



**Synthesis and characterization of crosslink-free highly sulfonated multi-block poly(arylene ether sulfone) multi-block membranes for fuel cells**

Journal:	<i>Journal of Materials Chemistry A</i>
Manuscript ID:	TA-COM-11-2014-005887.R1
Article Type:	Communication
Date Submitted by the Author:	25-Nov-2014
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## COMMUNICATION

# Synthesis and characterization of crosslink-free highly sulfonated multi-block poly(arylene ether sulfone) multi-block membranes for fuel cells

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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**A block sulfonated poly(arylene ether sulfone) copolymer (SPAES) was synthesized through nucleophilic aromatic substitution between hydrophilic and hydrophobic oligomeric precursors. Highly sulfonated hydrophilic block polymers were designed and the resultant block membrane showed very high proton conductivity even under low RH: 0.48 and 0.035 S cm<sup>-1</sup> at 90 and 40% RH, respectively, at 80 °C; these values were higher than that of a commercial PFSA membrane. The fuel-cell performance reached 250 mA cm<sup>-2</sup> at 0.7 V at 120 °C, 40% RH, and atmospheric conditions.**

Proton-exchange membrane fuel cells (PEMFCs) have received considerable attention because of their high efficiency and lack of carbon-dioxide emission. PEMFCs generate electricity via an electrochemical reaction between hydrogen and air. Perfluorinated sulfonic acid (PFSA) membranes, such as Nafion® (DuPont) and Aquivion (Solvay), are commonly used because of their high ionic conductivities and excellent mechanical properties; however, their high manufacturing cost and low thermal stability are major drawbacks.

Heat-resistant and inexpensive aromatic hydrocarbon-based membranes seem to be successful potential alternatives to PFSA membranes.<sup>1,2</sup> Although different types of membranes have been tried,<sup>3-6</sup> sulfonated poly(arylene ether sulfone) (SPAES) polymers have mainly been studied in their random or multi-block structures. Recently, multi-block membranes have proven to be successful possibilities for alternative hydrocarbon membranes, although the proton conductivity of random polymers was strongly dependent on RH.<sup>7-9</sup> Well-developed phase separation provided good pathways for water diffusion; hence, improved proton conductivity has been reported even under low RH. More recently, the introduction of highly sulfonated hydrophilic blocks (almost one sulfonic acid per benzene ring) resulted in comparable proton conductivity to

those of PFSA membranes. The higher local concentration of sulfonic acid resulted in well-defined phase separation between the hydrophilic and hydrophobic blocks, and some examples had higher proton conductivity than Nafion throughout the entire RH range.<sup>6,10-13</sup> However, most of these compounds contained crosslinks because decafluorobiphenyl or hexafluorobenzene chain-extenders were used. Crosslinking during polymerization resulted in undesirable low solubility and defects. Without perfluorinated-benzene end-capping reagents, a high molecular weight was very difficult to obtain because of the low reactivity due to the extremely high hydrophilicity of the sulfonated segment blocks.

In this study, we succeeded in synthesizing high-molecular weight SPAES multi-block polymers free from perfluorinated end-groups and crosslinking defects. By increasing the purity of the oligomers and determining the optimum solvent for each segment, polymerization successfully generated high-molecular weight polymers without perfluorinated chain-extenders (Figure 1). The resulting block SPAES membrane showed very high proton conductivity and comparable fuel-cell performance to PFSA membranes under low-RH and high-temperature conditions.

Fluorine-terminated hydrophilic oligomers were synthesized by nucleophilic aromatic substitution under a nitrogen atmosphere [Figure S1]. <sup>1</sup>H and <sup>19</sup>F NMR spectra of the hydrophilic oligomers are shown in Figures S2 and S3, respectively. The small peaks (1, 2, and 3) in the <sup>1</sup>H NMR spectrum represented the end-groups of the aromatic fluorine, and the single peak that appeared in the <sup>19</sup>F NMR spectrum at 103.2 ppm was assigned to the fluorine groups. The progress of the experiment was monitored by gel-permeation chromatography (GPC) [Figure S4]: The targeted molecular weight was obtained after 8 h of reaction. The combination of detailed monitoring and dialysis gave highly pure oligomers with a low polydispersity index (PDI). Owing to the over-estimated molecular weight in the GPC, which

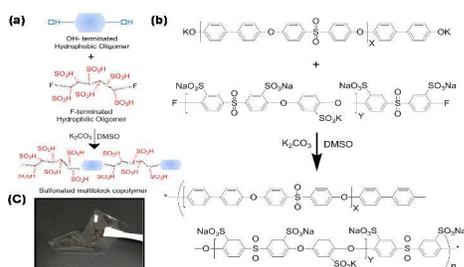


Figure 1. (a) Concept for the multi-block copolymer, (b) synthesis of block SPAES, and (c) block SPAES membrane after casting

originated from repulsion between sulfonic acid groups, a number-average molecular weight was obtained via NMR and was determined to be 5.8 kDa with 1.3 PDI ( $Y = 11$ ) [Table 1].

