Reaction of Hydroxyl Radicals with Sulfonated Phenylated Polyphenylenes

by

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Faculty of Science

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Abstract

The perceived poor durability of non-fluorous, hydrocarbon solid polymer electrolyte membranes in the presence of reactive hydroxyl radicals remains a significant hurdle for their integration into electrochemical systems such as fuel cells. However, recent reports point to sulfonated phenylated polyphenylenes (sPPP) being considerably stable in accelerated fuel cell tests. In order to investigate the possible reaction of hydroxyl radicals with this promising class of hydrocarbon polymer electrolytes, a structurally-analogous oligophenylene model compound was synthesized and its degradation route was studied in the presence of hydroxyl radicals. Using NMR spectroscopy and mass spectroscopy, all significant degradation products are characterized and based on their chemical structures, along with changes in concentration over time, a degradation route is proposed. Hydroxyl-radical degradation was observed and found to be initiated by the oxidation of pendant phenyl rings to form fluorenone sub-structures which, upon further oxidation, lead to ring-opening of a main chain phenyl ring which, if occurring in sPPP, leads to chain-scission of the polymer backbone. In keeping with this hypothesis, molecular weights of sPPP were found to decrease when subject to hydroxyl radicals. Although degraded polymer NMR spectra remain unchanged, resonances consistent with the elimination of sulfobenzoic acid emerge. The results outlined in this work point towards a promising future for sPPP membranes and suggest a simple modification which should enhance their lifetime within fuel cell systems.

Keywords: Fuel Cells; Polymer Electrolyte Membrane; Degradation; Oxidation; Polyphenylenes; Solid Polymer Electrolyte
Dedication

To my wife, parents and family,

whose love and support have inspired and motivated me
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### List of Acronyms

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<th>Definition</th>
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<tbody>
<tr>
<td>AST</td>
<td>Accelerated stress test</td>
</tr>
<tr>
<td>ATR-IR</td>
<td>Attenuated total reflection infrared</td>
</tr>
<tr>
<td>BHT</td>
<td>Butylated hydroxytoluene</td>
</tr>
<tr>
<td>$D$</td>
<td>Polydispersity index ($M_n/M_w$)</td>
</tr>
<tr>
<td>DCE</td>
<td>Dichloroethane</td>
</tr>
<tr>
<td>DMPO</td>
<td>5,5-Dimethylpyrroline N-oxide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>ESR</td>
<td>Electron spin resonator</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
</tr>
<tr>
<td>IEC</td>
<td>Ion exchange capacity</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>LC/MS</td>
<td>Liquid chromatography-mass spectroscopy</td>
</tr>
<tr>
<td>$M_n$</td>
<td>Number average molecular weight</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Weight average molecular weight</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectroscopy</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>N211</td>
<td>Nafion 211</td>
</tr>
<tr>
<td>OCV</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>PEM</td>
<td>Proton exchange membrane</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Proton exchange membrane fuel cell</td>
</tr>
<tr>
<td>PFCA</td>
<td>Perfluorocarboxylic acid</td>
</tr>
<tr>
<td>PFSA</td>
<td>Perfluorosulfonic acid</td>
</tr>
<tr>
<td>PPP</td>
<td>Phenylated polyphenylene</td>
</tr>
<tr>
<td>PSSA</td>
<td>Polystyrene sulfonic acid</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>SPEEEK</td>
<td>Sulfonated polyether ether ketone</td>
</tr>
<tr>
<td>sPP</td>
<td>Sulfonated phenylated polyphenylene model compound</td>
</tr>
<tr>
<td>sPPP</td>
<td>Sulfonated phenylated polyphenylene</td>
</tr>
<tr>
<td>TEA</td>
<td>Triethyl amine</td>
</tr>
<tr>
<td>TFE</td>
<td>Tetrafluoroethylene</td>
</tr>
</tbody>
</table>
Chapter 1.

Introduction

1.1. Fuel Cells

Fuel cells are electrochemical devices which are used to convert chemical energy into electrical energy. In comparison to batteries which contain a limited amount of energy, fuel cells may continuously supply energy as long as fuel is available. Although the basic principle of a fuel cell was first demonstrated by Sir William Grove in 1839, their application as a power source was not demonstrated until 100 years later, when NASA used fuel cells for auxiliary power for the Apollo space missions. In simple terms, fuel cells contain an anode, cathode, and an electrolyte. The fuel (H₂) is oxidized at the anode, the oxidant (O₂) is reduced at the cathode, and the electrolyte transports ions between the anode and the cathode.

Fuel cells do not contain any moving parts and therefore do not require significant maintenance. Other benefits of fuel cells include quiet operation, low power to mass ratio, and quick refuelling times. Compared to combustion engines, which are limited in efficiency by the Carnot cycle, fuel cells are roughly two times as efficient. These advantages are leading to a wide range of fuel cell applications in both stationary and transportation energy applications.

1.2. Proton Exchange Membrane Fuel Cells

Of the various types of fuel cell systems available, proton exchange membrane fuel cells (PEMFC) are the most common. As their products are water and heat, PEMFCs are considered a clean energy conversion device. Their low operating temperature (typically 80°C) gives them quick start-up times. Furthermore, their low weight and small size give PEMFCs the highest weight (W kg⁻¹) and volumetric (W cm⁻¹) power densities among all fuel cell variants. For these reasons, fuel cells have been used in many kinds of transportation applications such as forklifts, buses, cars, and in aerospace applications. In 2013, Hyundai introduced the first commercially-produced PEMFC car, the Tucson.
Since then, many automotive manufacturers, such as Honda, Mercedes-Benz, and Toyota, have commercialized fuel cell vehicles.

The basic concept of a fuel cell involves the oxidation of hydrogen gas on a catalyst, forming water, and heat as by-product. By separating each half reaction and allowing the electrons to travel through an external circuit, power is generated. A general schematic of a fuel cell, along with both half reactions is outlined below (Figure 1.1).

Figure 1.1: Schematic of a proton exchange membrane fuel cell with relevant reactions.

On the anodic side of a fuel cell, hydrogen gas reacts on the catalyst, converting hydrogen gas (H₂) into two protons (H⁺) and two electrons (e⁻). The electrons travel through an external circuit from the anode to the cathode, while the protons travel across the proton exchange membrane (PEM). Once the electrons reach the cathode, they recombine with the protons and reduce oxygen to water.
1.3. Proton Exchange Membranes

A central component of PEMFCs is the PEM, a membrane that acts as an electronic insulator, facilitates the transport of protons from the anode to the cathode, and acts as a barrier to the reactant gases (H₂ and O₂). PEMs are typically composed of membranes containing sulfonic acid groups, due to their high acidity and ease of synthesis. Under normal operating conditions, PEMs are exposed to a wide range of harsh operating conditions that slowly degrade PEMs. Specifically, PEMs must be able to function under strongly oxidizing and reducing conditions, highly acidic conditions, high temperatures, high chemical potentials, high electric current, and large potential differences.

The first well-known use of PEMFCs came in the 1960's when NASA employed a membrane based on polystyrene sulfonic acid (PSSA), developed by General Electric, for the Gemini Space Program. The membrane, however, only lasted for ~500 hours of operation at 60°C. Subsequent analysis of the waste water revealed a large amount of low molecular weight PSSA oligomers, indicating the membrane had undergone a significant amount of degradation. This was the first sign of the need for highly durable membranes due to the harsh environment within an operating fuel cell, as previous studies using these membranes for electrodialysis at the same temperature showed only minimal signs of degradation. Due to their limited lifetimes, future space missions were forced to use alternative technologies until more durable PEMs could be developed.

The development of perfluorosulfonic acid (PFSA) ionomer membranes such as Nafion® in the 1960's significantly extended the lifetime of PEMFCs. Nafion® is comprised of a poly(tetrafluoroethylene) (PTFE) backbone, with pendant perfluoroether side chains which terminate with perfluorosulfonic acids (see Figure 1.2). The high durability of PFSA polyelectrolytes can be attributed to their PTFE backbone. When compared to their hydrocarbon analogues which have C-H bond strengths of 410 kJ mol⁻¹ (431 kJ mol⁻¹ for aromatics), the high bonding energy of C-F bonds (typically 540 kJ mol⁻¹) gives PFSA polyelectrolytes remarkable chemical and physical stability. Since Nafion® was first developed by DuPont, several commercial PFSA polyelectrolytes have been developed by companies such as Solvay, 3M or Gore.
Although PFSA ionomers such as Nafion® have remained as the dominant membranes for PEMFC applications, they are not without their drawbacks. Compared to their hydrocarbon analogues, PFSA membranes exhibit substantially higher rates of gas crossover which can lead to degradation (see following section), and result in reduced lifetimes.\textsuperscript{13–16} Furthermore, their inability to operate at high temperatures, requirement for constant humidification, high cost of manufacturing, combined with increased environmental concerns related to their disposal have led researchers to seek alternative PEMs for fuel cell applications. A significant amount of research has thus been directed to investigating hydrocarbon PEMs.

Many of the problems which are associated with the use of perfluorinated PEMs, such as their high gas permeability along with high cost, may be solved through the use of hydrocarbon-based PEMs. As hydrocarbon PEMs do not contain any fluorine atoms, their decomposition products do not release HF gas or perfluorocarboxylic acids (PFCA) which are classified as both toxic and persistent chemicals by Environment Canada.\textsuperscript{17,18} Additionally, hydrocarbon-based PEMs display much lower rates of gas crossover, and their synthesis is generally much easier and less expensive. Although hydrocarbon PEMs are promising alternative to PFSA polymers, their poor durability in fuel cell systems has hindered their integration into commercial fuel cell systems, and still remains a significant hurdle.

