

### Article

## On the Stability of Hydrocarbon Fuel Cell Membranes: Reaction of Hydroxyl Radicals with Sulfonated Phenylated Polyphenylenes

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1	On the Stability of Hydrocarbon Fuel Cell Membranes: Reaction of Hydroxyl
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# Abstract

The perceived poor durability of hydrocarbon polymer electrolyte membranes remains a significant hurdle for the integration of non-fluorous, solid polymer electrolytes into electrochemical systems such as fuel cells. In order to elucidate the mechanism of free radical degradation in a promising class of hydrocarbon polymer electrolyte membranes based on sulfonated phenylated polyphenylenes (**sPPP**), we synthesized and studied the degradation of a structurally-analogous oligophenylene model compound in the presence of hydroxyl radicals using NMR spectroscopy and mass spectrometry. Degradation is demonstrated to be initiated by the oxidation of pendant phenyl rings to carboxylic acids, which form fluorenone substructures via intramolecular reaction with a juxtaposed phenyl ring. Upon further oxidation, these substructures can lead to ring-opening of a core phenyl ring which, if occurring in **sPPP**, leads to chain-scission of the polymer backbone. In keeping with this hypothesis, molecular weights of **sPPP** are found to decrease when subject to hydroxyl radicals. Although degraded polymer NMR spectra remain unchanged, resonances consistent with the elimination of sulfobenzoic acid emerge.

#### **Chemistry of Materials**

## Introduction

Since their introduction in the 1960's, perfluorosulfonic acid (PFSA) ionomers such as Nafion<sup>®</sup> have remained the benchmark proton exchange membrane (PEM) for solid polymer electrolyte fuel cells and electrolyzers. Although PFSA ionomer membranes display high chemical stability, good mechanical toughness, and high proton conductivity, their high cost of manufacturing, high gas permeability, combined with increasing environmental concerns related to their disposal, have led researchers to seek alternative PEMs for fuel cell applications.<sup>1–4</sup> A significant amount of research has thus been directed to investigating hydrocarbon membranes based on functionalized polystyrene,<sup>2,5–7</sup> poly(arylene ether ketone),<sup>8–10</sup> poly(imide),<sup>11–13</sup> and poly(phenylene) polymer backbones.<sup>14–21</sup>

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,<sup>18,19,21</sup> and their low solubility in polar solvents.<sup>22</sup> Phenylated polyphenylenes (**PPP**) such as those prepared by Stille,<sup>23–26</sup> Kallitsis,<sup>27</sup> and Müllen<sup>28</sup> 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.<sup>14,15,29</sup> Recently, we 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.<sup>16,17,30</sup>

*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 *in situ* durability relative to Nafion<sup>®</sup> N211 references.<sup>16</sup> 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 *in situ* accelerated degradation tests have reported similar results.<sup>21</sup> *In situ* degradation is often attributed to a combination of mechanical and chemical processes that include membrane swelling and shrinking caused by temperature and relative humidity cycling, as well as the presence of generated radicals.<sup>1,31</sup> However, the fundamental aspects of hydrocarbon PEM degradation in the presence of free radicals alone remains relatively unknown. While numerous extensive performance and degradation studies have been reported for PFSA-based membranes,<sup>1,32–36</sup> similarly comprehensive studies on polyaromatic hydrocarbon membranes, in general, are relatively sparse,<sup>1,30,37–41</sup> and reports on their degradation even more so.<sup>2,5,39,42–45</sup>

In previous reports on **sPPP**,<sup>17,30</sup> we showed that **sPPP** membranes possessing high ion exchange capacities (IEC) exhibited no signs of degradation by mass loss or <sup>1</sup>H NMR after exposure to Fenton's reagent for 1 hour (3 ppm FeSO<sub>4</sub>, 3% H<sub>2</sub>O<sub>2</sub>, 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.<sup>46</sup> 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 1) was designed to mimic the structural motifs of the polymer. Although Fenton's reagent is commonly employed as an accelerated oxidative stability test for PEMs, the radicals generated therein are in relatively high concentration ( $k = 63 \text{ M}^{-1}\text{s}^{-1}$  for Fe<sup>2+</sup>).<sup>37,47</sup> which promotes secondary degradation pathways and creates difficulty in detecting potentially vital intermediates.<sup>48,49</sup> To counter this, a milder route to free radical formation was employed which involved the thermal decomposition of  $H_2O_2$  (k =  $1.2 \times 10^{-7}$  s<sup>-1</sup>).<sup>37,50,51</sup> This method was previously employed to elucidate the oxidative degradation route of a sulfonated poly(arylene ether ketone) (sPEAK) model compound, which shed meaningful light on the degradation pathways and chemical sensitivities of analogous polymers.<sup>39,43</sup>



Figure 1: Chemical Structure of sulfonated phenylated polyphenylene (sPPP) and the corresponding model compound (sPP).