The hydroxyl-terminated hydrophobic oligomer [Figure S5] was synthesized using the same method as for the hydrophilic oligomer except without dialysis. The reaction was monitored by GPC and conducted for 4 h. The  $^1\text{H}$  NMR spectrum [Figure S6] showed the chemical structure of the hydrophobic oligomer and confirmed the presence of hydroxyl end-groups (small peaks 5, 6, 7, and 8). Also, GPC monitoring confirmed that the molecular weight of the hydrophobic oligomer gradually increased [Figure S7]. Finally, we obtained hydrophobic oligomers with a molecular weight of 6.8 kDa and PDI of 2.4; the repeating unit was calculated to be 12 from the GPC results and ratio between the end-group and main-chain peaks in the  $^1\text{H}$  NMR spectrum.

Figure 2 shows the chemical structure and  $^1\text{H}$  NMR spectrum of multi-block SPAES. The spectrum proved the disappearance of the end-group peaks associated with the starting oligomers, confirming successful polymerization (inverse-triangle and star mark in Figure 2). The GPC monitoring results shown in Figure S8 also proved increasing molecular weight with increasing reaction time. The molecular weight did not increase in the single-solvent system (DMAc or DMSO) because of the different solubility of each oligomer. The combination of different solvents for the hydrophilic and hydrophobic oligomers enhanced the reactivity and increased the molecular weight of the block

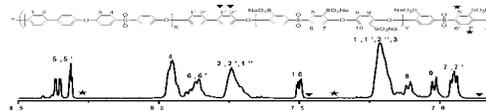


Figure 2.  $^1\text{H}$  NMR spectrum of block SPAES in dimethyl sulfoxide- $d_6$

SPAES (See ESI Figure S10 and Table S1). Their weight-average molecular weight reached 270 kDa, which was sufficient to form robust membranes. We believed that the polymerization was successful in the absence of perfluorinated chain extenders because of the high purity of the oligomers and the two-solvent system. Dialysis was also important to increase the purity of the hydrophilic oligomers; however, this added time and cost to the process. Therefore, more advanced methods are needed before commercial application and scale-up.

The ion-exchange capacity measured from titration was 2.9 meq/g; this value correlated with the NMR results [Table 1] and was similar to the expected value, which reflected successful block copolymerization.

Figure 3 shows the RH dependence of proton conductivity at 80 °C. The proton conductivity was 0.48 and 0.005  $\text{S cm}^{-1}$  at 90 and 20% RH, respectively. Surprisingly, the measured proton conductivity was much higher than that of commercial Nafion and Aquivion membranes: Nafion and Aquivion membranes showed proton conductivities of about 0.11  $\text{S cm}^{-1}$  at 80 °C, which were four times lower than that of SPAES block membranes. The high proton conductivities of the SPAES block membranes were mainly due to the highly localized sulfonated blocks, which could induce highly developed phase separation between the hydrophilic and hydrophobic blocks. The well-formed phase separation might have facilitated the formation of proton pathways within the block copolymers. Similar results were also found in recent research that introduced locally and sulfonated random<sup>14,15</sup> or block copolymers<sup>10,11,13</sup>. However, most of these membranes showed around 0.1 ~ 0.2  $\text{S cm}^{-1}$  at 90 % RH, which was lower than the SPAES membranes.

Lead-stained block SPAES was observed by TEM in order to

Table 1. Properties of oligomers and copolymers

Hydrophobic oligomer			Hydrophilic oligomer			Mn <sup>a</sup> (kDa)	Mw <sup>a</sup> (kDa)	Expected IEC (meq g <sup>-1</sup> )	Experimental IEC (meq g <sup>-1</sup> ) <sup>c</sup>		Water uptake(%) <sup>e</sup>
Mn <sup>a</sup> (kDa)	PDI <sup>a</sup>	X <sup>b</sup>	Mn <sup>b</sup> (kDa)	PDI <sup>a</sup>	Y <sup>b</sup>				NMR	Titration <sup>d</sup>	
6.8	2.4	12	5.8	1.3	11	100	270	2.8	3.1	2.9	390