1.4. Degradation of Polymer Electrolyte Membranes

The design and development of highly durable PEMs able to withstand the harsh environment within PEMFC systems poses a fundamental challenge.\textsuperscript{13–16} Under normal operating conditions, PEMFCs typically display a slow steady decrease in their power output, followed by a sudden failure.\textsuperscript{8} The degradation of PEMs is categorized as either chemical or mechanical. Chemical degradation is often the result of radical species.
formed through side-reactions within fuel cells, whereas mechanical degradation is often attributed to tears or cracks within membranes induced by external stresses such as fluctuations in humidity or temperature. When membranes are subjected to a combination of mechanical and chemical stresses, each mode of degradation is exacerbated.

Within fuel cells, there exists a trade-off between performance and durability and as a result, a balance between the two must often be met. The drive to develop PEMFC systems with increased performances is often achieved through a) increasing the ion exchange capacity (IEC) (the number of acidic groups per gram of polymer) or b) by using thinner membranes.\textsuperscript{19} Increasing the IEC of membranes has previously been shown to reduce the chemical stability of PEMs.\textsuperscript{20} Therefore, the development of chemically robust membranes which possess high IEC values poses a significant challenge to researchers. Similarly, the use of thin PEMs results in a decrease in the mechanical properties of the membrane, and also increases its permeability to reactant gases, which can lead in chemical degradation, as will be discussed in the following sections.\textsuperscript{21}

### 1.4.1. Mechanical Degradation

Over the course of their lifetime, fuel cells are expected to operate under a wide variety of operating conditions, which can impose mechanical stresses on the membrane and may lead to cracks, pinholes, or tears within the membrane. Mechanical stresses can be imparted by changes in humidity, temperature, or start-up/shutdown cycles. The addition of hydrophilic sulfonic acid groups to PEMs leads to membrane swelling when exposed to high humidity environments (Figure 1.3). The effect of swelling becomes more prominent as IEC values are increased. Since membranes are confined within the membrane electrode assembly, continuous cycles of swelling/de-swelling can impose a large amount of stress on the membrane.
1.4.2. Chemical Degradation

Since the first application of PEMFC systems in the Gemini space mission, the chemical stability of PEMs has remained a significant issue for fuel cell systems. Chemical degradation of PEMs is caused by radicals which are generated in situ and attack the membrane. While hydrogen peroxide (H$_2$O$_2$) has been known to play a significant part in the chemical degradation of PEMs since the 1960s,$^{10,23}$ it was not until recently that the presence of free radicals was detected in situ through the use of 5,5-dimethylpyrroline N-oxide (DMPO) as a spin trapping agent, and by placing a miniature fuel cell inside an electron spin resonator (ESR).$^{24,25}$ Hydroxyl radicals (HO•), hydroperoxyl radicals (HOO•), as well as hydrogen radicals (H•) have all been detected in situ, however, HO• and HOO• are generally regarded as the most prominent species involved in the degradation process. In terms of reactivity, HO• is regarded as the most reactive radical species as reflected by its oxidative strength ($E^\circ = 2.72$ V)$^{26}$, followed by H• ($E^\circ = 2.32$ V)$^{27}$, and HOO• ($E^\circ = 1.46$ V)$^{28}$. 

While there is no agreement regarding what mechanisms lead to the formation of radical species, the decomposition of H$_2$O$_2$ within fuel cells is assumed to play a large role in the formation of radicals. Experiments measuring the concentration of H$_2$O$_2$ in an operating fuel cell have shown that membrane thickness strongly influences the rate of H$_2$O$_2$ formation,$^{21}$ suggesting that gas crossover (H$_2$ and O$_2$) leads to the formation of
H₂O₂, and consequently to the formation of radical species. Whether radical species are generated chemically or electrochemically has been the subject of a long debate. H₂O₂ may be formed electrochemically through the two electron oxygen reduction reaction (equation 1), or chemically via reaction of H₂ and O₂ on a platinum catalyst (equation 2).¹⁰,²⁸

\[
2H^+ + O_2 + 2e^- \rightarrow H_2O_2 \quad (E^o = 0.68 \text{ V})^{30} \quad (1)
\]

\[
H_2 + O_2 \xrightarrow{Pt} H_2O_2 \quad (2)^{10,31}
\]

Under open circuit voltage (OCV) conditions which are typically used for accelerated degradation experiments, H₂O₂ formation at the cathode is not expected to occur due to the absence of Faradic current as well as the high cathode potential of >0.9 V.³² Previous in situ ESR experiments have detected HO• radicals under load conditions, however under OCV conditions no HO• radicals were detected which gives support for equation 1. In 2010, Ghassemzadeh et al. exposed a catalyst coated membrane to both hydrogen and oxygen gas and found that degradation was most prominent in H₂-rich conditions, which mimics the anodic side of the fuel cell and gives evidence for the chemical mechanism outlined in reaction 2.²⁸,³³

Once formed, H₂O₂ may react with trace metals within the membrane such as Fe²⁺ which result in the formation of HO• (reaction 3). Alternatively, H₂O₂ may also undergo thermal decomposition (reaction 5), however this reaction occurs at a much lower rate (k = 1.2 x 10⁻⁷ s⁻¹). In situ detection of H₂O₂ was first reported by Liu and Zuckerbrod who reported concentrations of 23 ppm (1100 μM) using a 25 μm membrane, and 2 ppm (100 μM) using a 140 μm membrane.²¹

\[
H_2O_2 + Fe^{2+} + H^+ \rightarrow HO^• + Fe^{3+} + H_2O \quad (k = 60 \text{ M}^{-1}\text{s}^{-1})^{34} \quad (3)
\]

\[
Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^• + H^+ \quad (k = 4 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1})^{35} \quad (4)
\]

\[
H_2O_2 \xrightarrow{\Delta} 2HO^• \quad (k = 1.2 \times 10^{-7} \text{ s}^{-1})^{28,36} \quad (5)
\]
\[ HO^* + H_2 \rightarrow H^* + H_2O \quad (k = 4.3 \times 10^7)^{37} \]  \hspace{1cm} (6)

\[ H^* + O_2 \rightarrow HOO^* \quad (k = 1.2 \times 10^{10} \text{ M}^{-1} \text{s}^{-1})^{37} \]  \hspace{1cm} (7)

\[ HO^* + H_2O_2 \rightarrow HOO^* + H_2O \quad (k = 2.7 \times 10^7 \text{ M}^{-1} \text{s}^{-1})^{37} \]  \hspace{1cm} (8)

\[ HOO^* + H_2O_2 \rightarrow HO^* + O_2 + H_2O \quad (k = 0.6 \text{ M}^{-1} \text{s}^{1})^{37} \]  \hspace{1cm} (9)

Other radical species which have been detected \textit{in situ} include HOO• and H•.\textsuperscript{25} The formation of H• is assumed to be due to the reaction of HO• with H\textsubscript{2} gas (reaction 6), and H• has been detected at both the anode and cathode in an operating fuel cell. Similarly, HOO• may be formed via the reaction of H• with O\textsubscript{2} (reaction 7), or through reaction of HO• with H\textsubscript{2}O\textsubscript{2} (reaction 8).\textsuperscript{28}

\textbf{1.4.3. Ex-Situ Chemical Degradation Mechanisms}

The degradation of PEMs \textit{in situ} typically occurs over the course of thousands of hours. Therefore, long-term durability tests are generally impractical and expensive. To circumvent this, accelerated stress tests (AST) have been used in order to accelerate the understanding of key durability issues. \textit{Ex situ} degradation methods such as Fenton’s reagent tests have previously been used to provide valuable information on the degradation pathways and chemical sensitivities of PEMs such as Nafion and PSSA.\textsuperscript{33,38–40} Outlined below is a description of some common \textit{ex situ} accelerated chemical degradation techniques which have previously been used.

