therefore, being analogous to, e.g., polymer nanocomposites, a more effective ‘dispersion’ of the hydrophilic nanophase in the polymer matrix is beneficial and improves conductivity, which can be achieved via smaller and more densely grafted polystyrene domains.

**7.5. Conclusion**

In summary, we studied a thus far unexplored degree of freedom in the design of irradiation grafted copolymers: The graft density and molecular weight can be scaled in specific manner through the irradiation dose and graft level. Based on a straightforward model, we designed and synthesized ion-containing graft-copolymer membranes via electron pre-irradiation. Evidence suggesting that scaling the dimensions of the copolymer architecture was successful was obtained through small-angle neutron and X-ray scattering as well as ion conductivity analyses correlating domain structure, water uptake, and ion conductivity.
7. Grafting Design: Structural Investigation

**Figure 7.4:** Illustration of structural differences found between L (low-dose) and H (high-dose) membranes: graft density increased with irradiation dose, and the size of the grafted chains increased with graft level. These parameters enabled to scale the size and the number density of PS(SA) domains (in green).

### 7.6. Supporting Information

#### 7.6.1. Membrane Synthesis

The base polymer poly(ethylene-alt-tetrafluoroethylene) (ETFE) was purchased from DuPont (Tefzel® 100LZ, Circleville, USA, 25 μm thickness). Reagents used during membrane synthesis are styrene (98%, Fluka), 2-propanol (PROLABO®, VWR), acetone (PROLABO®, VWR), chlorosulfonic acid (98%, Fluka) and dichloromethane (PROLABO®, VWR). All reagents and the monomer were used as received without removal of inhibitor.

The ETFE base films were pre-irradiated in air by an electron beam with different deposited doses (MeV class accelerator, Leoni-Studer AG, Däniken, Switzerland). After exposure the irradiated films were stored at −80°C until further processing. All grafting reactions were carried out with 7 cm × 7 cm pre-irradiated ETFE films in glass reactors (3 cm diameter, 18 cm height, 60 ml capacity) under nitrogen atmosphere. A degassed mixture of 20% (v/v) styrene, 70% (v/v) isopropanol and 10% (v/v) ultra-pure water served as grafting solution for the low dose system (3 kGy, type L). For the synthesis of type H (high dose system, 30 kGy) a solution of 7% (v/v) styrene was used while the ratio of isopropanol to ultra-pure water was kept constant. The reaction temperature was 55°C for type L (low-dose) and 50°C for type H (high-dose). For a GL of 25% the reaction was stopped after 1.58 h and 26 h, respectively, followed by an
7. Grafting Design: Structural Investigation

extraction of the grafted films with toluene for 16 h to remove residual monomer and homopolymer not covalently attached to the base film. The films were dried at 60°C under reduced pressure and weighed. The grafting level of each film was gravimetrically determined using the following equation:

$$GL = \frac{m_g - m_0}{m_0} \cdot 100\%$$

(7.7)

where $m_0$ and $m_g$ represent the weight of the sample before and after grafting, respectively.

Subsequent sulfonation was performed in a 2 L glass reactor using 2% (v/v) chlorosulfonic acid in dichloromethane. The films were separately placed in the solution and possible gas bubbles were carefully removed with a PTFE rod before the reactor was closed and protected against light with a PVC shielding. After stirring for five hours at room temperature the sulfonated films were removed from the reaction mixture and repeatedly washed with ultra-pure water. Hydrolysis of the functionalized films to sulfonic acid groups was performed in water at 80°C for 15 h.

![Scheme 7.1: Synthesis of electron beam grafted membranes with styrene as example.](image)

7.6.2. Ex-Situ Characterization

Ex-situ fuel cell relevant properties, such as the ion exchange capacity (IEC), proton conductivity, water uptake, and hydration number were determined in fully swollen state at ambient conditions. The IEC is defined as

$$IEC = \frac{n(H^+)}{m_{dry}}$$

(7.8)

where $n(H^+)$ is the molar number of acid protons and $m_{dry}$ is the dry mass of the membrane. After a proton/potassium exchange (stirring in 1 M KCl for 12 h at room temperature) the free accessible protons were titrated with a 0.05 M KOH solution by means of a SM Titrino 702 instrument (Metrohm, Herisau, Switzerland). The water
uptake ($W$) of the membrane displays its ability to absorb water and can be calculated according to the following equation:

$$ W = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \cdot 100\% $$  (7.9)

The hydration number ($\lambda$) is the molar ratio between water and sulfonic acid groups and is calculated from the IEC and the water uptake values according to:

$$ \lambda = \frac{n(\text{H}_2\text{O})}{n(\text{SO}_3\text{H})} = \frac{W}{\text{IEC} \cdot M_{\text{H}_2\text{O}}} $$  (7.10)

The degree of sulfonation ($s$), which is defined as the percentage of styrene units bearing sulfonic acidic groups, was estimated from the ratio of measured ion exchange capacity and the calculated IEC of the polymer.

$$ s = \frac{\text{IEC}_{\text{exp}}}{\text{IEC}_{\text{th}}} \cdot 100\% $$  (7.11)

$$ \text{IEC}_{\text{th}} = \frac{GL}{M_{\text{Styrene}} + (M_{\text{Styrene}} + M_{\text{SO}_3}) \cdot GL} $$  (7.12)

The through-plane conductivity in dependence of the relative humidity (r.h.) was measured with the 740 Membrane Test System from Scribner Associates Inc. (North Carolina, USA) at 80°C temperature using gas diffusion electrodes from E-TEK DivisionSM (ELAT HT-140E-W).222

### 7.6.3. SEM and EDX Analysis

In order to analyze the through-plane distribution of the grafted chains, sulfonated films were swollen in water for 2 h, subsequently frozen in liquid nitrogen and fractured to obtain a sharp cross-section area without smearing. SEM pictures were taken with a FESEM Ultra 55 (Carl Zeiss, Oberkochen, Germany) and energy dispersive X-ray analysis was performed using a compatible accessory (EDAX TSL, AMETEK).

### 7.6.4. Through-Plane Homogeneity Optimization

A tenfold or even higher increase in irradiation dose leads not only to much faster kinetics but also to a pronounced front mechanism that impairs the through-plane homogeneity of graft distribution. Therefore, the synthesis of type H (high-dose) membranes had to be optimized in order to obtain the same through-plane homogeneity as present in type L (low-dose) membranes.314 For this, the parameters of monomer concentration in the grafting solution as well as reaction temperature and applied dose had to be optimized. The best parameters found were 7% (v/v) styrene, 170
50°C and 30 kGy. After this optimization, sulfur micro-probing showed similar through-plane distribution profiles for both types of membrane (Figure 7.5).

Figure 7.5: Comparison of sulfur distribution profiles in through-plane direction for membranes of type L and type H (GL of ~25%).

7.6.5. Small-Angle Neutron Scattering

Small-angle neutron scattering (SANS) experiments were performed on the SANS II and SANS I instruments at the Paul Scherrer Institute (PSI). On these instruments a quasi-continuous beam is monochromatized by a velocity selector. In the case of SANS II the applied wavelength (\(\lambda\)) values were 0.518 and 1.035 nm with a wavelength spread (\(\Delta \lambda / \lambda\)) of \(\sim 10\%\). In the case of SANS I the applied wavelength (\(\lambda\)) was 0.45 nm with a wavelength spread (\(\Delta \lambda / \lambda\)) of \(\sim 10\%\). The samples were mounted on a conventional temperature controlled sample changer directly (in case of base films) or in 1 mm quartz cuvettes (fully swollen or nominally dry sulfonated membranes). The neutron beam was defined with a \(10 \times 7\) mm\(^2\) aperture (corners covered with a \(d = 10\) mm circular aperture) in front of the sample (SANS II) or with a \(10 \times 5\) mm\(^2\) aperture (SANS I). Scattered neutrons were detected with a position-sensitive \(^3\)He detectors with \(128 \times 128\) pixels, with a pixel size of \(4.3 \times 4.3\) mm\(^2\) (SANS II) or \(7.5 \times 7.5\) mm\(^2\) (SANS I). The sample to detector distance and collimation were 1.1 m and 3 m (at \(\lambda = 0.518\) nm), 4 m and 4 m (at \(\lambda = 0.518\) nm), and 6 m and 6 m (at \(\lambda = 1.035\) nm) offering a \(Q\)-range coverage of \(0.3 - 2.9\) nm\(^{-1}\), 0.09-0.8 nm\(^{-1}\) and 0.03 – 0.27 nm\(^{-1}\) on SANS II, while on SANS I a sample to detector distance of 1.6 m and collimation of 3 m, with an off-centered detector position was offering a \(Q\)-range coverage of 0.75 – 7.4 nm\(^{-1}\).

In order to follow the influence of the relative humidity on the structural features of the membranes we performed SANS experiments also under defined relative humidity...
conditions. For this, samples were equilibrated for 14 days in a sealed container with a saturated salt solution maintaining a specified r.h. at 25°C (MgCl$_2$: 33% r.h.; Mg(NO$_3$)$_2$: 52.8% r.h.; NaCl: 75% r.h.)$^{224,225}$. For 0% r.h., the samples were dried under reduced pressure at 80°C for 24 h. Afterwards the samples were transferred to aluminum cells which were sealed using IceCube elastomer (Freudenberg). The windows of the cells were made of Si wafer (Figure 7.6) and used for measurements on SANS II. On SANS I experiments were performed exclusively on nominally dry or D$_2$O swollen membranes.

![Figure 7.6: Photographs showing the main components of the humidity cell (from left to right)](image)

1) The frames of the cells are made of aluminum. 2) Ice cube sealing seals the contact between the aluminum and the Si wafer windows. 3) The Si wafer windows are almost transparent for neutrons. 4) The thickness of the sample space is defined by the Ice cube which seals the contact between the two aluminum frames. 5) The cell is closed and airtight.

Data treatment was performed with the “Graphical Reduction and Analysis SANS program” package (GRASP) (developed by C. Dewhurst, ILL). The 2D data was corrected for background and dark counts according to standard procedures, and 1D scattering curves were obtained by azimuthally averaging either in a 360° sector around the direct beam position or in two 90° sectors along the machining and the transverse direction of the sample (SANS II), or in a 180° sectors along horizontal direction of the sample (off-centered detector position on SANS I).

### 7.6.6. Quantification of the Semi-Crystalline Structural Differences

We quantified the semi-crystallinity related structural features of the grafted films and membranes via applying the Bragg equation on the characteristic peak position observed in the SANS scattering curves. A possible approach for the estimation of the position of the characteristic peak would be via finding the local maxima in the peak region. This method however cannot be applied for ill-defined peaks lacking local maxima; this is often the case for the investigated membranes, especially at high humidity. In order to
overcome this obstacle we relied on the anisotropic nature of the SANS scattering signals. The characteristic peaks are significantly more pronounced along the machining direction than along the transvers direction. Consequently if the latter is subtracted from the former – resulting in the cancellation of any isotropic signal – the difference spectrum is expected to exhibit a better-defined characteristic peak. We have to note that the characteristic distances obtained via this method are corresponding mainly to distances in and around the machining direction. Scattering curves averaged radially in two 90° sectors along the transverse direction of the sample were subtracted from the ones averaged along the machining direction. The resulting difference spectrum exhibits a peak with clear maxima at the position of the original correlation peak both for the low and the high dose system both at 25 % GL. The center position of the characteristic peak was determined via fitting a Gaussian function in the 0.1-0.26 nm\(^{-1}\) momentum transfer region (0.19-0.35 nm\(^{-1}\) in the case of the base film).