## **Experimental**

## Reagents

The following reagents were purchased and used as received: Triethylamine (99%, Combi-Blocks), 1,4diiodobenzene (98%, Combi-Blocks Inc.), *n*-butanol (Fisher Scientific), hydrogen peroxide (30%, Fisher Scientific), potassium hydroxide (Caledon Laboratories), nitrobenzene (Sigma Aldrich),

#### **Chemistry of Materials**

dimethylformamide (HPLC grade, Sigma Aldrich), acetonitrile (HPLC grade, Fisher Scientific)
diphenylphosphineferrocene palladium dichloride (Strem Chemicals), trimethylsilylethyne (Tokyo
Chemical Industry Co.), trimethylsilyl chlorosulfonate (99%, Sigma Aldrich), 1,3-(diphenyl)propan-2one (98%, Tokyo Chemcial Industry Co.), bisbenzyl (98%, Tokyo Chemcial 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 disulfoanted tetracyclone were prepared according to previously
reported literature procedures.<sup>16,17,30</sup> All experiments were performed using deionized water which was
further purified using Millipore Milli-Q water purification system (≥18MΩ·cm).

## Synthesis

Sulfonated phenylated polyphenylene (sPPP).<sup>17</sup> A 60 mL Schlenk tube equipped with a stir bar was charged with 2.50g (1.77 mmol) of a tetrasulfonated bistetracyclone triethylammonium salt, 24 mL of nitrobenzene, and 0.23g (1.79 mmol) 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 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<sup>+</sup> 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<sup>+</sup> was placed in a 250 mL round bottom flask containing 75 mL of H<sub>2</sub>O, then 25 ml of 2M H<sub>2</sub>SO<sub>4</sub> was added dropwise and sPPP precipitated. The mixture was stirred for 2 hours, then collected via suction filtration, washed with cold H<sub>2</sub>O 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).

*Sulfonated Phenylated Phenylene* (**sPP**).<sup>17</sup> A 100 ml round bottom flask equipped with a stir bar was charged with 8.00g (10.7 mmol) of disulfonated tetracyclone triethylammonium salt, 1.12g (10.9 mmol) phenylacetylene, and 40 mL of nitrobenzene. The 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**<sup>+</sup> 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 H<sub>2</sub>O in a 500 mL round bottom flask equipped with a stir bar and 50 mL of 2M H<sub>2</sub>SO<sub>4</sub> 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%).<sup>1</sup>H NMR (601 MHz, Methanol-d<sub>4</sub>)  $\delta$  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). <sup>13</sup>C NMR (151 MHz, Methanol-d<sub>4</sub>)  $\delta$  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]<sup>-</sup> Calculated for C<sub>66</sub>H<sub>45</sub>O<sub>12</sub>S<sub>4</sub><sup>-</sup> 1157.1796, found 1157.1676, [M-2H]<sup>2-</sup> 578.0863, [M-3H]<sup>3-</sup> 385.0556, [M-4H]<sup>4-</sup> 288.5400.

## Equipment

<sup>13</sup>C NMR spectra were recorded on a Bruker AVANCE II 600 MHz NMR spectrometer equipped with a 5 mm QNP cryoprobe. <sup>1</sup>H, 2D (COSY), and 1D NOE 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<sub>2</sub>O and 10% acetonitrile (solvent A), and 5mM ammonium acetate in 95% acetonitrile and 5% H<sub>2</sub>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).

### **Degradation Procedure**

Degradation experiments were performed similar to previously reported literature procedures.<sup>39,40</sup> 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

#### **Chemistry of Materials**

 $(H_2O_2/sPP)$ , and at concentrations of 0.07 - 0.70 vol.%  $H_2O_2$ . Typical experiments were performed with volumes of 10 cm<sup>3</sup>. After each reaction, samples were withdrawn for HPLC and LCMS analysis, or freeze-dried for NMR experiments.

## **Results and Discussion**

### **Degradation of sPPP Polymer - Analyses**

Preliminary degradation experiments on **sPPP** with 0.35%  $H_2O_2$  at 80°C for 100 hours indicated **sPPP**  $M_w$  and  $M_n$  decreased from 156,400 to 82,800 Da, and 109,900 Da to 77,600 Da, respectively. Despite this decrease in molecular weight, NMR spectra recorded a minimal change, with only two small doublets appearing at 8.08 and 7.91 ppm in the NMR spectrum (see following section). Model compound **sPP** was therefore examined as a means to shed light on the radical degradation pathway of **sPPP** polymers.