\textbf{Fenton’s Reagent}

The chemical reactions which occur within a Fenton’s reagent are outlined above in equations 3, 4, 8, and 9. The decomposition of H\textsubscript{2}O\textsubscript{2} by transition metals (typically Fe\textsuperscript{2+}, ppm range) is known as the Fenton’s reaction and produces hydroxyl radicals (reaction 3). The catalytic cycle is completed through reaction 4, which typically occurs very slowly and is often the rate-determining step for the generation of radicals. Reactions 8 and 9 describe the Haber-Weiss cycle which slowly consumes H\textsubscript{2}O\textsubscript{2}, and is dependent on the concentration of H\textsubscript{2}O\textsubscript{2}.\textsuperscript{41}
Fenton’s reagent tests have been widely used as quick and inexpensive chemical stability tests for PEMs. Compared with other degradation methods, the radicals that are generated therein are in relatively high concentration.\textsuperscript{28,34} Furthermore, the influence of membranes and degradation products on the reactivity of iron is not well understood. Previous work by Chen et al. has shown that quinone intermediates which are involved in the chemical degradation mechanism of benzene can accelerate Fenton’s reagent tests by converting Fe$^{3+}$ back to Fe$^{2+}$.\textsuperscript{42} In 2009, Mikhailenko and co-workers introduced (+)-catechin, a biologically active flavonoid antioxidant, into a sulfonated polyether ether ketone (SPEEK) membrane in order to improve its oxidative stability. However, the antioxidant appeared to decrease the stability of the membrane when subjected to Fenton’s reagent tests. The author therefore concluded that (+)-catechin appears to exhibit a radical-generating quality, however, instead, it may be that (+)-catechin, which contains a hydroquinone group, may act as an accelerator for the Fenton’s reagent reactions by facilitating the conversion of Fe$^{3+}$ to Fe$^{2+}$.\textsuperscript{43}

**Ultraviolet Photolysis**

Ultraviolet (UV) photolysis results in the homolytic decomposition of H$_2$O$_2$ to produce two hydroxyl radicals. An advantage of this method is that it is able to operate over a wide range of pH values and the radicals generated are not bound to metal catalysts. While this method has not been used as extensively as the Fenton’s test, it has previously been used to outline the chemical degradation mechanism of sulfonated aromatic model compounds. This method, however, has also been shown to degrade model compounds in the absence of H$_2$O$_2$ and therefore may induce secondary degradation pathways.\textsuperscript{44}

**Thermal**

When compared with other the other \textit{ex situ} degradation methods outlined above, thermal decomposition generally occurs much slower ($k = 1.2 \times 10^{-7}$).\textsuperscript{28,36} This method has been previously employed to elucidate the oxidative degradation route of a sulfonated poly(arylene ether ketone) model compound, along with a corresponding polymer which will be further discussed below.\textsuperscript{45,46}
1.4.4. Mechanisms of Chemical Degradation

Since their introduction in the 1960’s, perfluorosulfonic acid (PFSA) ionomers such as Nafion® have remained the benchmark PEMs for fuel cell applications. For this reason, the chemical degradation mechanisms of Nafion® have been well studied.\textsuperscript{12,13,28,33,39,47–50} One of the first degradation mechanisms of Nafion® reported by Curtin and co-workers was termed the un-zipping mechanism and is outlined in Scheme 1.\textsuperscript{50} According to this mechanism, residual carboxylic acid groups left over from the formation process react with HO•, forming a carboxyl radical, which liberates CO\textsubscript{2} and forms a fluorocarbon radical that leads to the formation of a fluoroalcohol. Upon elimination of HF, the fluoroalcohol is converted to an acyl fluoride, which readily hydrolyzes into a carboxylic acid. Reformation of the carboxylic acid allows the reaction to further propagate upon reaction with another hydroxyl radical.\textsuperscript{50}

\[
\begin{align*}
R_f\text{-}CF_2\text{COOH} + \cdot \text{OH} & \rightarrow R_f\text{-}CF_2\cdot + \text{CO}_2 + \text{H}_2\text{O} \\
R_f\text{-}CF_2\cdot + \cdot \text{OH} & \rightarrow R_f\text{-}CF_2\text{OH} \rightarrow R_f\text{-}\text{COF} + \text{HF} \\
R_f\text{-}\text{COF} + \text{H}_2\text{O} & \rightarrow R_f\text{-}\text{COOH} + \text{HF}
\end{align*}
\]

Scheme 1.1: Main chain unzipping mechanism of PFSA polymers proposed by Curtin et al.
(Adapted with permissions from reference 50. Copyright 2004 Elsevier B.V.)

According to the mechanism proposed by Curtin et al. (Scheme 1.1), reactive carboxylic acid end groups also act as radical scavengers, as each cycle consumes two equivalents of HO•. Although this mechanism has been widely accepted,\textsuperscript{8,28,33,50} given the low concentration of HO• \textit{in situ} (~10\textsuperscript{-16} M) when compared with other reactive species such as H\textsubscript{2}O\textsubscript{2} (~0.5 mM) or O\textsubscript{2} (~7.5 mM),\textsuperscript{28} it is highly unlikely for HO• and R\textsubscript{f}-CF\textsubscript{2}\cdot to react together. Therefore, a modified chain unzipping mechanism is proposed (Scheme 1.2). According to this mechanism, reactive R\textsubscript{f}-CF\textsubscript{2}\cdot groups are presumed to react with dissolved O\textsubscript{2}, yielding a perfluoroperoxy radical, which upon reaction with H\textsubscript{2}O\textsubscript{2}, reproduces HO• and forms a perfluoroalcohol, which may decompose to reproduce a perfluorocarboxylic acid. Unlike the chain unzipping mechanism (Scheme 1.1) proposed by Curtin et al. which suggests carboxylic acid groups scavenge radicals, the modified chain unzipping mechanism (Scheme 1.2) proposed here suggests HO• instead catalytically decomposes reactive carboxylic acid functional groups.
In order to improve their stability, Nafion® membranes were chemically stabilized using a radical fluorination process to convert carboxylic acid and other reactive end groups into stable -CF₃ end groups.¹²,³⁸,⁴⁸,⁵¹ Membranes which were subjected to post-fluorination were reported to degrade at least 1 order of magnitude slower, yet chemical degradation of membranes was still observed.⁴⁸ It therefore became clear that other degradation mechanisms existed.

Using a combination of theoretical calculations, along with experimental work on both Nafion® membranes and model compounds, Zhou and co-workers found that side-chain cleavage may be a significant degradation pathway.⁴⁸ Further studies by Ghassemzadeh et al. using electron beam irradiation to selectively generate HO• and H• radicals confirmed that HO• radicals can attack O-CF₂ bonds, and H• may attack tertiary carbon atoms, as outlined in Scheme 1.3.³³,³⁹,⁵²

**Scheme 1.2: Proposed modified chain unzipping mechanism of PFSA polymers.**
(Adapted with permissions from reference 50. Copyright 2004 Elsevier B.V.)
High synthetic cost, combined with environmental concerns related to their disposal, have led researchers to explore hydrocarbon membranes as alternatives to PFSA membranes for fuel cell applications. Hydrocarbon membranes have remained attractive due to their expected lower cost of synthesis, as well as lower gas permeability which consequently lowers the rates of free radical formation that are derived there from. Since PSSA membranes were first used in the Gemini space missions, the chemical durability of hydrocarbon membranes has remained a significant hurdle for their integration into fuel cell systems.

Upon further analysis, PSSA polymers were shown to be highly susceptible to chain-scission, due to the presence of a weak benzylic hydrogen atom which is easily abstracted. This observation was made first made by Hodgdon in 1966. Although it has been estimated that only ~20% of hydroxyl radicals lead to chain scission, with the majority of radicals resulting in the formation of phenolic species, this small amount is still substantial enough to hinder the applications of PSSA membranes within fuel cells.
The oxidation of polymers containing sp\(^3\) hybridized carbon atoms is expected to follow the same general mechanism in which lipids are oxidized and become rancid. This mechanism is initiated through the introduction of a peroxide group and becomes accelerated (Scheme 1.4) through reaction with \( \text{O}_2 \) and the decomposition of peroxide groups. Initiation occurs through H-abstraction by a radical (\( \text{HO}^\bullet \)), forming a radical on the polymer chain (\( \text{R}^\bullet \)). Propagation occurs through the reaction with \( \text{O}_2 \), forming a dioxyl radical (\( \text{ROO}^\bullet \)), followed by H-abstraction, and finally reproducing a peroxide group (\( \text{ROOH} \)). An important point is that this mechanism leads to an increase in the number of propagating reactive radicals which can continuously degrade the polymer.\(^{53,54}\)
Today, most hydrocarbon PEMs are based on high performance aromatic polymers due to their high thermal stability (when compared with polymers such as polyethylene), as well as high chemical stability due to the absence of sp\(^3\) hybridized carbon atoms. Due to their ease of synthesis and low cost, a significant amount of research has thus been devoted to investigating polyarylene polymer backbones containing various heteroatom groups such as poly(arylene ether ketone), poly(arylene sulfone), poly(amide), or poly(phenylene) membranes. A general chemical structure for these membranes is outlined in Figure 1.5.

**Figure 1.5:** General structure of high performance polymers.

Previous studies have shown that the oxidation of aromatic compounds by hydroxyl radicals originates by either abstraction of H\(^•\) (see Scheme 1.5) to form a phenyl radical (A) and water, or through an addition reaction to form a hydroxy cyclohexadienyl radical (B). The latter of the two mechanisms has been shown to be the dominant pathway. Once formed, intermediate B has a high probability of reacting with O\(_2\), to form phenol (C).
and HOO•; alternatively, it may undergo an intramolecular reaction forming a bicyclic compound (E) which leads to ring-opening bond scission.44,71–76

Scheme 1.5: Oxidative degradation mechanism of benzene.73,74,76

Recently, the impact of heteroatom functional groups, such as those outlined in Figure 1.5, have been the subject of debate amongst researchers.70 In 2009, Perrot et al. used a sulfonated polyarylene ether ketone model compound to study the aerobic oxidative degradation mechanism of sPAEK polymers (Scheme 1.6). In their study, they proposed that the degradation mechanism is initiated through HO• addition to non-sulfonated phenyl rings with ether bonds, which upon further oxidation lead to chain-scission of the polymer backbone. Therefore, they concluded that a potential way to improve the stability of PEMs could be through the removal of ether bonds.45
Recently, polyphenylene membranes have attracted renewed attention because of their high oxidative stability, mechanical properties and proton conductivity; however, their synthesis is perceived as difficult due to the challenges associated with preparing high molecular weight polymers using traditional transition metal-catalyzed polycondensation reactions, and their low solubility in polar solvents. Phenylated polyphenylenes (PPP) such as those prepared by Stille, Kallitsis, and Müllen have attracted attention due to their simpler synthesis, aided by the polymer’s solubility in common organic solvents. These polymers may be sulfonated to form sulfonated phenylated polyphenylene (sPPP), as demonstrated by the Sandia National Laboratory research group. Recently, the Holdcroft group reported the syntheses of sPPP-
based polymers through a strategy utilizing pre-functionalized monomers, yielding structurally well-defined sPPP architectures which possessed high degrees of functionalization, as well as high molecular weights (Scheme 1.7).\textsuperscript{65,66,85}