### 7.6.7. Small-Angle X-ray Scattering

Small-angle X-ray scattering (SAXS) spectra of the investigated samples were recorded at room temperature by using a NanoMax-IQ camera (Rigaku Innovative Technologies, Auburn Hills, MI USA). Raw data were processed according to standard procedures, and the scattering spectra are presented as a function of the momentum transfer \( Q = 4\pi\lambda \cdot \sin(\theta/2) \), where \( \theta \) is the scattering angle and \( \lambda = 0.1524 \text{ nm} \) is the photon wavelength.

### 7.6.8. Estimation of the Degree of Polymerization and Graft Density of the Side Chains

We calculated the expected average number of styrene monomers building up a single grafted chain (\( P \)) and the number of “ETFE units” (\( \text{C}_2\text{H}_2\text{F}_2 \)) (\( D \)) between neighboring grafted chains attached to the same ETFE molecule for the case of the grafted films prepared with the two different preparation protocols. For this we relied on the dose dependent spin concentration measurements of Mitov et al.\(^{312}\) – considering an ETFE irradiation in air, we can estimate a radical concentration of roughly \( c_{R,\text{low}} = 0.39\cdot10^{-6} \text{ mol g}^{-1} \) in the 3 kGy samples and \( c_{R,\text{high}} = 3.7\cdot10^{-6} \text{ mol g}^{-1} \) in the 30 kGy samples before grafting. From this the average number of ETFE units between two radicals \( \langle n_{\text{ETFE}} \rangle \) can be calculated as follows

\[
\langle n_{\text{ETFE}} \rangle = \frac{1}{c_{R} \cdot M_{\text{ETFE}}} = \frac{1}{c_{R} \cdot 64 \text{ g mol}^{-1}}
\]  

(7.13)
yielding for the low dose system on average \( \langle n_{\text{ETFE}} \rangle_{R_{\text{low}}} = 4 \cdot 10^4 \) ETFE units between radicals, while in the high dose system \( \langle n_{\text{ETFE}} \rangle_{R_{\text{high}}} = 4.2 \cdot 10^3 \) units.

For the estimation of the average number of styrene monomer units in the grafted chains the crystallinity (\( \chi \)) of the base film also has to be taken account (36% in the case of the DuPont base film used).\(^{313}\) We consider that all the grafting happens in the remaining 64% amorphous region. This constraint does not influence the number of ETFE units between radicals \( \langle n_{\text{ETFE}} \rangle \), only the number of monomers in a single graft chain. If \( n_S \) is the number of styrene molecules grafted on \( m_{\text{ETFE}} \) of base film, the average number of monomers in a single graft (polymerization level) can be calculated as follows:

\[
\langle n_S \rangle = \frac{n_S}{(1-\chi)m_{\text{ETFE}}c_R} = \frac{\langle n_{\text{ETFE}} \rangle}{(1-\chi)m_{\text{ETFE}}c_R} = \frac{G_L m_{\text{ETFE}}}{(1-\chi)c_R M_S} = \frac{G_L}{(1-\chi)c_R M_S} \tag{7.14}
\]

yielding for the low dose system on average \( \langle n_S \rangle_{R_{\text{low}}} = 9.6 \cdot 10^3 \) number of monomers in a single graft, while in the high dose system \( \langle n_S \rangle_{R_{\text{high}}} = 1.0 \cdot 10^3 \) monomers.

**Figure 7.7:** Azimuthally averaged SAXS curves of dry Cesium exchanged membranes at 25% GL for the entire investigated momentum transfer range (a) and for the low momentum transfer region (b).
Figure 7.8: SAXS curves of dry Cesium-exchanged membranes at 25% GL in the 2.2 nm\(^{-1}\) – 6.5 nm\(^{-1}\) momentum-transfer range. Since the curves for the low and the high dose membranes almost perfectly overlap in this range, the scattering from the low dose (left axis) and high dose (right axis) membranes are vertically shifted for the sake of clarity.

Figure 7.9: Azimuthally averaged SANS curves of the D\(_2\)O-swollen membranes at 25% GL for the high momentum transfer range. This $Q$-range fitted best against the phenomenological mathematical model expressed by the linear combination of a power and a Lorenzian function. The ionomer peak is centered around 2.55 nm\(^{-1}\) and 2.53 nm\(^{-1}\) for the low and high dose membrane, respectively. Applying the Kinning-Thomas model to the SANS curves did not reveal any significant difference between the low- and high-dose membranes. (Measurements performed on SANS I instrument.)
7. Grafting Design: Structural Investigation

Figure 7.10: Two-dimensional SANS patterns of type L (left) and type H (right) grafted films. Arrows mark the orientation of the films: MD (machining direction) and TD (transverse direction). Red lines mark the boundaries of the sectorial averaging. (Measurements performed on SANS II instrument.)

7.6.9. Estimation of Polystyrene Volume Fraction

In the following equations $m_o$, $m_g$ and $m_{PS}$ represent the mass of the pristine and grafted base film, and the mass of the PS in the grafted films, respectively. $V_{PS}$ and $V_{ETFE}$ are the volume of the PS and the ETFE, respectively, in the grafted films. $\rho_{PS} = 1.05 \ \text{g/cm}^3$ and $\rho_{ETFE} = 1.7 \ \text{g/cm}^3$ are the density of the PS and the ETFE, respectively.

\[
m_{PS} = m_g - m_o = GL \cdot m_o \tag{7.15}
\]

\[
\phi_{PS} = \frac{V_{PS}}{V_{ETFE}+V_{PS}} = \frac{\frac{GL \cdot m_o}{\rho_{PS}}}{\frac{m_o}{\rho_{ETFE}} + \frac{GL \cdot m_o}{\rho_{PS}}} = GL \cdot \frac{1}{\frac{1}{\rho_{ETFE}} + \frac{GL}{\rho_{PS}}} \tag{7.16}
\]

\[
\phi_{PS} = GL \cdot \frac{1 \ \text{cm}^3}{\frac{1 \ \text{cm}^3}{1.05 \ \text{g}} + \frac{GL \ \text{cm}^3}{1.7 \ \text{g}}} \tag{7.17}
\]

where $\phi$ stands for volume fraction. Therefore, the estimated volume fraction of PS is ~0.29 and ~0.45 for the grafted films with 25% GL and 51% GL, respectively.

7.6.10. Distribution of Grafted Domains in Dry Membranes

Here we estimate the distribution of the individual grafted domains originating from the different radical centers in the dry membranes prepared with the two different grafting protocols. As detailed above, we can predict a radical concentration of roughly...
\[ c_{R_{\text{low}}} = 0.39 \cdot 10^{-6} \text{ mol g}^{-1} \] in the 3 kGy samples and \[ c_{R_{\text{high}}} = 3.7 \cdot 10^{-6} \text{ mol g}^{-1} \] in the 30 kGy samples before grafting. Considering a mass increase of \( GL \cdot (M_{\text{Styrene}} + M_{\text{SO3}}) / M_{\text{Styrene}} = 44\% \), the number density of the grafted domains starting from different radical sites is maximum \( 0.27 \cdot 10^{-6} \text{ mol g}^{-1} \) in the 3 kGy samples and \( 2.6 \cdot 10^{-6} \text{ mol g}^{-1} \) in the 30 kGy samples, which corresponds to a number density \( (n) \) of \( 0.23 \cdot 10^{-3} \text{ nm}^{-3} \) and \( 2.18 \cdot 10^{-3} \text{ nm}^{-3} \) in the low and high dose system, respectively. Considering the law of average distance of the nearest neighbors in a random distribution of particles: \( (0.55 n^{-1/3}) \), an average distance between center of the nearest grafting domain neighbors is higher than 9.1 nm in the case of low dose system and higher than 4.3 nm for the high dose system. These values are a few times smaller than the characteristic distances of the crystalline-amorphous separation, observed in the small-angle scattering studies, showing that several grafted domains are present between neighboring crystallites in the grafted films and membranes.

**Figure 7.11:** Characteristic scattering peak positions calculated from the SANS curves measured at various humidity levels.
7. Grafting Design: Structural Investigation

Figure 7.12: Azimuthally averaged SANS curves along (a) and perpendicular (b) to the machining direction for membranes (25% GL) at 75% H₂O relative humidity. (Measurements performed on SANS II instrument.)

Figure 7.13: Water uptake and hydration level of type L and H membranes. Low dose data is given as a trend line to indicate the dependence of these properties on the grafting level.
7.11. **Through-Plane Proton Conductivity as a Function of Relative Humidity**

**Table 7.1:** The results of the statistical significance test (Student’s t test) of the conductivity difference between the L and H type membranes at different relative humidity values.

<table>
<thead>
<tr>
<th>r.h. [%]</th>
<th>p-value (significance level: 0.05)</th>
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<tr>
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<td>10</td>
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<td>30</td>
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<tr>
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<td>0.011</td>
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</table>

**Table 7.2:** Sets of through-plane proton conductivity values measured at systematically varied relative humidity values for the type L membranes.

<table>
<thead>
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<th>Conductivity [mS cm⁻¹]</th>
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<tr>
<td>5</td>
<td>0.07 0.05 0.15 0.05</td>
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<tr>
<td>10</td>
<td>0.27 0.19 0.35 0.21</td>
</tr>
<tr>
<td>30</td>
<td>4.55 3.47 4.33 3.87</td>
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<tr>
<td>35</td>
<td>6.66 5.23 6.28 5.63</td>
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<tr>
<td>50</td>
<td>18.27 15.78 17.47 15.72</td>
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<tr>
<td>55</td>
<td>24.80 20.59 22.81 20.82</td>
</tr>
<tr>
<td>70</td>
<td>55.49 50.18 51.97 50.38</td>
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</table>
### 7. Grafting Design: Structural Investigation

<p>| | | | |</p>
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<tr>
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<td>169.15</td>
<td>184.59</td>
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</table>

#### Table 7.3: Sets of through-plane proton conductivity values measured at systematically varied relative humidity values for the type H membranes.