## Degradation of sPP model compound - Analyses and proposed mechanism

Previous studies have shown that the oxidation of aromatic compounds by hydroxyl radicals originates by either abstraction of H• (see Scheme 1) 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, 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.<sup>42,52–57</sup>



Scheme 1: Oxidative degradation mechanism of benzene.54,55,57

In order to observe the formation of intermediates, degradation experiments were initially conducted on **sPP** using low concentrations of  $H_2O_2$  (0.35%) at 130 and 80°C for 24 and 100 hours, respectively, to ensure complete decomposition of  $H_2O_2$ .<sup>39</sup> After subjecting **sPP** to 4 equivalents of  $H_2O_2$  at 0.35% and 130°C for 24 hours, it was found that < 10% of **sPP** had degraded, as characterized by HPLC analysis (see **Figure S28** for details). For comparison, it is reported in the literature that a model compound of sulfonated poly(arylene ether ketone) degraded by 53% under the same

#### **Chemistry of Materials**

conditions.<sup>39</sup> Due to the low degradation rate observed, **sPP** was subject to harsher conditions (10 equivalents of 0.70% H<sub>2</sub>O<sub>2</sub>) for a total of 120 hours. Every 24 hours, an aliquot was withdrawn for analysis, and additional H<sub>2</sub>O<sub>2</sub> was added to continue the degradation experiment. A chromatographic overlay of the HPLC response obtained is provided in **Figure 2**. Each 24-hour period consumed  $\leq$  30% of **sPP**. After 120 hours, approx. 83% of **sPP** had been consumed.



Figure 2: HPLC chromatographic overlay of sPP degraded for 120 hours, initiated by reaction with 10 equivalents of 0.7% H<sub>2</sub>O<sub>2</sub> at 130°C. H<sub>2</sub>O<sub>2</sub> was replenished every 24 hours. Arrows and numbers highlight compounds that were collected and further characterized. Refer to Figure 5 for respective chemical structures. <sup>a</sup> Denotes products with more than one isomer.

Preparative HPLC was used to separate each significant degradation product. 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 3**). As illustrated in **Figure 3b**, the [M-H]<sup>-</sup> 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]<sup>2-</sup>, [M-3H]<sup>3-</sup>, and [M-4H]<sup>4-</sup> peaks, respectively; suggesting the compound still contained four acidic groups. HRMS was then employed to obtain a molecular weight of 1108.135  $\pm$  0.001 Da, which was used to calculate a chemical formula of C<sub>61</sub>H<sub>40</sub>O<sub>13</sub>S<sub>4</sub>. In the <sup>1</sup>H NMR spectrum of **sPP** (**Figure S4**). A series of four doublets (1-4) were observed, and the corresponding 2D COSY spectrum (**Figure S21**) 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

#### **Chemistry of Materials**

aromatic protons (5-8), attributed to an *ortho*-substituted aromatic ring. Lastly, a resonance at 191.7 ppm observed in the <sup>13</sup>C NMR spectrum (**Figure S23**) suggests that **a3** contains a ketone. With this information, it is proposed that **a3** contains a fluorenone substructure as shown in **Figure 3d**. An unusually low chemical shift at 6.2 ppm was observed for  $H_5$  of **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 NOE, as outlined in **Figure 3c**. A similar compound (**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** (with the exception of compounds **a1/b1** and **a4/b4**) were characterized. The total characterization for each compound is provided in the Supporting Information.



Figure 3: Characterization of degradation product a3. (a) <sup>1</sup>H NMR spectrum; (b) MS spectrum; (c) Selective <sup>1</sup>H 1D NOE irradiation; (d) Chemical structure of b3.

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.<sup>39,50,58,59</sup> The oxidation of phenyl rings

#### **Chemistry of Materials**

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** 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<sub>3</sub><sup>-</sup>, however no evidence for this degradation product was detected.<sup>52</sup>

HPLC was used to analyze the evolution of each degradation product over the course of 120 hours (Figure 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.<sup>39</sup> 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 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 sPP.



Figure 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<sub>2</sub>O<sub>2</sub> at 0.70% and 130 °C. H<sub>2</sub>O<sub>2</sub> was added every 24 hours. See Scheme 2 for respective chemical structures.

The major degradation routes of **sPP** appear to originate at both the sulfonated phenyl (**Scheme** 2, route a) and non-sulfonated phenyl rings (**Scheme 2**, route b). Even when exposed to  $H_2O_2$  at much lower concentrations and temperatures (e.g., 4 equivalents, 0.30%, and 80°C), the degradation route of **sPP** did not change (see Figure S31). In all cases, it began with the oxidation of a pendant phenyl ring, initiated by radical addition of HO• to form a hydroxycyclohexadienyl radical, which then leads to the formation of hydroxylated **sPP** (**a1** and **b1**) via elimination of H• (as HOO• through reaction with  $O_2$ ).



Scheme 2: HO<sup>•</sup> radical-induced oxidative degradation of sPP. <sup>a</sup> Products detected only by Mass Spectrometry.