\textit{In situ}, accelerated stress tests performed on sPPP membranes operated in fuel cells under open circuit potential, at 30\% RH and 90°C have demonstrated that these membranes possess excellent \textit{in situ} durability relative to Nafion\textsuperscript{®} N211 references.\textsuperscript{65} This is in part due to the low rates of gas crossover through sPPP membranes, which consequently lowers the rates of free radical formation that are derived therefrom. Similar studies on polyphenylene PEMs using \textit{in situ} accelerated degradation tests have reported similar results.\textsuperscript{70} While the chemical degradation mechanisms of PFSA-based membranes have been thoroughly studied,\textsuperscript{13,33,39,47–49} only few similar studies on polyaromatic hydrocarbon membranes have been performed.\textsuperscript{14,44–46,86–88}

The perceived poor chemical durability of hydrocarbon polymer electrolyte membranes has remained a significant hurdle for their integration into fuel cell systems. For this reason, chemically-robust hydrocarbon polymer electrolyte membranes are highly sought after as alternatives to perfluorosulfonic acid membranes due to their high cost of manufacturing, combined with increased environmental concerns related to their disposal.

\section*{1.5. Research Objective}

The purpose of this work was to determine the hydroxyl radical induced chemical degradation mechanism of sPPP membranes. Due to the complexity of characterizing sPPP polymers at the molecular level, an oligophenylene model compound sPP (see Scheme 1.8 below) was designed to mimic the structural motifs of the polymer. While sPPP membranes have demonstrated their high stability within fuel cell systems through \textit{in situ} accelerated degradation tests,\textsuperscript{65} the hydroxyl radical induced degradation mechanism of these membranes has yet to be studied. A proper understanding of the hydroxyl radical induced degradation mechanism of sPPP oligomers and polymers may aid future researchers in the design and development of highly durable hydrocarbon polymer electrolyte membranes. The model compound sPP and polymer sPPP were both synthesized by the author starting from 1,4-diodobenzene according to previously reported literature procedures, and their synthesis is outlined in Scheme 1.7 and 1.8.\textsuperscript{65,66}
Scheme 1.7: Synthetic pathway for the synthesis of (a) dieneophile monomer (b) diene monomer and (c) (sPPP) polymer.\textsuperscript{56} Reagents and Conditions: (i) Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, Cul, HNEt\textsubscript{2}, 56°C, 6 h; (ii) K\textsubscript{2}CO\textsubscript{3}, Et\textsubscript{2}O/MeOH (3/1), room temperature (RT), 6 h; (iii) I\textsubscript{2}, DMSO, 150°C, 8 h; (iv) KOH, EtOH, 80°C, 3 h; (v) TMS-O-SO\textsubscript{2}-Cl, dichloroethane (DCE), RT, 8 h; (vi) NEt\textsubscript{3}, n-BuOH, 4 h, RT; (vii) nitrobenzene, 195°C, 18 h; (viii) NaOH, MeOH, 4 h, RT; (ix) H\textsubscript{2}SO\textsubscript{4}, H\textsubscript{2}O, 4 h, RT.
Scheme 1.8: Synthetic pathway for the synthesis of model compound (sPP).\textsuperscript{66}

Reagents and Conditions: (i) KOH, EtOH, 80°C, 3 h; (ii) TMS-\(\text{SO}_2\)-Cl, DCE, RT, 8 h; (iii) NEt\(_3\), n-BuOH, 4 h, RT; (iv) nitrobenzene, 195°C, 18 h; (v) NaOH, MeOH, 4 h, RT; (vi) H\(_2\)SO\(_4\), H\(_2\)O, 4 h, RT.
Chapter 2.

Reaction of Hydroxyl Radicals with Sulfonated Phenylated Polyphenylenes

The work described in this chapter has been published in cooperation with Thomas J. G. Skalski, Michael Adamski, and Dr. Steven Holdcroft in Chem. Mater. 2019, 31, 4, 1441-1449.

Thomas Skalski and Michael Adamski aided and helped oversee the synthesis of the polymers used in this study. Dr. Holdcroft supervised the work reported in this chapter. Dr. Eric Yee helped perform selective 1D NOESY 1H NMR spectroscopy. The remaining experimental work reported in this chapter was performed by the author.

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2.1. Introduction

The development of chemically robust polymer electrolyte membranes (PEMs) has typically focused on the commercialization of perfluorosulfonic acid (PFSA) membranes due to their high chemical and thermal stabilities, as outlined in Chapter 1. As a result, numerous extensive performance and degradation studies have been reported for PFSA-based membranes, similarly comprehensive studies on polyaromatic hydrocarbon membranes, in general, are relatively sparse, and reports on their degradation even more so.

Previous studies on sulfonated phenylated polyphenylenes (sPPP) have showed that these membranes which possess a high ion exchange capacities (IEC) exhibited no signs of degradation by mass loss or 1H NMR spectroscopy after exposure to Fenton’s reagent for 1 hour (3ppm FeSO₄, 3% H₂O₂, 80°C), however after 4-6 hours all samples displayed a substantial amount of degradation. In contrast, a phenylated, sulfonated polyarylene ether exhibited a mass loss of 20% after 1 hour under similar conditions. In order to gain further insight into the stability of sPPP to oxidative free radicals, the polymer was exposed to hydroxyl radicals for prolonged periods to observe
changes in the chemical structure. Due to the complexity of characterizing sPPP polymers at the molecular level, an oligophenylene model compound sPP (Figure 2.1) was designed to mimic the structural motifs of the polymer.

![Figure 2.1: Chemical structure of sulfonated phenylated polyphenylene (sPPP) and the corresponding model compound (sPP).]

2.2. Experimental

2.2.1. Equipment

$^{13}$C NMR spectra were recorded on a Bruker AVANCE II 600 MHz NMR spectrometer equipped with a 5 mm QNP cryoprobe. $^1$H, 2D (COSY), and 1D NOESY were recorded on Bruker AVANCE II 600 MHz NMR spectrometer equipped with a 5 mm TCI cryoprobe. Mass spectra were recorded either on a Bruker Maxis Ultra-High Resolution tandem TOF (UHR-Qq-TOF) mass spectrometer or with an Agilent 6210 TOF LC/MS. Size exclusion chromatography analyses were obtained using a Malvern Instruments (Houston, Texas, USA) system with Viscotek D6000M column equipped with a refractive index, UV, and light scattering detectors. The mobile phase consisted of HPLC grade DMF (0.01M LiBr) as eluent at 298K with a flow rate of 1 ml/min, calibrated using a poly(methyl methacrylate) standard ($M_w = 51092$ Da, $M_n = 49231$ Da).

HPLC analysis was obtained using an Agilent 1100 HPLC equipped with a PDA detector at 210 and 254 nm, equipped with an autosampler and fraction collector. A reverse phase Kinetex 5u C18 150x10 mm column was used. The mobile phase was composed of 5mM ammonium acetate in 90% H$_2$O and 10% acetonitrile (solvent A), and 5mM ammonium acetate in 95% acetonitrile and 5% H$_2$O. The mobile flow rate was set
to 2 ml/min; linear solvent gradient 0-1 minute 5% (solvent B), 1-40 min 5-30% (solvent B), 40-45 min 30% (solvent B).

### 2.2.2. Reagents

The following reagents were purchased and used as received: Triethylamine (99%, Combi-Blocks), 1,4-diiodobenzene (98%, Combi-Blocks Inc.), n-butanol (Fisher Scientific), hydrogen peroxide (30%, Fisher Scientific), potassium hydroxide (Caledon Laboratories), nitrobenzene (Sigma Aldrich), dimethylformamide (HPLC grade, Sigma Aldrich), acetonitrile (HPLC grade, Fisher Scientific) diphenylphosphineferrocene palladium dichloride (Strem Chemicals), trimethylsilylethynyl (Tokyo Chemical Industry Co.), trimethylsilyl chlorosulfonate (99%, Sigma Aldrich), 1,3-(diphenyl)propan-2-one (98%, Tokyo Chemical Industry Co.), bisbenzyl (98%, Tokyo Chemical Industry Co.), copper iodide (99.9%, Santa Cruz Biotechnology), dichloroethane (Caledon Laboratories Ltd.), phenylacetylene (98%, Combi-Blocks Inc.), and ammonium acetate (ACP Chemicals). Tetrasulfonated bistetracyclone triethylammonium, and disulfonated tetracyclone were prepared through a multi-step synthesis according to previously reported literature procedures. All experiments were performed using deionized water which was further purified using Millipore Milli-Q water purification system (≥18MΩ·cm).