<table>
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<tr>
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<th>Conductivity [mS cm⁻¹]</th>
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<tr>
<td>5</td>
<td>0.11 0.11 0.11 0.15 0.25</td>
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<tr>
<td>10</td>
<td>0.36 0.37 0.33 0.39 0.49</td>
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<tr>
<td>30</td>
<td>5.61 5.56 5.21 5.64 5.74</td>
</tr>
<tr>
<td>35</td>
<td>8.24 8.17 7.62 8.16 8.24</td>
</tr>
<tr>
<td>50</td>
<td>21.74 21.81 20.54 23.11 23.15</td>
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</tr>
<tr>
<td>70</td>
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<tr>
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<tr>
<td>95</td>
<td>224.11 224.22 180.64 229.69 217.56</td>
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</tbody>
</table>

#### 7.6.12. Correlation between Microstructure and Grafting Kinetics

The structural conclusion derived above from the SANS experiments represent a statistically averaged information over the entire sample volume probed by the neutron beam. Here we show that the SANS experiments also carry information about the through-plane grafting homogeneity of the investigated samples.

As reported earlier, in order to achieve a homogeneous through-plane graft distribution in the case of high dose systems, we investigated how the system parameters influence the grafting front mechanism. The different grafting protocols are represented by the following notation: dose [kGy]/reaction temperature [°C]/monomer...
concentration [v/v %]. For the high dose system at 25% GL the most homogeneous through-plane graft distribution was obtained for the film 30/50/7 (referred as type H in the present article) (Figure 7.14)

**Figure 7.14:** Comparison of the sulfur distribution profiles in through-plane direction for membranes of high dose type at GL of ~25%. The notation \(x/y/z\) corresponds to \(x\): dose (kGy); \(y\): reaction temperature (°C); \(z\): monomer concentration (vol%).

For the high dose system at 51% GL the graft conditions 30/55/9 and 30/50/9 were tested and the 30/50/9 sample was found to be more homogeneous (Figure 7.15). We performed SANS experiments to reveal if at a constant dose and graft level we can observe structural differences in the films upon varying reaction temperature and monomer concentration. For the azimuthally averaged SANS curves see Figure 7.16 (25% GL) and Figure 7.17 (51% GL). Difference curves (obtained as detailed in the paragraph “Quantification of the semi-crystalline structural differences”) between the MD and TD directions are shown in Figure 7.18.

From the difference curves we determined the characteristic peak positions (Figure 7.19), and corresponding characteristic distances for the membranes prepared with different grafting protocol. As shown in Figure 7.19 among the high dose systems at 25% GL the lowest characteristic lengthscale was observed for the 30/50/7 system and at 51% GL for the 30/50/9 system i.e. on the systems which show the highest homogeneity of grafting across the film. This observation can be explained if we consider that the GL results in the shift of the characteristic peak towards lower momentum transfer values. When a specific average GL is achieved in an inhomogeneous system via combination of high and low local GL, in the scattering signal the part of the membrane with high GL (i.e. the one with lower characteristic...
peak position) will dominate, due to the higher contrast between the amorphous and crystalline domains.

**Figure 7.15:** Comparison of the sulfur distribution profiles in through-plane direction for membranes of high dose type at GL of ~51%. The notation \(x/y/z\) corresponds to \(x\): dose (kGy); \(y\): reaction temperature (°C); \(z\): monomer concentration (vol%).

Although a SANS experiment performed on fuel cell membranes oriented perpendicular to the neutron beam can provide direct structural information only parallel to the membrane plane, it can indirectly reveal the level of grafting inhomogeneity across the membrane, when several samples with the same GL are compared. It is also important to note that – as stated in the main article – independently from their through-plane inhomogeneity, all grafted films prepared with the high dose protocol show higher characteristic peak positions and lower characteristic distances when compared to the films prepared with the low dose protocol.
Figure 7.16: Azimuthally averaged SANS curves along (a) and perpendicular (b) to the machining direction for 25% grafted films, prepared with different grafting protocol and for the base film. (Measurements performed on SANS II instrument.) The notation \( x/y/z \) corresponds to \( x \): dose (kGy); \( y \): reaction temperature (°C); \( z \): monomer concentration (vol%).

Figure 7.17: Azimuthally averaged SANS curves along (a) and perpendicular (b) to the machining direction for 51% grafted films, prepared with different grafting protocol and for the base film. (Measurements performed on SANS II instrument.) The notation \( x/y/z \) corresponds to \( x \): dose (kGy); \( y \): reaction temperature (°C); \( z \): monomer concentration (vol%).
Figure 7.18: Influence of the grafting protocol on the grafted film structure. Difference of azimuthally averaged SANS curves along and perpendicular to the machining direction ($I_{MD} - I_{TD}$) for the grafted films at 25% GL (a) and at 51% GL (b) along with the difference spectra of the base film. (Measurements performed on SANS II instrument.) The notation $x/y/z$ corresponds to $x$: dose (kGy); $y$: reaction temperature ($^\circ$C); $z$: monomer concentration (vol%).

Figure 7.19: Characteristic peak positions (a) and corresponding characteristic distances (b) for the low and high dose grafted films prepared with various grafting protocols along with the corresponding base film data. The notation $x/y/z$ corresponds to $x$: dose (kGy); $y$: reaction temperature ($^\circ$C); $z$: monomer concentration (vol%).
Chapter 8. Swift Heavy Ion Induced Structuring

Most commonly, $\gamma$-radiation and accelerated electrons are the types of ionizing radiation used for the synthesis of radiation grafted membranes. Applying this activation technique, grafting results in the statistical formation of a random morphology with phase-separated hydrophilic / hydrophobic domain structure, in which case the tortuosity of the aqueous phase places an inherent limitation on the conductivity of the material. In this chapter an approach to reduce this tortuosity and create polymer electrolytes with proton conducting domains aligned in through-plane direction of the membrane is presented. This type of membrane was prepared via swift heavy ion (SHI) irradiation and the effect of this irradiation on the structure and fuel cell relevant properties of a PEM including performance measurements on the device (cell) level are thoroughly discussed. Membranes were synthesized with various densities of proton conducting channels, which were identified via elemental mapping and electrochemical AFM. These membranes showed superior proton conductivity and fuel cell performance.

The present chapter consists of a reproduction of a manuscript prepared for submission to the following journal:

8. Swift Heavy Ion Induced Structuring

8.1. Abstract

Proton exchange membranes (PEMs) attracted great interest as key elements in various electrochemical devices, such as fuel cells, electrolyzers or flow batteries. The structure of commonly used PEMs consists of a random arrangement of proton conducting domains, formed by phase separation of hydrophilic ionomer constituents from the hydrophobic polymer backbone. This paper presents an approach for the synthesis of polymer electrolytes with proton conducting domains aligned in through-plane direction of the membrane, prepared via swift heavy ion (SHI) irradiation followed by graft copolymerization and sulfonation to introduce proton conducting motifs. This paper presents a comprehensive discussion of the effect of SHI irradiation on the structure and fuel cell relevant properties of a PEM including performance measurements on the device (cell) level. Membranes were synthesized with various densities of proton conducting channels, which were identified via elemental mapping and electrochemical AFM. These membranes showed superior proton conductivity and fuel cell performance.

8.2. Introduction

Polymer electrolyte fuel cells (PEFCs) offer an environmentally friendly and efficient way for electrochemical energy conversion, which can also be applied in zero-emission cars, such as the Toyota Mirai, which has been commercialized in 2015.321 The proton exchange membrane (PEM) is one of the key components in these PEFCs, fulfilling requirements of high proton conductivity while acting as separator to prevent electric shorting and the mixing of reactant gasses.1, 3, 236 Despite being the center of investigation for decades, current membranes still do not fulfill all targeted requirements. Even the most commonly used PEMs in fuel cell applications – PFSA (perfluorosulfonic acid) membranes, such as DuPont’s Nafion® – show deficits when it comes to ‘dry’ operating conditions (< 50% r.h.) and temperatures above 90°C.3, 8, 62 Together with the high costs for such perfluorinated membranes this triggers further development of alternative PEMs. Among many different types of membranes which have been proposed and assessed (for more information see, for example, the reviews of Kerres8 and Devanathan322), radiation grafted membranes offer a versatile approach to modify commercially available base films. Different types of radiation can be used to generate radicals in the bulk of the base polymer film, which initiate the subsequent polymerization process. This approach allows the combination of chemically stable and non-reactive materials, e.g., ethylene-alt-tetrafluoroethylene (ETFE) or polyvinylidene fluoride (PVDF), with the desired property of another polymer – in this case high
proton conductivity - by covalent bonding. Nevertheless, the knowledge and understanding of the structure-property correlation in these membranes and the influence of polymer architecture on the final membrane performance is still rather limited. Hydrophilic channels, in which the protons are transported, form as a result of nanophase separation of the hydrophobic backbone and the hydrophilic side chains bearing acidic moieties. The morphology thereby adopted is determined by factors such as the extent of dissimilarity between incompatible polymer, the chain length of each constituent and their volume ratio. An increased content of sulfonic acid groups (expressed by a higher ion exchange capacity, IEC) leads to a higher water content resulting in an increased effective proton mobility and thus higher proton conductivity. The effective proton mobility includes factors such as the tortuosity and the degree of dissociation of the acid. Therefore, a lower degree of tortuosity, corresponding to a more direct conduction pathway, leads to a higher effective conductivity and, hence, to a lower resistance of the membrane.

Most commonly, γ-radiation and accelerated electrons are the types of ionizing radiation used. This kind of irradiation leads to a homogenous distribution of energy throughout the bulk of the material, which is described by a low LET value (average linear energy transfer (LET) of a 1 MeV electron or a 60Co γ-ray in water is around 0.3 keV/μm). Another kind of radiation which can be used to initiate the grafting process are swift heavy ions (SHI). In contrast to electron and γ-radiation, SHI irradiation is associated with a high LET (e.g. 4He2+, 100 keV/μm or more in H2O) which leads to the formation of a continuous and strongly localized track of ion-polymer interaction. Along the trajectory of the heavy ion a cylindrical damage zone with reduced material density (latent track) is created that consists of free radicals and groups (peroxides and hydroperoxides) formed therefrom through oxidation in air. These active groups can be found in the latent track. Its diameter ranges between 3 and 30 nm, depending on the ion used and analytical method employed for characterization. The activation extends to the surrounding area (halo, radius ~50-200 nm) and can be used as initiator for the grafting reaction.

The advantage in this approach lies in the possible formation of macroscopically oriented grafted domains. Electron (and γ-) induced grafting results in the statistical formation of a random morphology with phase-separated hydrophilic / hydrophobic domain structure, in which case the tortuosity of the aqueous phase places an inherent limitation on the conductivity of the material. Using SHI irradiation, however, offers the prospect of forming conduction pathways with low tortuosity, as grafting starts from the area around the latent track that has a macroscopic orientation (Figure 8.1), which is expected to lead to an improved through-plane conductivity of the membrane.
8. Swift Heavy Ion Induced Structuring

![Image](image_url)

**Figure 8.1:** Schematic sketch to illustrate the conceptual difference in hydrophilic (green) – hydrophobic (black) phase distribution and orientation between electron irradiation grafting (left) and grafting after SHI irradiation (right).