Having established that carboxylic acids a2 and b2, fluorenones a3 and b3, and dicarboxylic acids 5 and 6 (Scheme 2) are intermediate species in the degradation process, and that they arise from oxidation of pendant phenyl rings, it is postulated that carboxylic acids **a2** and **b2** may be formed through the oxidation of phenols **a1** and **b1**, or via ring-opening of a hydroxycyclohexadienyl radical intermediate (see B, Scheme 1). Once formed, a2 and b2 undergo an acid-catalyzed intramolecular Friedel-Crafts acylation reaction forming fluorenones a3 and b3. Similar acylation reactions have previously been observed for aromatic polymers.<sup>60–62</sup> Upon reaction with H<sub>2</sub>O<sub>2</sub>, fluorenones **a3** and **b3** undergo a Baever-Villiger oxidation to form lactones a4 and b4, which were only detectable via mass spectrometry. In the presence of H<sub>2</sub>O<sub>2</sub> and under acidic conditions, fluorenone has been shown to undergo a Baeyer-Villiger reaction forming the corresponding lactone.<sup>63</sup> It is proposed that upon further oxidation, lactones **a4** and **b4** 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.

#### **Chemistry of Materials**

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 ( $k = 1.6 \times 10^9$ ).<sup>64</sup> 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 a degradation product, while oxidation of a sulfonated phenyl ring may lead to the 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 3: 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 3) 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 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.<sup>53–55</sup>

## **Degradation of sPPP polymer – Mechanism**

Having rationalized a degradation mechanism for **sPP**, the analogous **sPPP** polymer was subjected to degradation experiments using  $H_2O_2$  concentrations of 0.07%, 0.15%, and 0.35%, and heated to 80°C for 100 hours to ensure complete decomposition of  $H_2O_2$  and to ensure radicals were generated at a relatively low rate. The results from this experiment are outlined in **Figures 5** and **6**. After degrading **sPPP** with 0.35%  $H_2O_2$ , two doublets were observed in the <sup>1</sup>H NMR spectrum (**Figure 5b**) at 7.9 and 8.1 ppm, matching the NMR pattern for sulfobenzoic acid. No other significant changes  in the <sup>1</sup>H NMR spectra were observed. ATR-IR analysis (**Figure 5c**) revealed a broad carbonyl stretch near 1690 cm<sup>-1</sup>, 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 H<sub>2</sub>O/H<sub>3</sub>O<sup>+</sup> deformation mode. After degradation with H<sub>2</sub>O<sub>2</sub>, observed changes in the GPC chromatograms (**Figure 5a** and **Table 1**) show minimal changes in peak shape, with small shifts of the entire peak. Upon degrading **sPPP** with 0.07% H<sub>2</sub>O<sub>2</sub>, GPC analysis revealed a decrease in the *M<sub>w</sub>* from 156,400 Da to 98,500 Da, and the *M<sub>n</sub>* from 109,900 to 95,700. When the amount of H<sub>2</sub>O<sub>2</sub> was increased by a factor of 5 to 0.35% H<sub>2</sub>O<sub>2</sub>, the *M<sub>w</sub>* and *M<sub>n</sub>* only decreased to 82,800 Da and 77,600 Da, respectively.



Figure 5: Hydroxyl radical-induced changes in sPPP after reaction with H<sub>2</sub>O<sub>2</sub> at 80°C for 100 hours. (a) GPC (UV) curves; (b) <sup>1</sup>H NMR spectrum; (c) ATR-IR spectrum.

Table 1: GPC molecular weight data of sPPP after reaction with H<sub>2</sub>O<sub>2</sub> at 80°C for 100 hours.

H <sub>2</sub> O <sub>2</sub>	$M_{\rm w}({\rm Da})$	$M_{\rm n}$ (Da)	Ð
(%)			
0	156,400	109,900	1.42
0.07	98,500	95,700	1.03
0.15	90,500	86,900	1.04
0.35	82,800	77,600	1.07

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 14

### **Chemistry of Materials**

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 4**). 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 4: Proposed hydroxyl radical-induced oxidative degradation route of sPPP polymers.

## Conclusion

In summary, we elucidate the route of free radical degradation of sulfonated phenylated polyphenylenes (**sPPP**) using a structurally-analogous oligophenylene model compound **sPP** which mimics the structural motifs of sPPP. 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. The results obtained in this paper suggest the addition of electron withdrawing groups to phenyl rings may serve to enhance the chemical stability of hydrocarbon polymer electrolyte membranes. 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.

## **Associated Content**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 15

All characterization data for sPPP, degraded sPPP, sPP, a2, b2, a3, b3, 4, 5, 6, 7, 8, and 9,

HPLC traces for **sPP** and degraded **sPP**, FTIR-ATR for **sPPP** and degraded **sPPP**.

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Page 19 of 23

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# **TOC Graphic**

