Accelerated Simulation of the Degradation Process of Poly(arylene ether ketone)s Containing Alkylsulfonated Side Chain Used as a Proton Exchange Membrane

Dong Liu$^a$, Jiamin Li$^a$, Jiangpeng Ni$^a$, Xiongzhi Xiang$^a$, Bin Liu$^{a,b,*}$, Lei Wang$^{a,b,*}$

$^a$ Shenzhen Key Laboratory of Polymer Science and Technology, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China

$^b$ Guangdong Research Center for Interfacial Engineering of Functional Materials, Shenzhen University, Shenzhen 518060, China

Corresponding author:

Lei Wang, E-mail: wl@szu.edu.cn; Bin Liu, E-mail: bliu@szu.edu.cn

Manuscript [to be] submitted to RSC Advances
**Synthesis of poly(arylene ether sulfones) containing methoxy groups, MPAEK.**

To a 50 mL round-bottom three-neck flask fitted with a magnetic stirrer, nitrogen inlet/outlet, Dean-stark trap, and condenser were added BPF (0.9387 g, 2.68 mmol), DMHF (0.6208 g, 1.32 mmol), DFBP (0.8726 g, 4.00 mmol), anhydrous potassium carbonate (0.828 g, 6.00 mmol), toluene (12.0 mL), and DMAc (10.0 mL). The reaction mixture was stirred for 10 min under nitrogen. The reaction mixture was heated at 150 °C (oil bath temperature) for approximately 4 h to remove water and then at 180 °C for 12 h to remove toluene. To the resulting thick mixture was added 5 mL of DMAc, and the prepared polymer was precipitated by slowly pouring the mixture into 100 mL of a mixed solution of deionized water, methanol and 2 mL of HCl. To remove inorganic salts, the precipitates were repeatedly washed with deionized water. The white solid polymer was dried at 110 °C under vacuum for 24 h (yield: 90%). $^1$H NMR (400 MHz, CDCl$_3$; ppm): 7.86-7.68 (m, 3.84H), 7.56-7.51 (d, 0.57H), 7.48-7.29 (m, 3.65H), 7.26-7.20 (d, 1.67H), 7.04-6.84 (m, 4.31H), 6.56-6.47 (s, 1H), 3.84-3.54 (m, 3.2H).

**Synthesis of poly(arylene ether sulfones) containing hydroxyl groups, HPAEK.**

To a 250 mL three-neck flask fitted with a magnetic stirrer maintained under a flow of nitrogen was charged 5.0 g of MPAEK and 100 mL of CH$_2$Cl$_2$. BBr$_3$ (3 mL) was diluted with CH$_2$Cl$_2$ (30 mL) and dropped cautiously into the MPAEK solution in an ice bath over 6 h. The resultant solid copolymer (HPAEK) was filtered, washed with water and methanol, and dried for 24 h at 100 °C under vacuum (yield: 93%). $^1$H NMR (400 MHz, DMSO-$d_6$; ppm): 9.53-9.30 (m, 1H), 8.32-6.64 (m, 10H), 6.48-6.00
Synthesis of poly(arylene ether sulfones) containing alkylsulfonated side chains, SPAEK. One gram of HPAEK and 0.3 g of NaOH were added to 30 mL of DMSO under a nitrogen atmosphere and then stirred at room temperature for 2 h. The reaction was heated to 100 °C for an additional 12 h and then charged with 1 mL of 1,4-butanesultone. The resultant mixture was slowly poured into boiling deionized water and then dried under vacuum atmosphere at 100 °C for 24 h. 1H NMR (400 MHz, DMSO-\textit{d}_6; ppm): 8.09-7.80 (s, 2H), 7.79-7.53 (s, 4H), 7.52-7.25 (m, 5H), 7.24-7.11 (s, 2H), 7.09-6.93 (m, 4H), 6.92-6.53 (m, 1H), 3.98-3.59 (s, 2H), 2.46-2.14 (m, 2H), 1.86-1.28 (m, 4H).

Characterization of MPAEK, HPAEK and SPAEK

The 1H NMR spectrum (in CDCl₃) of the MPAEK polymer is shown in Figure S1. The occurrence of peaks at approximately 3.55 ppm indicates that the copolymers contained a DMHF moiety. The –OCH₃ groups were converted to reactive –OH groups using BBr₃ in CH₂Cl₂. Although the MPAEKs were readily soluble in CH₂Cl₂, the resultant HPAEKs remained undissolved due to the chemical polarity of the –OH groups. MPAEK turned into HPAEK (Scheme 1) and resulted in precipitation from the solution of CH₂Cl₂ [1].

As shown in Figure S2, comparing the 1H NMR spectra of the MPAEK and HPAEK copolymers reveals that the proton peaks (–OCH₃) at 3.55 ppm completely disappeared, and the proton peaks (–OH) appeared at 9.43 ppm. Varieties of side-
chain PEMs with sulfoalkyl functional groups in each hydrophilic monomer have been synthesized using a copolymerization method [2, 3] or by subsequently chemically introducing neo-pendant groups to polymers [4-6]. SPAEK was prepared by adding 1,4-butanesultone to HPAEK in NaOH. The chemical structures of SPAEK were verified by \(^1\)H NMR (Figure S3). As expected, the peak (–OH) at 9.43 ppm completely disappeared, and the peaks of the four sulfobutyl methylene groups (H\(_j\), H\(_k\), H\(_l\), H\(_m\)) appeared at lower frequencies.

**Density, ion-exchange capacity (IEC), dimensional stability and water uptake.**

The related properties of the membranes were measured according to methods reported in the literature [7]. The IEC (1.43 mequiv. g\(^{-1}\), Table S1) corresponded to its theoretical value, indicating an almost quantitative sulfobutylation reaction. As shown in Figure S4, the swelling ratio and water uptake (wt%) of the membrane demonstrate the relatively good dimensional stability of the membrane at different temperatures.
Table S1 Properties of Nafion 117 and the SPAEK membrane

<table>
<thead>
<tr>
<th></th>
<th>Conductivity ($10^{-2}$ S cm$^{-1}$)</th>
<th>Density (g cm$^{-3}$)</th>
<th>Oxidation Stability (h)</th>
<th>Tensile Strength (MPa)</th>
<th>IEC (meq g$^{-1}$)</th>
<th>IEC (meq g$^{-1}$)</th>
<th>Mw$^b$ ($\times 10^5$)</th>
<th>Mn$^b$ ($\times 10^5$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPAEK</td>
<td>15.60</td>
<td>1.24$^B$</td>
<td>35$^C$</td>
<td>26.55</td>
<td>1.8085</td>
<td>1.4303</td>
<td>7.34</td>
<td>6.47</td>
</tr>
<tr>
<td></td>
<td>10.08$^E$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nafion 117</td>
<td>1.98$^E$</td>
<td>&gt;8$^E$</td>
<td></td>
<td>25.7$^E$</td>
<td>0.91$^E$</td>
<td>0.91$^E$</td>
<td>NR</td>
<td>NR</td>
</tr>
</tbody>
</table>

$^A$ Measured at 30 °C. $^B$ Based on a dry state. $^D$ Measured at room temperature. $^E$ Data taken from Ref.[8]. $^C$ Measured at room temperature and 100% relative humidity (RH) for the hydrated membrane samples. $^F$ The theoretical IEC. $^G$ The experimental IEC. NR, not reported.
Figure S1 $^1$H NMR spectrum of MPAEK
Figure S2 $^1$H NMR spectrum of HPAEK
Figure S3 $^1$H NMR spectrum of SPAEK
Figure S4 Water uptake and swelling ratio of the membrane
References