Most commonly, the radicals created by SHI irradiation are directly used for further modification (**Figure 8.2**). The group around N. Betz and her successors intensively investigated this “*direct approach*”, mostly using PVDF as base film for their grafting reactions.\(^{330-333}\) Besides the grafting modification, also the technique of track-etching (removal of damaged material in the latent tracks and halo by chemical etching) is a widely used method to prepare membranes from SHI irradiated films (e.g. PET or PC) in industrial scale. Track-etched membranes offer a very uniform pore size with a tunable diameter (30 nm to 20 \(\mu\)m).\(^{334}\) Another approach is to combine both above mentioned concepts and fill the etched pores with graft polymers using either the remaining radicals after the etching process \(^{335-338}\) or activate the film in a second step with electron or \(\gamma\)-irradiation \(^{339, 340}\). Recently, an approach was followed by Yoshida et al. where the macroscopic structuring effect of SHI (damaged area in latent tracks with reduced material density, no subsequent etching procedure) was combined with the homogenous activation of \(\gamma\)- and electron beam irradiation.\(^{341, 342}\)

![Image](image_url)

**Figure 8.2:** Schematic sketch to illustrate the approach of SHI irradiation induced polymer film modification. The base film is irradiated with swift heavy ions (SHI, e.g. Kr\(^{16+}\)) to generate...
latent tracks. The radicals generated during this irradiation are directly used for further modifications, e.g. grafting or track-etching, yielding a highly structured (functionalized) film.

From a conceptual point of view, when grafting is initiated by the radicals created upon SHI irradiation, one can expect a pronounced separation between the grafted tracks and the remaining bulk material. On a more detailed level, however, radicals are not only created in the tracks but also in the surrounding area (‘halo’). Therefore, for ion fluences commonly used the grafting does not only occur within the created tracks but also in the material between the tracks, though not to the same extent.

In the present work we compare SHI membranes with membranes produced according to the standard electron irradiation based protocol. In the course of our structure-property correlation studies, ETFE-g-PSSA (PSSA: polystyrene sulfonic acid) membranes are used as model system to investigate the impact of SHI irradiation and the macroscopic structuring. For this four different fluences were tested (100 × 10⁶ ions cm⁻², 320 × 10⁶ ions cm⁻², 960 × 10⁶ ions cm⁻² and 2560 × 10⁶ ions cm⁻²). The overall mass ratio of PS(SA) and ETFE (expressed by the grafting level, GL) was kept constant for all membranes (~25% GL), therefore different properties can be attributed to the different distribution of PSSA within these membranes. With our structure-property correlation studies we aim to highlight different aspects contributing to the performance of radiation grafted membranes, which are expected to be of a general nature and applicable to more complex grafting systems involving multi-monomer grafts. This leads to a deeper understanding of radiation grafted membranes and helps to optimize PEMs.

### 8.3. Experimental Section

#### 8.3.1. Chemicals

The base polymer, poly(ethylene-alt-tetrafluoroethylene) (ETFE), was purchased from DuPont (Tefzel® 100LZ, Circleville, USA) as a film of 25 μm thickness. The reagents used during membrane synthesis included styrene (98%, Fluka), 2-propanol (PROLABO®, VWR), acetone (PROLABO®, VWR), chlorosulfonic acid (98%, Fluka) and dichloromethane (PROLABO®, VWR). The reagents and the monomer were used as received without removal of inhibitor.
8.3.2. **Membrane Synthesis**

The SHI irradiation of the ETFE base films was conducted by Oxyphen AG (Wetzikon, Switzerland). The films were irradiated under vacuum with high-energy ions of Kr (\(^{84}\text{Kr}^{16+}\)) at a specific energy of 383 MeV. Four different fluences of the ion-beam were investigated: 100 × 10^6 ions cm\(^{-2}\), 320 × 10^6 ions cm\(^{-2}\), 960 × 10^6 ions cm\(^{-2}\) and 2560 × 10^6 ions cm\(^{-2}\), which will be abbreviated following the notation \(K_{xy} (= xy \times 10^6 \text{ ions cm}^{-2})\). For comparison purposes, untreated ETFE base films were electron irradiated using a MeV class accelerator and a dose of 5 kGy. All films were stored at -80°C until used.

The method of grafting styrene onto ETFE base films was the same as reported elsewhere\(^{262}\) using 20% (v/v) styrene monomer in a mixed isopropanol / water solvent followed by subsequent sulfonation in 2% (v/v) chlorosulfonic acid in dichloromethane.\(^{262}\)

The grafting level of each film was gravimetrically determined according to:

\[
GL = \frac{m_g - m_0}{m_0},
\]  

(8.1)

with \(m_0\) and \(m_g\) representing the mass of the sample before and after grafting, respectively. To obtain a grafting level of ~25%, the reaction time for electron irradiated samples was 1.42 h. For the direct approach ~25% GL were obtained after 1.42 h (K2560), 2.25 h (K960), 4.73 h (K320) and 17.5 h (K100).

Nafion® PFSA membrane (NR-212, solution cast) was purchased from DuPont and was used as received.

8.3.3. **Sample Characterization**

Various techniques were applied to characterize films and membranes: SEM and EDX analyses were applied to characterize surface and cross-sectional structuring effects in the distribution of grafted polystyrene chains. Electrochemical atomic force microscopy (EC-AFM) was used to investigate the topography of the synthesized membranes correlated with local proton conductivity measurements. Further \textit{ex-situ} characterization comprises ion-exchange capacity and water-uptake as well as the through-plane proton conductivity in dependence of relative humidity. First fuel cell tests and hydrogen permeation measurements complement the characterization and provide a proof of concept on the device level. A detailed description of the used analytical methods can be found in the Supporting Information.
8.4. Results and Discussion

8.4.1. Graft Distribution

The reaction kinetics for the different ion densities used in this investigation is shown in the Supporting Information, Section 8.6, Figure 8.11. The radicals initiating the grafting process were generated during the SHI irradiation and are therefore strongly localized. These radicals are distributed either inside or in the area around the tracks created by Kr\textsuperscript{16+} (halo). Due to this structuring, the grafting originates in the tack / halo and not within the bulk of the material as in the standard electron irradiated membrane. To evaluate the success of base film structuring by ion irradiation EDX analysis was chosen as the most suitable method. The grafting of styrene onto an ETFE base film is a diffusion controlled process which in the case of the electron irradiated standard membrane (5 kGy, Std.e-) leads to an inhomogeneous distribution of grafts in through-plane direction (cf. Supporting Information, Section 8.6, Figure 8.12). As the irradiation with Kr\textsuperscript{16+} creates tracks with damaged base film material and lower density the diffusion of the styrene monomer into these tracks is expected to be enhanced. Therefore, the grafting is facilitated in these zones of reduced material density. Upon incorporation of polystyrene into ETFE, the diffusion of the monomer into the film is faster. In this concept, the created tracks of lower density should form a pathway for an enhanced diffusion of the styrene monomer into the bulk of the base film, thereby reducing the through-plane inhomogeneity or even leading to a completely homogenous graft density perpendicular to the plane of the membrane. EDX spectroscopy offers the possibility to investigate the transverse concentration profile using a sulfur mapping as a tracer for graft distribution.

Sulfur mappings of the cross-sections show significantly improved through-plane homogeneity for membranes synthesized by heavy ion irradiation at a GL of ~25% (Figure 8.3a). The lower ion densities, K100 and K320, yield a completely homogeneous transverse concentration profile while the sample irradiated with the highest ion density, K2560, features a small gradient towards the center of the film. However, this gradient is much less pronounced than in the standard system, Std. e-, without structuring (Figure 8.3b), proving the impact of the enhanced diffusion along the tracks generated by the SHI irradiation. The comparison between the different ion densities shows the same trend as that long known for electron irradiated systems.\textsuperscript{262, 344} The higher the accumulated dose (more initiation points for grafting), the faster the target GL is reached, but the more pronounced are the so-called grafting fronts resulting in an inhomogeneous distribution of grafts in through-plane direction. Nevertheless, even in case of K2560 and Std.e- (both having identical reaction times to reach
~25% GL) the SHI membrane shows strongly improved through-plane homogeneity (Figure 8.3b). The systems K100 and K320 even offer homogenous grafting at very low GL, e.g. 5% (cf. Supporting Information, Section 8.6, Figure 8.13 for distribution profiles of all ion densities at different GL).

![Figure 8.3](image)

**Figure 8.3:** Overlaid sulfur distribution profiles (through-plane direction) for membranes synthesized with different ion densities (a) and a graft level of ~25%. The distribution profiles were normalized to 25.0% GL for comparison. b) Overlaid sulfur distribution profiles of the K2560 membrane (showing the highest degree of inhomogeneity within the SHI treated series) versus the standard electron irradiated system (std. e-).

An interesting effect could be seen in the cross-sectional EDX-mappings of the system irradiated with the lowest ion density, K100. Under this condition the tracks created by the irradiation with Kr^{16+} seem to have sufficient distance from each other to permit a distinction between the higher grafted areas in close proximity to these tracks and the surrounding material which is functionalized to a lower level. **Figure 8.4a** shows an overlay of the sulfur mapping (graft propagation tracer, magenta) and fluorine mapping (higher concentration for less modified base film, blue) of the cross-section of a K100 membrane with a GL of 25%. When two elemental mappings are overlaid in one image each pixel gets the color assigned to the element with the highest content (sulfur – magenta; fluorine – blue) and no mixed colors are formed.

The separate sulfur and fluorine distribution profiles in lateral direction of the membrane cross-section taken from the separate elemental mappings are displayed in **Figure 8.4b.** K100 shows the desired structuring effect with elongated features in through-plane direction of the membrane, that is in strong contrast to the S and F distribution in Std. e- (Figure 8.4a, inset), which shows the aforementioned grafting front characteristic (structuring parallel to the plane of the membrane).
Figure 8.4: a) Overlaid EDX mappings of sulfur (magenta) and fluorine (blue) for the cross-section of a K100 membrane with 25% GL. The inset shows the analog for the standard electron irradiated system (cf. Supporting Information for more information). b) Sulfur and fluorine distribution profiles measured along the direction of the plane of the membrane.

The higher local content of sulfur reflects the structure that is expected due to the more localized distribution of radicals and tracks of lower material density upon heavy ion irradiation. As the hydrophilic phase is formed from the functionalized graft component, this is the first indication that a macroscopic orientation of the hydrophilic phase might have been successfully created in the present case. The analysis of different GL can be found in the Supporting Information (Section 8.6, Figures 8.14 – 8.19).