The following section outlines the detailed experimental procedure for the last step in the preparation of polymer sPPP and model compound sPP.
2.2.3. Synthesis

Preparation of sulfonated phenylated polyphenene (sPPP)

![Diagram of sPPP](image)

Compound sPPP was prepared according to a previously reported literature procedure as outlined in Scheme 1.66 A 60 mL Schlenk tube equipped with a stir bar was charged with 1.77 mmol (2.50g) of a tetrasulfonated bistetracyclone triethylammonium salt, 24 mL of nitrobenzene, and 1.79 mmol (0.23g) of 1,4-diethynyl benzene. The mixture was stirred for 15 minutes at room temperature, then heated to 185°C. After 48 hours, the reaction mixture was allowed to cool to room temperature and precipitated into ethyl acetate (500 mL) and refluxed for 4 hours, then filtered and washed twice with boiling ethyl acetate, and once with boiling acetone. The polymer was dried overnight in a vacuum oven at 80°C. Next, the polymer was added to a 250 mL round bottom flask containing 70 mL of methanol and stirred for 4 hours, then 25 mL of 2M KOH in methanol was added dropwise and the polymer sPPP-K⁺ precipitated and was stirred for 2 hours then was collected via suction filtration, washed with cold methanol and diethyl ether, and dried in a vacuum oven. Lastly, sPPP-K⁺ was placed in a 250 mL round bottom flask containing 75 mL of H₂O, then 25 mL of 2M H₂SO₄ was added dropwise and sPPP precipitated. The mixture was stirred for 2 hours, then collected via suction filtration, washed with cold H₂O and diethyl ether, then dried in a vacuum oven at 80°C to yield sPPP as a dark brown solid (1.65g, 81% yield). GPC analysis: $M_w = 154,400$ Da and $M_n = 109,900$ Da ($D = 1.31$).
Preparation of sulfonated phenylated phenene (sPP)

Compound sPP was prepared similar to previously reported literature procedures as outlined in Scheme 1. A 100 ml round bottom flask equipped with a stir bar was charged with 10.7 mmol (8.00g) of disulfonated tetracyclone triethylammonium salt, 10.9 mmol (1.12g) phenylacetylene, and 40 mL of nitrobenzene. The reaction mixture was stirred for 15 minutes at room temperature, then heated to 185°C. After 8 hours, the mixture was allowed to cool, then precipitated into 500 mL of ethyl acetate and refluxed for 2 hours, then collected via suction filtration and washed twice with boiling ethyl acetate and once with boiling acetone. The powder was dried in a vacuum oven at 80°C for 2 hours, then dissolved into 200 mL of methanol in a round bottom flask equipped with a stir bar and 50 mL of 2M KOH in methanol was added dropwise and a sPP-K⁺ precipitated. The mixture was stirred for 2 hours, then collected via suction filtration and washed with cold methanol and diethyl ether, then dried in a vacuum oven at 80°C for 2 hours. Lastly, the powder was dissolved in 200 mL of H₂O in a 500 mL round bottom flask equipped with a stir bar and 50 mL of 2M H₂SO₄ was added dropwise and sPP precipitated. The mixture was stirred for 2 hours then collected via suction filtration and washed with cold water and diethyl ether, followed by drying in a vacuum oven at 80°C to yield sPP (5.61g, 85%).¹H NMR (601 MHz, methanol-d₄) δ 7.64 (d, J = 8.3 Hz, 4H), 7.50 (d, J = 8.1 Hz, 4H), 7.47 (s, 2H), 7.25 (d, J = 8.3 Hz, 4H), 6.97 (s, 4H), 6.96 – 6.81 (m, 24H).¹³C NMR (151 MHz, methanol-d₄) δ 145.20, 143.89, 143.76, 143.33, 143.31, 141.74, 141.56, 141.17, 140.89, 140.68, 140.09, 132.65, 132.54, 132.49, 131.85, 130.91, 130.49, 128.10, 127.85, 126.94, 126.73, 126.30, 125.77. HRMS [M-H]⁻ Calculated for C₆₆H₄₅O₁₂S₄ 1157.1796, found 1157.1676, [M-2H]⁻ 578.0863, [M-3H]⁻ 385.0556, [M-4H]⁺ 288.5400.
2.2.4. Degradation Procedure

Degradation experiments were performed similar to previously reported literature procedures. Reactions were conducted in sealed glass pressure reactors, heated to 80 or 130°C and allowed to react for 100 or 24 hours, respectively. Reactions were performed with molar ratios of 1-10 (H₂O₂/sPP), and at concentrations of 0.07 – 0.70 vol.% H₂O₂. Typical experiments were performed with volumes of 10 cm³. After each reaction, samples were withdrawn for HPLC and LC/MS analysis, or freeze-dried for NMR experiments.

2.3. Results and Discussion

2.3.1. Polymer and Model Compound Synthesis

The polymer (sPPP) was prepared via a (4+2) Diels-Alder reaction between a tetrasulfonated bistetracyclone triethylammonium (TEA) salt and 1,4-diethynyl benzene as described in the literature. Similarly, the model compound (sPP) was prepared through a Diels-Alder reaction between a disulfonated tetracyclone TEA salt, and 1,4-diethynyl benzene. Both sPPP and sPP were converted into their acid forms in two steps as reported in section 2.2. Gel permeation chromatography (GPC) analysis indicated pristine sPPP possessed a $M_w$ of 156,400 Da and $M_n$ of 109,900 Da ($D = 1.31$).

2.3.2. Degradation Study of the Model Compound

In order to observe the formation of intermediates, degradation experiments were initially conducted on sPP using low concentrations of H₂O₂ (0.35%) at 130 and 80°C for 24 and 100 hours, respectively, to ensure complete decomposition of H₂O₂. After subjecting sPP to 4 equivalents of H₂O₂ at 0.35% and 130°C for 24 hours, it was found that < 10% of sPP had degraded, as characterized by HPLC analysis. For comparison, it is reported in the literature that a model compound of sulfonated poly(arylene ether ketone) degraded by 53% under the same conditions. Due to the low degradation rate observed, sPP was subject to harsher conditions (10 equivalents of 0.70% H₂O₂) for a total of 120 hours. Every 24 hours, an aliquot was withdrawn for analysis, and additional H₂O₂ was added to continue the degradation experiment. An overlay of the HPLC
chromatograms is provided in Figure 2.2. Each 24-hour period consumed ≤ 30% of sPP. After 120 hours, approx. 83% of sPP had been consumed.

Figure 2.2: HPLC chromatographic overlay of (sPP) degraded for 120 hours, initiated by reaction with 10 equivalents of 0.7% H$_2$O$_2$ at 130°C. H$_2$O$_2$ was replenished every 24 hours. Arrows and numbers highlight compounds that were collected and further characterized. Refer to Figure 5 for respective chemical structures. a Denotes products with more than one isomer.

Preparative HPLC was used to separate each significant degradation product. Although fractions were collected for all peaks, only the peaks in which enough compound could be collected for characterization are outlined in Figure 2.2. For each peak, over 100 fractions were collected and combined, then concentrated for further analysis. Each compound was subsequently characterized using NMR and MS techniques. A description of the analysis of compound a3 which eluted at 26.5 minutes is provided to highlight the methodology (see Figure 2.3). As illustrated in Figure 2.3b, the [M-H]$^-$ peak at 1107.13 (m/z) indicates that the molecular weight of a3 is 1108.14 Da. The peaks observed at 553.06, 368.37, and 276.03 (m/z) are indicative of [M-2H]$^{2-}$, [M-3H]$^{3-}$, and [M-4H]$^{4-}$ peaks, respectively; suggesting the compound still contained four acidic groups. HRMS was then employed to obtain a molecular weight of 1108.135 ± 0.001 Da, which was used to calculate a chemical formula of C$_{61}$H$_{40}$O$_{13}$S$_{4}$. In the $^1$H NMR spectrum, 9 new resonances were observed (labeled 1-9) when compared with the $^1$H NMR spectrum of sPP (see Section 2.2.3). A series of four doublets (1-4) were observed, and the corresponding 2D COSY spectrum (Figure A21) was used to outline correlations between doublets 1-2 and
3-4, which were assigned to the $\alpha$ and $\beta$ protons on the sulfonated phenyl ring. Next, the 2D COSY spectrum was used to identify a spin system comprised of 4 aromatic protons (5-8), attributed to an ortho-substituted aromatic ring. Lastly, a resonance at 191.7 ppm observed in the $^{13}$C NMR spectrum (Figure A23) suggests that $\textbf{a3}$ contains a ketone. With this information, it is proposed that $\textbf{a3}$ contains a fluorenone substructure as shown in Figure 2.3d. An unusually low chemical shift at 6.2 ppm was observed for $H_5$ of $\textbf{a3}$, which is caused by anisotropic effects of the adjacent phenyl ring and proven through the detection of $H_1$ and $H_2$ peaks at 7.94 and 7.32 ppm using selective 1D NOESY, as outlined in Figure 2.3c. A similar compound ($\textbf{b3}$) was also detected with a molecular weight of 1028.18 Da, which is also purported to possess a fluorenone substructure, but with a ketone replacing a sulfonated phenyl ring. Using a similar analytical strategy, all significant degradation products highlighted in Figure 2.2 (with the exception of compounds $\textbf{a1/b1}$ and $\textbf{a4/b4}$) were characterized. The total characterization for each compound is provided in the Supporting Information.

**Figure 2.3:** Characterization of degradation product ($\textbf{a3}$). (a) $^1$H NMR spectrum; (b) MS spectrum; (c) Selective $^1$H NOESY irradiation; (d) Chemical structure of $\textbf{a3}$. 