<sup>a</sup>Measured by GPC <sup>b</sup>Calculated from the  $^1\text{H}$  NMR spectra <sup>c</sup>Acid form <sup>d</sup>Titration using 0.01 M NaOH <sup>e</sup>Acid form in room temperature water

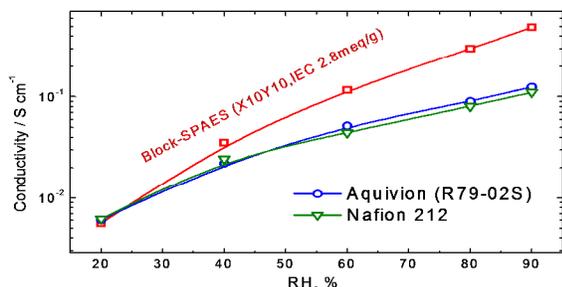


Figure 3. Proton conductivity of block SPAES, Aquivion, and Nafion membranes at 80 °C

investigate the morphology. Figure 4 shows a comparison of TEM images of multi-block SPAES and BPSH (biphenol-based sulfonated poly(arylene ether sulfone)) random polymers; the bright spots indicated hydrophobic clusters, and the dark spots indicate hydrophilic clusters. In contrast with the random polymer, bigger and more well-ordered hydrophilic clusters were evident in the block SPAES. Images of different magnifications also supported the phase separation [Figure S9]. Well-defined phase separation appeared to be responsible for the high proton conductivity even in the low-RH regions.

Fuel-cell performances of the block SPAES membranes were investigated, as shown in Figure 5, and compared with that of Aquivion at 120 °C and 40% RH under H<sub>2</sub>/O<sub>2</sub> atmospheric conditions. Applying the same catalyst layer gave us an exact comparison between the two membranes. The IV curves of both membranes are almost the same and the current density at 0.7 V was about 250 mA cm<sup>-2</sup>. The high proton conductivity of the block SPAES under low-RH and high-temperature conditions was verified by the fuel-cell test. The through-plane conductivity appeared to be as high as the in-plane conductivity. Although a higher FC performance of the block SPAES was expected, both membranes showed a similar performance. Slow water diffusion of the hydrocarbon-based SPAES might inhibit hydration of a membrane to result in lower FC performance. Nevertheless, to our knowledge, this is one of the best fuel-cell performances of a hydrocarbon-based membrane under these severe conditions ever published.

## Conclusions

A crosslink-free multi-block SPAES copolymer was successfully synthesized from hydrophilic and hydrophobic oligomers. Both highly purified oligomers and optimum solvent conditions were necessary to generate the high-molecular weight block SPAES. The presence of well-formed proton pathways from the hydrophilic clusters was confirmed by TEM; these explain the very high proton conductivity even under low RH conditions. The

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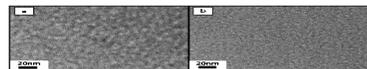


Figure 4. TEM image of (a) block SPAES (IEC 2.8 meq/g) and (b) random BPSH (IEC 2.08 meq/g) membranes.

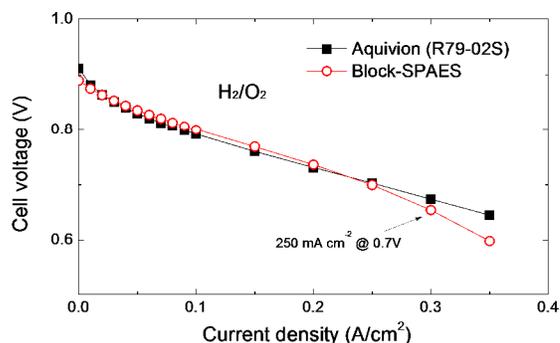


Figure 5. Cell performance of block SPAES (IEC 2.8 meq/g) compared to that of Aquivion (R79-02S) (at 120 °C, 40% RH, atmospheric conditions, same Nafion binders for An/Ca).

cell performance of SPAES was quite close to that of the state-of-the-art Aquivion membrane at 120 °C and 40% RH. This multi-block SPAES could be a strong candidate as an alternative to PFSA membranes for fuel-cell applications above 120 °C.

## Acknowledgements

This work was partly supported by the framework of the Research and Development Program of the Korea Institute of Energy Research (KIER) (B4-2413) and Korea Institute of Energy Technology Evaluation and Planning (KETEP) Grant (20113020030040 and 20123010010090).

## Notes and references

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†Electronic Supplementary Information (ESI) available: Synthetic procedures. See DOI: 10.1039/c00/0000x/

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Text

“Highly sulfonated hydrophilic block polymers were designed and the resultant block membrane showed very high proton conductivity even under low RH”