Apart from the cross-sections also the surface of the SHI membranes was analyzed with SEM and EDX. The SEM image shows a highly structured surface area for SHI membranes of K100 (Figure 8.5a) with ‘mushrooms’ with size of ~1 μm diameter (or larger if several were grown together). This structuring resembles the distribution of the created ion tracks, which form the center of highly grafted ETFE-g-PSSA domains, an observation that was already made for other materials. The elevations are caused by PSSA growing out of the track and ‘speading’ over the surface of the membrane. With increasing ion density and therefore closer proximity of the single tracks the surface is more and more covered by this second phase (cf. Supporting Information, Section 8.6, Figures 8.20 – 8.23). EDX measurements of sulfur and fluorine are in accordance with this assumption and show a higher sulfur content located in these features (Figure 8.5b). At the highest ion density of $2560 \times 10^6$ ions cm$^{-2}$ the sulfur mapping of the surface is completely homogenous and no structuring is discernible (Supporting Information, Section 8.6, Figure 8.23).
After EDX analysis giving a first confirmation of the different composition of the phases forming the structuring effects that were visible in SEM micrographs, further investigations on this issue were performed. A highly appealing method in this context is electrochemical atomic force microscopy (EC-AFM). This technique provides information on the topography of the surface and, at the same time, on the local proton conductivity. The experimental setup is shown in the Supporting Information, Section 8.6, Figure 8.24. All experiments were performed in an environmental chamber with humidified air on both sides of the cell. A water reservoir was used to ensure constant humidification of the membrane and enable stable measurements. The atmosphere was set to a relative humidity of 45 ± 3% and voltage is applied to measure a net current. This current is driven by electrochemical reactions on both sides of the membrane. At the anode water reacts at the Pt catalyst layer to form oxygen and protons. These protons are transported through the hydrophilic channels of the membrane and recombine with the oxygen from the air atmosphere at the Pt coated tip of the AFM probe (cathode side) to form water. Therefore, current is only measured when the conductive AFM-tip is in contact with such a hydrophilic channel or a cluster thereof.

The surface of K100 and K2560 membranes (~25% GL) was investigated in the described manner and showed clearly distinguishable areas. K100 features blurry elevations corresponding to the ‘mushrooms’ seen in the SEM micrographs. These elevations show good proton conductivity and are 200 – 400 nm in height (Figure 8.6 and Supporting Information, Section 8.6, Figures 8.25 – 8.26). The bright areas in the image indicate where a current is detected whereas the lower dark areas are non-conductive under the measured conditions and can be attributed to the ETFE
dominated hydrophobic regions. As already seen in the SEM image, the surface of a K2560 membrane, on the other hand, is largely covered with conductive material and just a few small depressions. The difference in height between these non-conductive depressions and the surrounding surface is only 20 – 60 nm. The different height can be rationalized as both films have the same grafting level, i.e., both contain the same amount of PSSA but distributed differently. In K100 the PSSA is located around a smaller number of tracks and fewer starting points (radicals) yield the same grafted mass as in K2560. This means that in K100 the grafted chains are growing longer than in K2560 but in fewer channels and therefore larger fractions of the PSSA chains are pushed out of the ETFE film compared to the shorter and more distributed grafts in K2560.

Figure 8.6: Simultaneously recorded current mapping overlaid over a 3D-image of the surface topography of K100 (a) and K2560 (c) membranes at ~25% GL. Figures b) and d) show the overlaid height and current line profiles corresponding to the blue lines in figures a) and b). For a better stability during the measurement a water reservoir was used to provide constant humidification. The brighter areas correspond to detected current whereas the dark regions show no measured conductivity under this condition.
The observed distance between the highly conductive areas in K100 is up to 1-2 μm (Figure 8.6a and b) whereas on the surface of K2560 membranes only non-conductive spots of ~0.2 μm diameter can be found (Figure 8.6c and d). This leads to a conductive area fraction of ~90% for membranes irradiated with the high ion density. In the highly structured K100 membrane, on the other hand, only 70% of the surface contributes to the conductivity under the conditions of the measurement (Supporting Information, Section 8.6, Figure 8.26). This fraction was even less (~60%, Supporting Information, Section 8.6, Figure 8.27g) when the measurements were performed without a water reservoir. Measurements without a water reservoir but with a higher humidification of the air atmosphere in the AFM chamber (~80% r.h.) were performed to obtain higher resolution and measure the membrane in a less swollen condition. Under these conditions it was possible to obtain more detailed images of the mushroom structure in K100. Figure 8.7 shows the local current distribution on the surface of this membrane. At the edge of the elevations small conductive features expand into the ETFE dominated regions and bridge most of the separated mushrooms (cf. Supporting Information, Section 8.6, Figure 8.27e).

![Image of mushroom structure](image)

**Figure 8.7:** Contact current measurement of the surface of a K100 membrane (~25% GL) without added water reservoir. The brighter areas correspond to detected current whereas the dark regions show no measured conductivity under this condition.

Furthermore, the cross-section of K100 and K2560 membranes was investigated. For this the membranes were embedded in polyurethane resin and cut with a microtome yielding thicknesses between 150 and 200 μm. The current was measured in the plane of the membrane (along that thickness) and perpendicular to the channel structure that was
obtained by SHI irradiation. Especially in the case of the low ion density this led to difficulties as the conductive channels have to be connected in the direction perpendicular to their orientation over the whole distance of ~200 μm and the density of the channels at a grafting level of 25% might not be sufficient for this. Nonetheless, local current measurements were successful and show not only differences between the two investigated ion densities but also a conductive area distribution for K100 that can clearly be assigned to the channel structure obtained by SHI irradiation (Figure 8.8). The cross-section of K2560, on the other hand, suggests a channel density high enough to ensure numerous contact ‘points’ between the channels leading to more homogenous distribution of in-plane conducting areas, which can be seen in Figure 8.8b.

![Figure 8.8](image)

**Figure 8.8:** Contact current measurements of the cross-section of a K100 (a) and K2560 (b) membrane at ~25% GL without added water reservoir. The brighter areas correspond to detected current whereas the dark regions show no measured conductivity under this condition. The channel structure in K100 is highlighted in blue. The picture without this modification can be found in the Supporting Information, Section 8.6, Figure 8.28.

8.4.2. Membrane Conductivity

Governing aspects for the proton conductivity of PEMs are the structure of the hydrophilic phase and the number of sulfonic acid groups per mass of dry polymer (ion exchange capacity, IEC). The latter depends on the graft level and shows no dependence on ion fluence (Supporting Information, Section 8.6, Figure 8.29). The IEC for Std.e- membranes and membranes irradiated with different ion densities is therefore the same for identical graft levels. The water-uptake of ion irradiated
membranes was also found to be similar to that in Std.e- (Supporting Information, Section 8.6, Figure 8.29). The macroscopic structure of the hydrophilic phase, however, should be different. Though one of the determining factors – the extent of dissimilarity between incompatible blocks – is the same as all compared membranes consist of the same material (ETFE and PSSA), other properties are affected by the SHI irradiation. Around the former tracks the PSSA to ETFE ratio is higher than in Std.e-, and this ratio also changes within the series of investigated SHI membranes. K100 represents the membrane with the most localized PSSA domains, which should have the highest local graft level along its former tracks, whereas K2560 has a much more homogenously distributed graft component but should still offer a higher degree of macroscopic orientation of the hydrophilic phase than the e- irradiated system due to the structuring created by SHI irradiation. Electron beam grafted standard membranes cannot have such a predefined orientation and therefore the hydrophilic phase is formed in a statistical manner, which leads to a higher tortuosity compared to the SHI membranes (Figure 8.1). Furthermore, the different radical concentration between the systems is likely to result – at the same GL – in different graft lengths. The extent of these differences has not been investigated, but proton conductivity measurements show their impact (Figure 8.9).

![Figure 8.9: Through-plane conductivity at 80°C and different relative humidity values plotted in a logarithmic scale. The inset shows the conductivity increase for SHI membranes compared to the standard electron grafted membrane (Std.e-) and Nafion. All measured radiation grafted membranes have a GL ~25%.](image)

All membranes synthesized after SHI irradiation show a better proton conductivity than the standard electron irradiated membranes (Std.e-) that were functionalized to the same
extent. This improvement of around a factor of 2 (K100 compared to Std.e-) clearly highlights the advantageous impact of the macroscopic alignment of the hydrophilic phase in SHI membranes. Although a more strongly localized PSSA content improves the proton conductivity, it does not influence the general dependence on relative humidity of ETFE-g-PSSA membranes. This seems to be inherent to the system and differs from e.g. Nafion NR 212 (Figure 8.9, inset and Supporting Information, Section 8.6, Figure 8.30).

A possible explanation might be the different structure of PSSA based membranes and Nafion-type ones. In Nafion the side chains are largely hydrophobic and the terminal sulfonic acid moiety is hydrophilic, while in PSSA based membranes the complete side chain contains these hydrophilic motifs. This may have an impact on the structure of the hydrophilic phase as in PFSA membranes the sulfonic acid groups tend to be found at the interface of the hydrophobic and hydrophilic domains with the rest of the side chain located in the hydrophobic phase. In PSSA based membranes, however, the total length of the side chain is surrounded by water, resulting in a most likely less homogenous aqueous phase than in Nafion-type membranes. Another important aspect for the strongly reduced proton conductivity of PSSA based membranes at low relative humidity values is the effect of ionic cross-linking. Due to the close proximity of the sulfonic acid moieties in the PSSA chain, the formation of ionic aggregates at low relative humidity values can be invoked, leading to a reduced number of available ionic charge carriers and therefore a strong decrease in proton conductivity.

8.4.3. **Cell Performance**

The four SHI membranes and the standard electron irradiated membrane were assembled in single cells and characterized under different relative humidity conditions (100%, 70% and 50% r.h., (Nafion NR 212 is included as a reference, Supporting Information, Section 8.6, Figure 8.31). Preliminary tests show an improved performance for SHI membranes compared to Std.e-. Under the most stringent conditions of 50% r.h. SHI membranes show not only a lower high frequency resistance (HFR) compared to the standard electron irradiated membranes but also a significantly improved cell performance (Figure 8.10). Despite a persistently lower HFR for all SHI membranes at all relative humidity values, this lower resistance seems not always to be fully translated into cell performance (Supporting Information, Section 8.6, Figure 8.31). This could be caused by a surface mismatch between the ETFE-g-PSSA membrane and the commercial electrode which contains perfluorosulfonic acid ionomer designed for Nafion-type membranes. This mismatch seems to be more strongly pronounced for SHI membranes. It is likely that the higher heterogeneity of the surface
contributes to this and that K100 membranes represent a limit regarding this surface heterogeneity. **Figure 8.10 c** shows the cell performance at 2000 mA cm$^{-2}$ for membranes synthesized with different ion densities (an ion density of 0 represents the standard electron irradiated sample). Despite having one of the lowest HFR, K100 membranes show the least improvement in cell performance. Further investigations have to be undertaken on this effect to improve the interface, in order to transfer the superior characteristics of HFR / proton conductivity into the final fuel cell performance.