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Addition products from the reaction of HO• with sPP to form phenolic compounds a1 and b1 were detected by MS, but only in trace amounts. This is not unexpected, as phenol-containing compounds are known to have relatively low oxidative stability.\textsuperscript{45,91–93} The oxidation of phenyl rings into carboxylic acids was consistently observed throughout this study, occurring at both sulfonated (b2), and non-sulfonated (a2) phenyl rings, as well as via the oxidation of multiple phenyl rings into carboxylic acids (5 and 6) (see Scheme 2.1 for full chemical structures). While the degradation product resulting from the oxidation of two non-sulfonated phenyl rings (5) was collected and characterized, no degradation product for the oxidation of two sulfonated phenyl rings was detected in this study. Similarly, the oxidation product of three or more phenyl rings was not detected. Benzoic acid (BA) and sulfobenzoic acid (SBA) were both consistently detected throughout the study, as well as compounds 7 and 8. A trace of ring-fused product (9) was also detected. Theoretical studies on polyaromatic hydrocarbon model compounds have indicated that the attack on the C1 atom of sulfonated aromatic compounds may lead to the breaking of C-S bonds, forming phenol and •SO\textsubscript{3}•, however no evidence for this degradation product was detected.\textsuperscript{71}

HPLC was used to analyze the evolution of each degradation product over the course of 120 hours (Figure 2.4). The plots provided the rate of increase and decrease of a particular compound. It is important to note that the relative amounts of each product should not be directly compared to one other due to discrepancies in their molar extinction coefficients.\textsuperscript{45} Instead, information was collected by analyzing the evolution of each individual degradation product over time. Each 24-hour degradation period degrades approximately 30% of sPP, and after a total of 120 hours, 83% of the original sPP had been degraded. Many of the degradation products, such as carboxylic acids a2 and b2, fluorenones a3 and b3, and dicarboxylic acids 5 and 6 (Figure 2.4) display a slow increase in their concentration over the first 48-72 hours, then decrease in concentration. These results are indicative of intermediate species involved in the degradation mechanism. Degradation product 7 shows a similar trend, reaching a maximum concentration between 72-96 hours. This would suggest 7 is a late-stage intermediate product. Only benzoic acid (BA), sulfobenzoic acid (SBA), and 8 continuously increase in their concentration throughout the entire oxidation process, indicating that these products are unlikely to undergo further oxidation once formed. Lastly, ring-fused compound 9 also displays a maximum concentration after 48 hours,
followed by a continuous decrease in concentration, indicating it has a lower oxidative stability than \( \text{sPP} \).

\[ \text{Figure 2.4: HPLC analysis data showing the evolution of (sPP) degradation products over the course of 120 hours in the presence of 10 equivalents of H}_2\text{O}_2 \text{ at 0.70}\% \text{ and 130 } ^\circ \text{C.} \]
\[ \text{H}_2\text{O}_2 \text{ was added every 24 hours. See Scheme 2 for respective chemical structures.} \]

The major degradation routes of \( \text{sPP} \) appear to originate at both the sulfonated phenyl (Scheme 2.1, route a) and non-sulfonated phenyl rings (Scheme 2.1, route b). Even when exposed to \( \text{H}_2\text{O}_2 \) at much lower concentrations and temperatures (e.g., 4 equivalents, 0.30\%, and 80°C), the degradation route of \( \text{sPP} \) did not change (see Figure A31). In all cases, it began with the oxidation of a pendant phenyl ring, initiated by radical addition of \( \text{HO}^\cdot \) to form a hydroxycyclohexadienyl radical, which then leads to the formation of hydroxylated \( \text{sPP} \) (\( \text{a1} \) and \( \text{b1} \)) via elimination of \( \text{H}^\cdot \) (as \( \text{HOO}^\cdot \) through reaction with \( \text{O}_2 \)).
Scheme 2.1: HO• radical-induced oxidative degradation of (sPP).

*a Products detected only by Mass Spectrometry.
Having established that carboxylic acids \( a_2 \) and \( b_2 \), fluorenones \( a_3 \) and \( b_3 \), and dicarboxylic acids 5 and 6 (Scheme 1.2) are intermediate species in the degradation process, and that they arise from oxidation of pendant phenyl rings, it is postulated that carboxylic acids \( a_2 \) and \( b_2 \) may be formed through the oxidation of phenols \( a_1 \) and \( b_1 \), or via ring-opening of a hydroxycyclohexadienyl radical intermediate (see B, Scheme 1.4). Once formed, \( a_2 \) and \( b_2 \) undergo an acid-catalyzed intramolecular Friedel-Crafts acylation reaction forming fluorenones \( a_3 \) and \( b_3 \). Similar acylation reactions have previously been observed for aromatic polymers.\(^{94-96}\) Upon reaction with \( \text{H}_2\text{O}_2 \), fluorenones \( a_3 \) and \( b_3 \) undergo a Baeyer-Villiger oxidation to form lactones \( a_4 \) and \( b_4 \), which were only detectable via mass spectrometry. In the presence of \( \text{H}_2\text{O}_2 \) and under acidic conditions, fluorenone has been shown to undergo a Baeyer-Villiger reaction forming the corresponding lactone.\(^{97}\) It is proposed that upon further oxidation, lactones \( a_4 \) and \( b_4 \) result in the formation of dicarboxylic acids 5 and 6. As no degradation compound possessing three carboxylic acids was detected, it is postulated that further oxidation of dicarboxylic acids 5 and 6 may result in the oxidation of a core phenylene ring, forming compound 7, benzoic acid, and sulfobenzoic acid in the process. It is important to note that the degradation of a core phenylene ring in compounds 5 and 6 would be the equivalent of a chain-scission process in the analogous polymer, sPPP. Lastly, further oxidation of 7 results in the formation of compound 8.

Although oxidation via hydroxyl radical attack is demonstrated to occur at both sulfonated and non-sulfonated phenyl rings, the latter is assumed to be the predominant route due to the much higher concentration of sulfobenzoic acid found compared to benzoic acid. This result is not unexpected, as hydroxyl radicals are known to undergo a higher rate of reaction with benzene \((k = 7.8 \times 10^9 \, \text{M}^{-1}\text{s}^{-1})\) than with benzenesulfonic acid \((k = 1.6 \times 10^9)\).\(^{37}\) It is worth noting that the oxidation of a non-sulfonated phenyl ring may lead to ring-opening, consuming said phenyl ring in the process. Further oxidation may ultimately result in the ring-opening of a core phenylene ring, which would result in the production of sulfobenzoic acid, as outlined in Scheme 2.2. That is, oxidation of a non-sulfonated phenyl ring may lead to the production of sulfobenzoic acid as a degradation product, while oxidation of a sulfonated phenyl ring may conversely lead to production of benzoic acid as a degradation product. As such, the addition of electron withdrawing groups to phenyl rings appears to enhance their chemical stability by lowering their rate of reaction with hydroxyl radicals.
Scheme 2.2: Proposed oxidative ring-fusion mechanism of (sPP) initiated through H• abstraction.
Note, multiple isomers are detected.

A trace amount of ring-fused product (9, Scheme 2.2) was detected; however, the amounts were minimal, and likely formed via H-abstraction from sPP by HO•, forming a phenyl radical that leads to the fusion of phenyl rings according to the mechanism shown in Scheme 2.3. This observation is in agreement with a theoretical study that suggests H-abstraction from phenyl rings by hydroxyl radicals is expected to play only a minor role in the degradation of aromatic compounds.72–74

2.3.3. Degradation of sPPP polymer – Mechanism

Having rationalized a degradation mechanism for sPP, the analogous sPPP polymer was subjected to degradation experiments using H2O2 concentrations of 0.07%, 0.15%, and 0.35%, and heated to 80°C for 100 hours to ensure complete decomposition of H2O2 and to ensure radicals were generated at a relatively low rate. The results from this experiment are outlined in Figure 2.5. After degrading sPPP with 0.35% H2O2, two doublets were observed in the 1H NMR spectrum (Figure 2.5b) at 7.9 and 8.1 ppm, matching the NMR pattern for sulfobenzoic acid. No other significant changes in the 1H NMR spectra were observed. ATR-IR analysis (Figure 2.5c) revealed a broad carbonyl stretch near 1690 cm⁻¹, however this peak is difficult to interpret as it may be due to a) the formation of carboxylic acid groups on the polymer formed by the oxidation of pendant phenyl rings; b) the formation of fluorenone-like structures; c) due to residual sulfobenzoic acid remaining in the polymer; or d) due to a stronger H2O/H3O+ deformation mode. After degradation with H2O2, observed changes in the GPC chromatograms (Figure 2.5a and Table 2.1) show minimal changes in peak shape, with small shifts of the entire peak. Upon degrading sPPP with 0.07% H2O2, GPC analysis revealed a decrease in the Mw from 156,400 Da to 98,500 Da, and the Mn from 109,900...
to 95,700. When the amount of H$_2$O$_2$ was increased by a factor of 5 to 0.35% H$_2$O$_2$, the $M_w$ and $M_n$ only decreased to 82,800 Da and 77,600 Da, respectively.

![Figure 2.5](image)

**Figure 2.5:** Hydroxyl radical-induced changes in (sPPP) after reaction with H$_2$O$_2$ at 80°C for 100 hours. (a) GPC (UV) curves; (b) $^1$H NMR spectrum; (c) ATR-IR spectrum.