**Figure 8.10:** a) Polarization curves of SHI membranes and Std.e- with a graft level of 25% at a low relative humidity of 50% (80°C; 2.5 bar$_a$ backpressure on both sides, H$_2$/O$_2$: flow rates on both sides: 2000 mL min$^{-1}$). b) The corresponding high frequency resistance curves of both types of membrane. c) Cell voltage at a current density of 2000 mA cm$^{-2}$ and different relative humidity values in dependence of the ion density of the corresponding membranes (0 ion density / empty symbol represents the standard electron irradiated membrane). The line serves as guide to the eye.
An important aspect for fuel cell operation is the gas crossover. One of the main degradation mechanisms of PSSA grafted as well as PFSA membranes is triggered by the oxidative attack of hydroxyl radicals formed during the operation of a fuel cell.\textsuperscript{281-283} The extent of radical formation is strongly connected to the gas crossover,\textsuperscript{81} which occurs mostly through the hydrophilic phase. As this phase is expected to be more localized and directed in SHI membranes – which is the reason for the enhanced proton conductivity – it also has to be expected to measure a higher gas crossover. Electrochemical hydrogen permeation measurements were used to investigate this behavior as the crossover of hydrogen gas is proportional to the crossover of oxygen.\textsuperscript{285} However, the observed hydrogen crossover of SHI membranes lies in the range of the electron irradiated membranes (Std.e-, \( \sim 10 \, \text{N} \mu \text{L min}^{-1} \text{cm}^{-2} \), at 2.5 bar) only being insignificantly higher and still below the hydrogen crossover of Nafion (NR 212, \( \sim 17 \, \text{N} \mu \text{L min}^{-1} \text{cm}^{-2} \), at 2.5 bar). Only K100 membranes showed a drastically increased hydrogen crossover (Supporting Information, \textbf{Section 8.6, Figure 8.32}), which can be rationalized by the pronounced heterogeneity of the membrane. As the total graft level is confined to “a few” channels, the local graft level within these channels is much higher than in the membranes with more homogeneously distributed grafts synthesized with higher fluences. Therefore, the gas permeation is enhanced in these much more hydrophilic channels. This could be overcome, however, by the incorporation of crosslinking agents and acrylonitrile based monomers, which are known to improve gas barrier properties.\textsuperscript{285}

SHI membranes show improved properties compared to standard electron irradiated membranes. This could also been shown in \textit{in-situ} performance tests in a fuel cell, where even at reduced relative humidity (50% r.h.) SHI membranes show a lower high frequency resistance and a correspondingly higher cell voltage compared to the standard membrane (Std.e-). The ion density used for K100 samples seems to represent a lower limit regarding the interaction with the catalyst layer and the heterogeneity of the membrane surface.

So far, SHI membranes were subjected to protocols and preparation conditions (e.g. MEA lamination pressure and temperature) that were created for standard electron irradiated membranes (Std.e-). Further experiments have to be conducted to find more suitable conditions for SHI membranes and to optimize the SHI type membrane itself (fluence, storage conditions, target graft level, etc.). After these first promising results a further improvement of the performance of SHI membranes is realistic.
8. Swift Heavy Ion Induced Structuring

8.5. Conclusion

In this work structure-property correlation aspects in radiation grafted membranes using swift heavy ion (SHI) irradiation with Kr\(^{16+}\) were investigated, which leads to membranes with an oriented structure of the grafted regions. The direct approach yielded membranes with superior properties compared to the standard electron radiation grafted membrane. The proton conductivity for membranes with the same functionalization level (~25% GL) could be increased by a factor ~2 (K100 versus Std.e-) via this method. The unique structure of track-initiated grafting could be verified by EDX cross-sectional analysis as well as the improved through-plane homogeneity of graft distribution compared to standard electron irradiated membranes. Furthermore, the obtained “2 phase” topography of SHI membranes could be correlated with local proton conductivity measurements using EC-AFM. Preliminary fuel cell measurements confirm the increased proton conductivity of SHI membranes displaying lower high frequency resistances. The cell performance of the K100 membrane, which shows the highest degree of heterogeneity, is lower than expected from the ohmic resistance of the membrane, which is most likely related to electrode regions that are inactive since they are facing insulating membrane regions. The gas permeation of SHI membranes was found to be in the range of Std.e- and below the value of NR 212, except for K100 membranes, which showed an increased gas permeation due to the fewer but more highly functionalized channels. This could be overcome by the incorporation of crosslinking agents and acrylonitrile based monomers, which are known to increase gas barrier properties. The membrane design concept shown here demonstrates that a polymer structure comprising ion-containing regions with oriented architecture can yield membranes with improved conductivity and fuel cell performance.

8.6. Supporting Information

8.6.1. EC-AFM Measurements

8.6.1.1. Sample Preparation

For surface measurements the membranes were taped on the AFM steel sample disc with conductive carbon adhesive tape, which was previously impregnated with nano-scaled (< 50 nm) Pt-particles (Sigma Aldrich). Additional measurements with a water reservoir beneath the conductive adhesive tape were taken to improve humidification. Relative humidity was set to (45 ± 3)%. For measuring cross-sections, the membranes
were embedded with Teroson 6700 2-component Polyurethane glue (Henkel). After curing 24 h at room temperature, the samples were cut by microtome into slices of 150-200 µm and fixed on a sample disk similarly to the surface measurements. To ensure sufficient humidification, all cross-section samples were equilibrated at 80% relative humidity for at least 1 h prior to the measurement. Figure S14 shows a schematic sketch of the setup.

**AFM-Measurements:** AFM-measurements were performed by a Multimode 8 atomic force microscope (Bruker) with a closed loop scanner (nPoint) in PeakForce TUNA™ mode. The current evaluated in tapping mode was averaged with a lock-in amplifier. The contact current is averaged over the tip-sample contact time whereas the TUNA current is averaged over the whole tapping period. Platinum coated OMCL-AC240TM AFM-probes (Olympus) were used. All measurements were executed in a gas tight chamber at (45 ± 3 for surface measurements with water-reservoir; 75 ± 5 for measurements without a water-reservoir) % relative humidity. The applied bias was varied between 1.5 and 2.3 V. The exact values for each measurement are noted in the results part. Images were taken with a resolution of 1024x1024 pixels and a scan rate of 0.25 Hz.

The data of Figures 6, S15 and S16 was obtained for measurements with attached water-reservoir while the data for Figures 7, 8, S17 and S18 was obtained without attached water-reservoir.

As previously mentioned elsewhere:

8.6.2. **SEM / EDX Analysis**

To analyze the through-plane distribution of the grafted polystyrene chains on the micrometer scale, sulfonated copolymer films were swollen in water for 2 h, subsequently frozen in liquid nitrogen and fractured to obtain a sharp cross-section area without considerable smearing. Scanning electron microscopy (SEM) images were taken with an FE-SEM Ultra 55 (Carl Zeiss, Oberkochen, Germany) and energy dispersive X-ray (EDX) analysis was performed using a compatible accessory (EDAX TSL, AMETEK) and analyzed with EDAX TEAM™ software (version V4.3). The standard gun-to-sample distance was 8.5 mm with a magnification of 1600 and an acceleration voltage of 10 kV, an aperture of 60 µm was used. The images were taken in the secondary electrons mode. For sulfur distribution profiles perpendicular to the plane of the membrane, ImageJ software (National Institutes of Health) was used.
8.6.3. **Ex-Situ Characterization**

The ion exchange capacity (IEC), proton conductivity, water uptake and hydration number were determined in fully swollen state at ambient conditions. The IEC is defined as

\[ \text{IEC} = \frac{n(H^+)}{m_{\text{dry}}} \]  

(8.2)

where \( n(H^+) \) is the molar number of acid protons and \( m_{\text{dry}} \) is the dry weight of the membrane. After a proton/potassium exchange (stirring in 1 M KCl for 12 h at room temperature) the free protons were titrated with a 0.05 M KOH solution by means of a SM Titrino 702 instrument (Metrohm, Herisau, Switzerland). The theoretical IEC can be calculated using the following equation, assuming that all styrene units carry one sulfonic acid group:

\[ \text{IEC}_{\text{th}} = \frac{GL}{M_S + M_{\text{SSA}} \cdot GL} \]  

(8.3)

where \( M_S \) and \( M_{\text{SSA}} \) denote the molar masses of styrene (104 g/mol) and styrene sulfonic acid (184 g/mol), respectively. The water uptake (Q) of the membrane, representing the ability to absorb water, is determined by gravimetric means using the following equation:

\[ Q = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \]  

(8.4)

The through-plane conductivity at different relative humidity values (r.h.) was measured with a 740 Membrane Test System from Scribner Associates Inc. (North Carolina, USA) at a temperature of 80 °C, using gas diffusion electrodes from E-TEK DivisionSM (ELAT HT-140E-W).222

8.6.4. **In-Situ Characterization**

Fuel cell tests were performed with membranes of a grafting level of ~25%. Nafion® (NR-212) was measured as reference. To form a membrane electrode assembly (MEA), membranes were laminated with gas diffusion electrodes from Johnson Matthey Fuel Cells (type ELE 0263-0983, loading: 0.4 mg Pt/cm²) in a hot-press at defined temperature, load, and duration (110°C/2.5 MPa/180 s).130 Subsequently, the MEAs were assembled into a single cell with a graphite flow field and an active area of 15.8 cm². Further details regarding the cell design can be found elsewhere.287 The MEAs were operated in a single cell mode at 80°C and 2.5 bar, backpressure on both sides with hydrogen and oxygen fed at a flow rate of 600 mL min⁻¹. After 12 h conditioning at
constant current density (0.5 A cm\(^{-2}\)) and 100% relative humidity, the first polarization curve was measured. Cell voltage and high frequency resistance (HFR, at 1 kHz, AC milliohm meter model 3566, Tsuruga, Japan) were continuously monitored over the entire length of the test protocol. The cell was conditioned at 70% r.h. for 2 h (gas flow rate: 2000 mL min\(^{-1}\), 0.1 A cm\(^{-2}\)) before the next polarization curve was taken; the same applies to the measurements at 50% r.h..

Electrochemical hydrogen permeation measurements based on the single cell configuration were conducted to assess the mechanical integrity and gas permeability of the membranes. After the described protocol (cf. above) hydrogen crossover through the membrane was measured by an electrochemical method\(^{237,238}\) under fully humidified conditions at 80°C and 2.5 bar\(_a\) backpressure on both sides. Fully humidified gasses (H\(_2\) and N\(_2\), flowrate 600 mL min\(^{-1}\)) were fed to the anode and cathode, respectively. After 2 h the hydrogen permeation was evaluated as a diffusion-limited hydrogen oxidation current density in the range of 200 – 800 mV.

Scheme 8.1: Reaction scheme for the synthesis of ETFE-g-PSSA membranes. In the irradiation step electron or swift heavy ion (SHI, Kr\(^{16+}\)) irradiation was used. For the grafting procedure the reaction mixture consisted of 20% (v/v) styrene monomer, 70% (v/v) iso-propanol and 10% (v/v) ultra-pure water. The reaction temperature was 55°C. The functionalization was performed with 2% (v/v) chlorosulfonic acid in dichloromethane solvent at room temperature (5.5 h) followed by a 18 h hydrolysis step at 80°C in ultra-pure water.
Figure 8.11: Grafting kinetics for the grafting of ETFE with styrene after irradiation with different ion densities.

Figure 8.12: Scanning electron micrograph of the standard electron irradiated membrane (Std. e-, ~25% GL, a) and EDX sulfur mapping thereof (b)).
Figure 8.13: Distribution profiles obtained from EDX sulfur mappings for SHI membranes irradiated with different ion densities (a) K2560, b) K960, c) K320, d) K100) and different graft levels (as marked in the legend).

Figure 8.14: Schematic sketch illustrating the area that was used for the analysis of the sulfur (magenta) and fluorine (blue) distribution profiles along the direction of the plane of the membrane.
8. Swift Heavy Ion Induced Structuring

7.5% GL

![Image of overlaid sulfur (magenta) and fluorine (blue) EDX mappings of a K100 membrane (7.5% GL).](image1)

![Image of overlaid sulfur (magenta) and fluorine (blue) EDX mappings on a SE image of the membrane.](image2)

![Graph showing sulfur and fluorine distribution profiles measured along the direction of the plane of the membrane.](image3)

**Figure 8.15:** a) Overlaid sulfur (magenta) and fluorine (blue) EDX mappings of a K100 membrane (7.5% GL). b) Overlaid sulfur (magenta) and fluorine (blue) EDX mappings on a SE image of the membrane. c) Sulfur and fluorine distribution profiles measured along the direction of the plane of the membrane.

25% GL

![Image of overlaid sulfur (magenta) and fluorine (blue) EDX mappings of a K100 membrane (25% GL).](image4)
Figure 8.16: a) Overlaid sulfur (magenta) and fluorine (blue) EDX mappings of a K100 membrane (25% GL). b) Overlaid sulfur (magenta) and fluorine (blue) EDX mappings on a SE image of the membrane. c) Sulfur and fluorine distribution profiles measured along the direction of the plane of the membrane.

29% GL
Figure 8.17: a) Overlaid sulfur (magenta) and fluorine (blue) EDX mappings of a K100 membrane (29% GL). b) Overlaid sulfur (magenta) and fluorine (blue) EDX mappings on a SE image of the membrane. c) Sulfur and fluorine distribution profiles measured along the direction of the plane of the membrane.

34% GL

Figure 8.18: a) Overlaid sulfur (magenta) and fluorine (blue) EDX mappings of a K100 membrane (34% GL). b) Overlaid sulfur (magenta) and fluorine (blue) EDX mappings on a
SE image of the membrane. c) Sulfur and fluorine distribution profiles measured along the direction of the plane of the membrane.

**Figure 8.19:** Rough estimation of correlation of the diameter of the initial track with the grafting level.

**Figure 8.20:** a) Scanning electron micrograph of a K100 membrane (25% GL). b) Overlaid sulfur (magenta) and fluorine (blue) EDX mappings on the SE image of the membrane. c) Overlaid sulfur (magenta) and fluorine (blue) EDX mappings. d) EDX sulfur mapping.
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Figure 8.21: a) Scanning electron micrograph of a K320 membrane (25% GL). b) Overlaid sulfur (magenta) and fluorine (blue) EDX mappings on the SE image of the membrane. c) Overlaid sulfur (magenta) and fluorine (blue) EDX mappings. d) EDX sulfur mapping.

Figure 8.22: a) Scanning electron micrograph of a K960 membrane (25% GL). b) EDX sulfur mapping of the membrane.
Figure 8.23: a) Scanning electron micrograph of a K2560 membrane (25% GL). b) EDX sulfur mapping of the membrane.

Figure 8.24: Schematic sketch of the experimental setup used for EC-AFM measurements when no water reservoir was used. For the measurements with a water reservoir this was attached below the gas diffusion layer (GDL).
8. Swift Heavy Ion Induced Structuring

**Figure 8.25:** EC-AFM measurements (setup including water reservoir) of K100 and K2560 membranes (~25% GL). a) and b) display the topography of K100 and K2560, respectively, with elevated areas marked in brighter colors. c) and d) show the corresponding local current measurements (TUNA). The brighter areas correspond to detected current whereas the dark regions show no measured conductivity under this condition.

**Figure 8.26:** Conductive area fractions for K100 (a), 70%) and K2560 (b), 90%) membranes with a grafting level of ~25%. TUNA current was used for the evaluation and the measurement setup was equipped with a water reservoir. Grey areas correspond to conductive fractions.
Figure 8.27: EC-AFM measurements (setup without water reservoir) of K100 and K2560 membranes (~25% GL). a) and b) show simultaneously recorded current mapping overlaid over a 3D-image of the surface topography of K100 and K2560, respectively. c) and d) display the topography of K100 and K2560, respectively, with elevated areas marked in brighter colors. c) and d) show the corresponding local current measurements (contact current). The brighter areas (in a, b, e and f) correspond to detected current whereas the dark regions show no measured conductivity under this condition. Figure e) highlights furthermore the fine bridges between the locally separated conducting elevations (magenta ellipses). g) and h) resemble the conductive area fractions for K100 (g, 56±4%) and K2560 (h, 95±2%) membranes. Grey areas correspond to conductive fractions. Figure i) shows the overlaid height and current line profiles corresponding to the blue line in figure e), the green borders mark the onset and offset of the elevation.
Figure 8.28: Contact current measurements of membrane cross-sections for K100 (a, c) and K2560 (b, d) membranes at 25% GL. Figure c) and d) show the conductive area fractions for the respective membranes within an area of 10 μm x 10 μm (K100: 44 ± 6%; K2560: 81 ± 9%).

Figure 8.29: Experimentally determined ion exchange capacity and water-uptake for SHI membranes synthesized after irradiation with different fluences and the standard electron irradiated membrane (0 x 10⁶ ion cm⁻²). All membranes had a GL of ~23%.
Figure 8.30: Through-plane conductivity measurement at 80°C and different relative humidity values plotted in a logarithmic scale (a). The inset is plotted linearly. The conductivity increase of SHI irradiated membranes compared to the standard electron irradiated system (Std.e-) and Nafion is highlighted in b). Figure c) is plotted in a double logarithmic scale. All measured radiation grafted membranes have a GL of \( \sim 25\% \).
Figure 8.31: Polarization curves of SHI membranes (K100, K320, K960 and K2560) and Std.e- with a graft level of 25% and Nafion NR 212 at different relative humidity values (80 °C; 2.5 bar, backpressure on both sides, \( \text{H}_2/\text{O}_2 \) flow rates on both sides for 100% r.h.: 600 mL min\(^{-1}\) and for 70% and 50% r.h.: 2000 mL min\(^{-1}\)).
Figure 8.32: Electrochemically determined hydrogen permeation values for SHI membranes synthesized after irradiation with different fluences, the standard electron irradiated membrane ($0 \times 10^6$ ion cm$^{-2}$) and Nafion (NR 212).
Chapter 9. Conclusion and Outlook

This thesis extended the research on structure-property correlations which are important for the design of high performing proton exchange membranes (PEMs) to the field of radiation grafted membranes. Radiation grafted membranes have the prospect to replace perfluorinated membranes in polymer electrolyte fuel cells as they were shown to outlast Nafion® membranes with a comparable performance under fully humidified conditions and potentially significantly less production costs. However, with the particularity of modifying a preformed film instead of ending with a casting procedure this method represents a special case. It is reasonable to assume that grafting in a preformed matrix will be accompanied by restrictions that are not present when synthesizing a graft polymer in solution and subsequent solution casting. These restrictions will most probably affect the obtained morphology and thus the properties of the final membrane. Therefore, it is crucial to investigate the correlations between polymer architecture and membrane performance in this type of membrane.

The well-defined model system of (sulfonated) polystyrene grafted into ethylene-alt-tetrafluoroethylene as a base film (ETFE-g-PS(SA)) was chosen and systematically modified regarding polymer architecture.

9.1. Influence of Base Film Structure

In radiation grafted membranes a hydrophilic functionalized polymer is grafted into a hydrophobic base film that provides mechanical and chemical stability. The structure and morphology of the final PEM and therefore also membrane properties such as proton conductivity are strongly influenced by the structure of the base film. It was shown that when the new polymer grows into the base polymer matrix it is strongly affected by the inherent anisotropy of the base film even when the mass ratio of functionalized polymer to base polymer is larger than one. This clearly influences the
transport properties of charge carriers (protons) and molecules such as water, which was shown via proton conductivity and pulsed field gradient NMR measurements in machining (MD) and transverse (TD) direction. In the studied base film ETFE this resulted in a preferred direction of growth and transport (TD). As the structure of the polymer is expected to be similar in through-plane direction and TD due to the extrusion process used for film fabrication, this could be an advantage regarding the function of the membrane in the fuel cell. Even variations in the arrangement of the crystalline phase, as it can be found in base films from two different suppliers that are otherwise chemically identical and have the same overall crystallinity, were found to affect the properties of the final membrane. Although scattering results and fuel cell relevant properties follow largely similar trends in graft copolymers prepared from the two different ETFE base films from DuPont and Saint-Gobain, some significant differences are observed. DuPont based membranes exhibited a better proton conductivity, in particular at low relative humidity. Furthermore, the DuPont based membrane was significantly more stable against degradation in the fuel cell subjected to relative humidity cycling. These phenomena could be attributed to differences in the morphology of the base film, such as smaller crystallites in the case of ETFE from Saint-Gobain. Therefore, it is essential for the development of new proton exchange membranes prepared via pre-irradiation grafting not only to investigate the chemical composition of the grafted membrane but also include microstructural analysis starting from the base film. It could be shown that the microstructure of the base polymer matrix clearly impacts the properties of the final membrane and that attention has to be paid to the careful design of base polymer material as its morphological features provides an important and essential degree of freedom to optimize properties, performance and stability characteristics of the final ion-conducting membrane.

9.2. Incorporation of Hydrophilic or Hygroscopic Moieties

The water uptake of a membrane is known to be one of the key parameters for high proton conductivity as a certain amount of incorporated water is needed to form a well-connected network of hydrophilic proton conducting channels. The conductivity of radiation grafted and most non-perfluorinated membranes, however, is known to be very sensitive towards relative humidity. Therefore, it was investigated whether the incorporation of a comonomer that is known for its hygroscopic properties would increase the water uptake of the model radiation grafted membrane and its capability to retain water at reduced relative humidity. Different amounts of a comonomer were introduced to the model system and it could be shown that the water uptake of the membrane increased with increasing content of hydrolyzed glycidyl methacrylate.
(GMA). This, however, did not translate into improved proton conductivity. An increasing GMA content even impaired the conductivity at reduced relative humidities compared to the pure sulfonated styrene grafted membrane, highlighting that the density of sulfonic groups in the grafts has a higher influence on the proton conductivity than the water content within the membrane. An approach to overcome this obstacle might lie in the application of monomers that bear a sulfonic acid moiety and other hydrophilic/hygrosopic moieties at the same time without significantly increasing the distance between the sulfonic acid groups.