**Table 2.1:** GPC molecular Weight Data of (sPPP) After Reaction with H$_2$O$_2$ at 80°C for 100 Hours.

<table>
<thead>
<tr>
<th>H$_2$O$_2$ (%)</th>
<th>$M_w$ (Da)</th>
<th>$M_n$ (Da)</th>
<th>$\bar{D}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>156,400</td>
<td>109,900</td>
<td>1.42</td>
</tr>
<tr>
<td>0.07</td>
<td>98,500</td>
<td>95,700</td>
<td>1.03</td>
</tr>
<tr>
<td>0.15</td>
<td>90,500</td>
<td>86,900</td>
<td>1.04</td>
</tr>
<tr>
<td>0.35</td>
<td>82,800</td>
<td>77,600</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Although the characterization of degraded sPPP still remains a significant issue, similarities between degraded sPPP and sPP can be seen. The high concentration of sulfobenzoic acid formed in both cases would suggest that degradation originates with the oxidation of non-sulfonated phenyl rings, forming phenolic rings. Once formed, these phenolic groups may be further oxidized, resulting in the formation of carboxylic acids, which upon reaction with adjacent phenyl rings may form fluorenone substructures. Further oxidation may then convert the fluorenes to their corresponding lactones, which upon further oxidation may culminate in chain-scission along the polymer backbone, forming sulfobenzoic acid in the process (Scheme 2.3). This hypothesis explains why the NMR spectra of the degraded polymer shows only minor changes with the appearance of sulfobenzoic acid, while the GPC results show a decrease in the molecular weight of the polymer.
Scheme 2.3: Proposed hydroxyl radical-induced oxidative degradation route of (sPPP) polymers.
2.3.4. Conclusion

In summary, the free radical degradation route of sulfonated phenylated polyphenylenes (sPPP) was elucidated, using a structurally-analogous oligophenylene model compound sPP which mimics the structural motifs of sPPP. Upon degradation with 10 equivalents of H₂O₂ at 0.70% and 130°C, the model compound was shown to degrade by ~30%. Each significant degradation product was isolated using preparative HPLC and subsequently characterized using NMR and MS techniques. Based on their chemical structure, along with their elution patterns, a degradation route is proposed. Degradation is demonstrated to occur primarily on non-sulfonated phenyl rings into fluorenone substructures, and upon further oxidation, may result in ring-opening of a core phenylene ring and lead to the formation of sulfobenzoic acid. In the analogous polymer, the same or similar oxidation of a fluorenone substructure would lead to chain-scission of the polymer backbone. Indeed, upon exposure of sPPP to hydroxyl radicals, the molecular weight is found to decrease substantially while the NMR spectra are relatively unchanged, save for the appearance of sulfobenzoic acid. A potential strategy to improve the oxidative stability of sPPP membranes lies in inhibiting the formation of the reactive fluorenone intermediates, which appear to promote chain-scission. Although hydrocarbon PEMs might never obtain the levels of ex situ chemical stability of their perfluorinated analogues, their generally observed lower gas crossover rates have led to several studies showing significantly longer in situ membrane lifetimes for hydrocarbon PEMs under accelerated OCV degradation conditions. Hence, the future in situ use of hydrocarbon PEMs remains promising.

2.3.5. Future Work

In keeping with the degradation mechanism outlined in this work, future work aimed at improving the chemical stability of sPPP membranes should focus on inhibiting the formation of reactive fluorenone intermediates which appear to promote chain scission. Due to the high stability of carbon-fluorine bonds, fluorine substitution is a method commonly used to selectively block specific locations within molecules which are highly reactive.98 Within sPPP membranes, the incorporation of fluorine atoms along the backbone of the polymer should inhibit the ability of phenylene rings to undergo electrophilic aromatic substitution, inhibiting the formation of fluorenone intermediates, and stopping the polymer from undergoing chain-scission. In the subsequent analysis of
the polymer, or analogous model compound, this should be displayed by a reduction in
the amount of sulfobenzoic acid eliminated after being degraded with hydrogen peroxide.
The synthesis of a modified sPPP polymer is outlined in Scheme 2.4 with the selective
incorporation of fluorine atoms onto the backbone of the polymer in order to inhibit the
formation of fluorenone intermediates.

![Scheme 2.4: Synthesis of (sPPP) polymer containing a fluorinated backbone.](image)

Although the incorporation of fluorine atoms onto the backbone of sPPP polymers
may improve their oxidative stability through inhibiting the formation of fluorenone
intermediates, it does not address the problem of decomposing, or terminating radical
species within fuel cell systems. The development of regenerative radical decomposition
catalysts still poses a fundamental challenge to researchers. While metal cation
scavengers such as Ce\(^{3+}\) (typically at 1 mol\%\) have been shown to improve the chemical
durability of PFSA membranes in situ\(^ {99,100}\), they are not expected to be as effective within
hydrocarbon membranes. The half-life of HO• within hydrocarbon membranes has been
estimated to be three orders of magnitude shorter than their perfluorinated anaoluges.\(^ {28}\)
Thus, in order to achieve the same level of HO• quenching, a higher concentration of Ce\(^{3+}\)
would be required, however Ce\(^{3+}\) ions are known to diminish membrane conductivity.\(^ {47}\)
The effectiveness of metal cations such as Ce\(^{3+}\) is still the subject of debate as some
groups have reported them to be ineffective within hydrocarbon membranes,\(^ {53}\) while
others have reported them to be effective.\(^ {101}\)

Phenolic derivatives have been widely used as antioxidants within plastics, due to
their higher rate of reaction with radical species.\(^ {54}\) As opposed to metal cations, phenolic
antioxidants do not hinder the performance of PEMs, however their application is limited as they become slowly consumed over time. In comparison to metal cations which terminate radical species, phenolic antioxidants act to temporarily trap radical species, or convert them into less reactive species such as hydroperoxides.\textsuperscript{102} Polymer-bond antioxidants have previously been incorporated into PSSA membranes by Buchmüller and co-workers. The incorporation of tyramine or glycidyl methacrylate were both shown to improve the chemical stability of membranes when subjected to \textit{in situ} accelerated stress tests.\textsuperscript{103}

The reaction of radical species with polymer chains ultimately leads to the propagation of radicals. Only upon recombination with another radical, or through reaction with a metal cation can radical termination occur. Therefore, to limit the amount of degradation radicals can incur on PEMs, future work may consider incorporating a polymer-bound antioxidant to temporarily trap radical species, along with metal cations which may terminate radical species. One of the most common antioxidants is butylated hydroxy toluene (BHT, Scheme 2.5), which is a synthetic analogue of vitamin E and was originally patented in 1947.\textsuperscript{104} Since it was first discovered, it has been used in a large number of applications as an antioxidant additive for polymers, foods, oils, and many other applications.\textsuperscript{102}

Scheme 2.5: Chemical structure of BHT and reaction with hydroxyl radicals.

When compared with hydroxyl radicals ($E^\circ = 2.72$), phenoxy radicals are much less reactive as reflected by their standard reduction potential ($E^\circ = 1.34$ V).\textsuperscript{105} Outlined in Scheme 2.6 is the synthesis of a copolymer which incorporates a hindered phenol antioxidant, similar to BHT, along with three pyridine rings to chelate metal cations and may inhibit them from being washed out of PEMs along with water.
Scheme 2.6: Synthesis of (sPPP) copolymers incorporating a phenolic antioxidant and a chelating agent.

As the conjugate acid of pyridine has a $pK_a$ of 5.25 which is above the operating pH of a fuel cell, pyridine rings, along with metal cations such as cerium, may neutralize acidic protons which may have adverse effects on the conductivity of PEMs. Thus, future work should consider adding these linkers in small amounts as a copolymer in order to ensure future membranes are still able to obtain high performance values.
References


(51) Roelofs, M. G. Methods to Prepare Chemically Stabilized Ionomers Containing Inorganic Fillers, November 27, 2008.


0191(00)00024-1.


Appendix.

Additional Figures

Figure A1: 1H NMR (601 MHz, methanol-d₄) spectrum of polymer (sPPP).
Figure A2: 1H NMR (601 MHz, methanol-$d_4$) spectrum of polymer (sPPP) degraded for 100 hours at 80 °C with 0.7 vol% $\text{H}_2\text{O}_2$. 
Figure A3: FTIR-ATR spectrum of polymer (sPPP) degraded for 100 hours at 80 °C with 0.7 vol% H$_2$O$_2$.
Figure A4: $^1$H NMR (601 MHz, methanol-\(d_4\)) spectrum of model compound (sPP).
Figure A5: $^{13}$C NMR (151 MHz, methanol-$d_4$) spectrum of model compound (sPP).
Figure A6: COSY (2D) NMR (601 MHz, methanol-$d_4$) spectrum of model compound (sPP).
Figure A7: \(^1\)H NMR (601 MHz, methanol-\(d_4\)) spectrum of fluorenone (b3).

\(^1\)H NMR (601 MHz, methanol-\(d_4\)) \(\delta\) 7.66 (s, 1H), 7.64 (d, \(J = 8.5\) Hz, 3H), 7.56 (d, \(J = 8.3\) Hz, 2H), 7.51 (d, \(J = 8.4\) Hz, 2H), 7.45 (s, 1H), 7.35 – 7.28 (m, 3H), 7.25 – 7.22 (m, 2H), 7.19 (dd, \(J = 7.7, 1.7\) Hz, 2H), 7.15 (td, \(J = 7.6, 1.3\) Hz, 1H), 7.00 – 6.79 (m, 18H), 6.09 (dt, \(J = 7.7, 0.8\) Hz, 1H).