9.3. Grafting Design – Tailoring Graft Lengths and Densities

In this part, a synthetic approach was developed to transfer the tunable design parameters of graft length and number density from “lab-scale” model systems as discussed in the introduction to radiation grafted membranes. Two model compounds were prepared – one comprising long graft chains and a low number density, the other having shorter grafts with a higher number density of grafts. The influence of synthesis parameter as applied irradiation dose, reaction temperature and monomer concentration were investigated for their impact on graft distribution. Despite the high irradiation dose and the proneness of the styrene monomer to form pronounced grafting fronts, a similar through-plane graft distribution profile was observed for both types of membranes and the optimized systems were compared regarding water uptake and proton conductivity at different relative humidity values and the impact on the phase segregated structure of the model system. The morphology of the system with a high number density of short grafts could be shown to comprise smaller ionic domains that were better connected. This resulted in increased through-plane proton conductivity over the whole relative humidity range. Especially in the low r.h. range, e.g. 30% r.h., this structure resulted in proton conductivities over 35% higher than the chemically identical membrane with long graft chains and a small number density thereof. With regard to the stringent target conditions for fuel cell applications stated in Section 1.2.1., the morphology resulting from short graft length and a high number density of grafts is clearly superior.

9.4. Proton Conducting Channels in Through-Plane Direction

Swift heavy ion (SHI, Kr^{16+}) irradiation was used to introduce proton conducting domains aligned in the required direction of proton transport. The standard electron or γ-irradiation induced grafting results in the statistical formation of a random morphology with phase-separated hydrophilic/hydrophobic domain structure, in
which case the tortuosity of the aqueous phase places an inherent limitation on the conductivity of the material. It could be shown that the SHI approach successfully reduced this limiting factor and resulted in a superior proton conductivity and fuel cell performance. The direct approach of using the activation generated by the SHI irradiation directly for the grafting procedure yielded membranes with superior properties compared to the standard electron radiation grafted membrane (Std.e-). The proton conductivity for membranes with the same functionalization level (~25% GL) could be increased by a factor ~2 (K100 versus Std.e-) via this method. The unique structure of track-initiated grafting could be verified by EDX cross-sectional analysis as well as the improved through-plane homogeneity of graft distribution compared to standard electron irradiated membranes. Furthermore, the obtained “2 phase” topography of SHI membranes (highly functionalized proton conducting channels aligned in through-plane direction and lower functionalized ETFE dominated surrounding material) could be correlated with local proton conductivity measurements using EC-AFM. Preliminary fuel cell measurements confirm the increased proton conductivity of SHI membranes displaying lower high frequency resistances. The cell performance of the K100 membrane, which shows the highest degree of heterogeneity, is lower than expected from the ohmic resistance of the membrane, which is most likely related to electrode regions that are inactive since they are facing insulating membrane regions. The gas permeation of SHI membranes was found to be in the range of Std.e- and below the value of NR 212, except for K100 membranes, which showed increased gas permeation due to the fewer but more highly functionalized channels. This could be overcome by the incorporation of crosslinking agents and acrylonitrile based monomers, which are known to increase gas barrier properties. The membrane design concept shown here demonstrates that a polymer structure comprising ion-containing regions with oriented architecture can yield membranes with improved conductivity and fuel cell performance.

9.5. Outlook

Several design principles for radiation grafted membranes have been found applying the model system of ETFE-g-PS(SA). The parameters to incorporate these principles into high performing radiation grafted membranes are yet to be found. Regarding the tailoring of graft lengths a combination of increased dose and RAFT (reversible addition-fragmentation chain transfer) procedure might be suitable to reduce and control the graft chain length in PSI Gen2 membranes while at the same time increasing the graft density. The RAFT procedure is necessary as PSI Gen2 membranes are already synthesized with a high accumulated dose but bears the obstacle of introducing further impurities (e.g. the RAFT agent itself) to the membrane. These impurities might
negatively affect the stability of the membrane in a fuel cell and have therefore to be removed.

To introduce proton conducting domains aligned in the required direction of proton transport was shown to significantly increase membrane performance. Although this approach is easily transferrable to other monomer and comonomer systems as PSI Gen2 parameters as the ideal channel density (corresponding to the applied fluence [ions cm\(^{-2}\)]) have to be adjusted for the new monomer system. Furthermore, a closer look has to be taken at the interface properties between the (SHI irradiation) grafted membrane and the catalyst layer. Another intriguing approach in this context is to decouple the degree of SHI structuring (density of introduced channels) and the applied dose. This could be achieved by a recombination step of SHI induced radicals and a second irradiation with e.g. electrons. It would allow a higher degree of freedom in the design of the desired membrane/film and might be of interest when monomers are used that require a high radical concentration to reach high grafting levels while at the same time only a low degree of base film structuring is desired.

Preliminary experiments were conducted to find conditions under which a recombination of the radicals which were created upon SHI irradiation was facilitated. However, under all tested conditions not only the radicals were eliminated but also the structuring effect of the SHI irradiation and no difference to standard electron irradiated membranes could be seen. Therefore, it would be interesting to pursue work in this context and e.g. change to a larger ion in the SHI irradiation.

Another topic that renders a deeper investigation necessary is the optimal base film microstructure. It could be shown that the structure of the base film affects membrane properties and that a larger crystallite size at the same overall crystallinity increases the stability of the final membrane towards humidity changes in a fuel cell. These first tests were conducted using commercially available base films from DuPont and Saint Gobain. In the next step, it would be interesting to adjust different crystallinity levels and crystallite sizes. Poly(vinylidene fluoride) (PVDF) is an example for a partially fluorinated base polymer which is similar to ETFE, e.g. regarding its stability towards radiation and radical yield, but is soluble in certain organic solvents. It can be solution cast into base films with different microstructure and crystallinity depending on the casting parameters or additives. To design an optimized base film for radiation grafted membranes possibly including the incorporation of additives to enhance stability or acid density is the next step in this context.
Chapter 10. Bibliography


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## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>BAM3G</td>
<td>trade name for a TFS based membrane</td>
</tr>
<tr>
<td>BPSH</td>
<td>group of poly(arylene ether sulfone)s investigated by Hickner <em>et al.</em></td>
</tr>
<tr>
<td>CTFE</td>
<td>chlorotrifluoroethylene</td>
</tr>
<tr>
<td>DIPB</td>
<td>diisopropylene benzene</td>
</tr>
<tr>
<td>DOE</td>
<td>department of energy (U.S.)</td>
</tr>
<tr>
<td>DP</td>
<td>DuPont</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>DVB</td>
<td>divinylbenzene</td>
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<tr>
<td>ETFE</td>
<td>ethylene-\textit{alt}-tetrafluoroethylene</td>
</tr>
<tr>
<td>ETFE-g-PSSA</td>
<td>sulfonated polystyrene grafted onto ETFE</td>
</tr>
<tr>
<td>FEP</td>
<td>fluorinated ethylene propylene</td>
</tr>
<tr>
<td>GDE</td>
<td>gas diffusion electrode</td>
</tr>
<tr>
<td>GL</td>
<td>grafting level</td>
</tr>
<tr>
<td>GMA</td>
<td>glycidyl methacrylate</td>
</tr>
<tr>
<td>IEC</td>
<td>ion exchange capacity (equivalent of sulfonic acid groups per gram dry polymer)</td>
</tr>
<tr>
<td>IPA</td>
<td>2-propanol</td>
</tr>
<tr>
<td>LSC-PFSA</td>
<td>long side chain perfluoro sulfonic acid</td>
</tr>
<tr>
<td>MD</td>
<td>machining direction</td>
</tr>
<tr>
<td>MEA</td>
<td>membrane electrode assembly</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>$M_w$</td>
<td>molecular weight</td>
</tr>
<tr>
<td>OCV</td>
<td>open circuit voltage</td>
</tr>
<tr>
<td>PBI</td>
<td>polybenzimidazole</td>
</tr>
<tr>
<td>PEFC</td>
<td>polymer electrolyte fuel cell</td>
</tr>
<tr>
<td>PEM</td>
<td>proton exchange membrane</td>
</tr>
<tr>
<td>PEN</td>
<td>polyethylene naphtalate</td>
</tr>
<tr>
<td>PFA</td>
<td>perfluoroalkoxy alkane</td>
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<tr>
<td>PFG-NMR</td>
<td>pulsed field gradient nuclear magnetic resonance</td>
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<tr>
<td>PFSA</td>
<td>polyfluorinated sulfonic acid</td>
</tr>
<tr>
<td>PFSA</td>
<td>perfluoro sulfonic acid</td>
</tr>
<tr>
<td>PSSA</td>
<td>polystyrene sulfonic acid</td>
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<tr>
<td>PTFE</td>
<td>polytetrafluoroethylene, Teflon</td>
</tr>
<tr>
<td>PTFE-g-TFSSA</td>
<td>sulfonated poly $\alpha$, $\beta$, $\beta$-trifluorostyrene grafted onto PTFE</td>
</tr>
<tr>
<td>PTFSSA</td>
<td>poly-$\alpha$, $\beta$, $\beta$-trifluorostyrene sulfonic acid</td>
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<tr>
<td>PVA</td>
<td>poly(vinyl alcohol)</td>
</tr>
<tr>
<td>PVC</td>
<td>poly(vinyl chloride)</td>
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<tr>
<td>PVDF</td>
<td>poly(vinylidene fluoride)</td>
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<tr>
<td>PVF</td>
<td>poly(vinyl fluoride)</td>
</tr>
<tr>
<td>QENS</td>
<td>quasi elastic neutron scattering</td>
</tr>
<tr>
<td>$R_\Omega$</td>
<td>ohmic resistance</td>
</tr>
<tr>
<td>S</td>
<td>styrene</td>
</tr>
<tr>
<td>SANS</td>
<td>small angle neutron scattering</td>
</tr>
<tr>
<td>SAXS</td>
<td>small angle X-ray scattering</td>
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<tr>
<td>SG</td>
<td>Saint Gobain</td>
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11. List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>sPEEK</td>
<td>sulfonated poly(ether ether ketone)</td>
</tr>
<tr>
<td>sPI</td>
<td>sulfonated polyimides</td>
</tr>
<tr>
<td>sPPS</td>
<td>sulfonated poly(phenylene) sulfone</td>
</tr>
<tr>
<td>SSC-PFSA</td>
<td>short side chain perfluoro sulfonic acid</td>
</tr>
<tr>
<td>TD</td>
<td>transverse direction</td>
</tr>
<tr>
<td>TFS</td>
<td>$\alpha,\beta,\gamma$-trifluorostyrene</td>
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</tbody>
</table>
Publication List

Peer Reviewed Publications


LEC Annual Reports

Contributed Talks

Sroll, V.; Schmidt, T.J.; Gubler, L., **Radiation grafted membranes for fuel cells: Understanding and improving polymer architecture.** University of Applied Sciences Esslingen, Esslingen (Germany), 2016.

Posters

Sroll, V.; Nagy, G.; Gasser, U.; Schmidt, T. J.; Gubler, L.; Balog, S., **Grafting design: a way to the optimized proton exchange membrane?** Fluoropolymer 2016, ACS Division of Polymer Chemistry, New Orleans, USA, October 2-5, 2016.


Sroll, V.; Gasser, U.; Nagy, G.; Balog, S.; Schmidt, T. J.; Gubler, L., **Structure-Property Correlations of Ion-Containing Polymers for Fuel Cell Applications.** IRaP 2014, Jeju, South Korea, October 5-9 2014.
Curriculum Vitae

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