ATR-IR: 1710, 1600, 1427 cm\(^{-1}\).
$^{13}$C NMR (151 MHz, methanol-$d_4$) δ 193.41, 146.12, 144.32, 143.70, 143.01, 142.88, 142.36, 142.27, 142.20, 141.94, 140.77, 140.66, 140.32, 140.25, 139.89, 139.88, 139.62, 138.81, 138.65, 138.01, 137.96, 134.63, 134.31, 133.25, 131.20, 131.16, 130.65, 130.39, 129.55, 129.47, 129.26, 128.79, 128.50, 128.23, 127.34, 126.67, 126.41, 125.47, 125.27, 124.95, 124.70, 124.46, 124.36, 123.46, 123.01.

**Figure A8:** $^{13}$C NMR (151 MHz, methanol-$d_4$) spectrum of fluorenone (b3).
Figure A9: COSY (2D) NMR (601 MHz, methanol-$d_4$) spectrum of fluorenone (b3).
Figure A10: 1D selective NOESY irradiation of fluorenone (b3) (101 MHz, methanol-\textit{d}_4).
Figure A11: $^1$H NMR (601 MHz, methanol-$d_4$) spectrum of carboxylic acid (7).

$^1$H NMR (600 MHz, methanol-$d_4$) $\delta$ 7.84 (d, $J = 8.4$ Hz, 2H), 7.65 (d, $J = 8.4$ Hz, 2H), 7.51 (s, 1H), 7.45 (d, $J = 8.2$ Hz, 2H), 7.30 (d, $J = 8.4$ Hz, 2H), 7.26 (d, $J = 8.4$ Hz, 2H), 7.01 (d, $J = 8.3$ Hz, 2H), 6.96 – 6.82 (m, 10H).


ATR-IR: 1704, 1605, 1430 cm$^{-1}$. 
Figure A12: $^{13}$C NMR (151 MHz, methanol-$d_4$) spectrum of carboxylic acid (7).

$^{13}$C NMR (151 MHz, methanol-$d_4$) δ 169.53, 147.61, 144.97, 144.38, 143.87, 143.54, 143.35, 141.78, 141.55, 141.45, 141.03, 140.84, 140.16, 132.56, 132.54, 132.50, 131.83, 131.09, 130.87, 130.30, 130.03, 128.15, 127.90, 127.02, 126.83, 126.39, 125.81.
Figure A13: COSY (2D) NMR (601 Mhz, methanol-\textit{d}_4) spectrum of carboxylic acid (7).
Figure A14: $^1$H NMR (601 MHz Methanol-$d_4$) spectrum of dicarboxylic acid (5).

$^1$H NMR (600 MHz, methanol-$d_4$) δ 7.85 (d, $J = 8.0$ Hz, 2H), 7.72 (d, $J = 8.1$ Hz, 2H), 7.65 (d, $J = 8.0$ Hz, 2H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 8.3$ Hz, 2H), 7.42 (s, 1H), 7.28 (s, 1H), 7.22 (dd, $J = 8.3$, 2.5 Hz, 4H), 7.00 – 6.77 (m, 16H).


ATR-IR: 1705, 1560, 1411 cm$^{-1}$. 
Figure A15: COSY (2D) NMR (601 MHz, methanol-d₄) spectrum of dicarboxylic acid (5).
Figure A16: $^1$H NMR (601 MHz methanol-$d_4$) spectrum of dicarboxylic acid (6).

$^1$H NMR (601 MHz, methanol-$d_4$) $\delta$ 7.92 (s, 1H), 7.61 (d, $J = 8.5$ Hz, 2H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 8.5$ Hz, 2H), 7.43 (s, 1H), 7.22 (d, $J = 8.4$ Hz, 2H), 7.12 (dd, $J = 8.0$, 1.7 Hz, 2H), 7.07 – 7.00 (m, 3H), 6.95 (d, $J = 8.4$ Hz, 2H), 6.93 – 6.77 (m, 18H).

HRMS [M-H]: Calculated for C$_{56}$H$_{37}$O$_{13}$S$_3$ $^{1013.1402}$, found [M-H] $^{1013.1392}$, [M-2H]$^{2-}$ $^{506.0680}$, [M-3H]$^{3-}$ $^{337.0431}$, [M-4H]$^{4-}$ $^{252.5310}$.

ATR-IR: 1705, 1600, 1392 cm$^{-1}$. 
Figure A17: COSY (2D) NMR (601 MHz, methanol-d₄) spectrum of dicarboxylic acid (6).
**Figure A18:** $^1$H NMR (601 MHz methanol-d$_4$) spectrum of carboxylic acid (b2).

$^1$H NMR (601 MHz, methanol-d$_4$) δ 7.75 (s, 1H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.50 (d, $J = 8.3$ Hz, 2H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.44 (s, 1H), 7.23 (d, $J = 8.5$ Hz, 2H), 7.08 – 6.74 (m, 28H).


ATR-IR: 1707, 1600, 1434 cm$^{-1}$. 

66
Figure A19: COSY (2D) NMR (601 MHz, methanol-d₄) spectrum of carboxylic acid (b2).
**Figure A20:** $^1$H NMR (601 MHz, methanol-$d_4$) spectrum of fluorenone (a3).

$^1$H NMR (601 MHz, methanol-$d_4$) $\delta$ 7.97 (d, $J$ = 8.3 Hz, 2H), 7.93 (d, $J$ = 8.4 Hz, 2H), 7.64 (d, $J$ = 8.3 Hz, 2H), 7.62 (d, $J$ = 8.5 Hz, 2H), 7.54 (d, $J$ = 8.4 Hz, 1H), 7.48 (d, $J$ = 8.4 Hz, 2H), 7.44 (s, 1H), 7.32 (d, $J$ = 8.4 Hz, 2H), 7.24 – 7.20 (m, 4H), 7.15 (td, $J$ = 7.6, 1.3 Hz, 1H), 7.00 (d, $J$ = 1.6 Hz, 4H), 6.97 – 6.78 (m, 12H), 6.24 (d, $J$ = 7.7 Hz, 1H).


ATR-IR: 1710, 1600, 1430 cm$^{-1}$. 

Figure A21: COSY (2D) NMR (601 MHz, methanol-\textit{d}_4) spectrum of fluorenone (a3).
Figure A22: 1D selective NOESY irradiation of fluorenone (a3) (601 MHz, methanol-d₄).
Figure A23: $^{13}$C NMR (151 MHz, DMSO-$d_6$) spectrum of fluorenol (a3).

$^{13}$C NMR (151 MHz, DMSO-$d_6$) $\delta$ 191.66, 147.90, 147.13, 146.11, 145.53, 142.97, 142.83, 141.88, 141.21, 140.00, 139.84, 139.54, 139.43, 139.31, 138.47, 137.38, 137.20, 136.99, 135.35, 134.37, 131.08, 131.00, 130.37, 129.35, 129.05, 128.87, 128.37, 127.07, 126.97, 126.73, 126.65, 126.00, 125.69, 125.02, 124.87, 124.35, 123.67, 122.80.
Figure A24: $^1$H NMR (601 MHz methanol-$d_4$) spectrum of carboxylic acid (8).

$^1$H NMR (601 MHz, methanol-$d_4$) δ 7.63 (d, $J = 8.5$ Hz, 2H), 7.62 (s, 1H), 7.57 (d, $J = 8.5$ Hz, 2H), 7.22 (dd, $J = 8.8$ Hz, 4H), 6.93 – 6.76 (m, 10H).


ATR-IR: 1706, 1575, 1395 cm$^{-1}$. 

Figure A25: COSY (2D) NMR (601 MHz, methanol-$d_4$) spectrum of carboxylic acid (8).
Figure A26: HPLC Chromatograms (254 nm) of (A) pristine sPP and (B) sPP degraded with 4 equivalents of H$_2$O$_2$ at 0.35 vol% and 130 °C for 24 hours.

Figure A27: The Chemical Structure of Compound a1/b1.

Note: Compound was only detected via mass spectroscopy.
HRMS [M-H]: Calculated for C_{66}H_{46}O_{13}S_{4} 1174.1821 not observed, found [M-2H]^{2-} 586.0872, [M-3H]^{3-} 390.3888, [M-4H]^{4-} 292.5397.

Figure A28: The Chemical structure of compound b4.
Note: Compound was only detected via mass spectroscopy.

HRMS [M-H]: Calculated for C_{61}H_{39}O_{11}S_{3}^{–} 1043.1660 not observed, found [M-2H]^{2-} 521.0853, [M-3H]^{3-} 347.0555.

Figure A29: The Chemical structure of compound a4.
Note: Compound was only detected via mass spectroscopy.

HRMS [M-H]: Calculated for C_{61}H_{39}O_{14}S_{4} 1124.1301 not observed, found [M-3H]^{3-} 373.7071, [M-4H]^{4-} 280.0307.
Figure A30: The Chemical structure of compound 7.

Note: Compound 7 was only detected via mass spectroscopy.

Figure A31: HPLC chromatographic overlay of sPPP degraded with a) 10 equivalents of 0.70% H₂O₂ for 24 hours b) 4 equivalents of 0.35% H₂O₂ at 80 °C.