

## Anion Exchange Membranes by Bromination of Benzylmethyl-containing Poly (fluorene ether sulfone)s

Wenhai Mei (梅文海), Jingling Yan (阎敬灵), \* and Zhen Wang (王震)

Polymer Composites Engineering Laboratory, Changchun Institute of Applied Chemistry,  
Chinese Academy of Science, Changchun, 130022, China.

\* Corresponding author; Email: jyan@ciac.ac.cn.

### 1. Introduction

Fuel cells are considered as promising energy conversion devices for both stationary and mobile applications. Anion exchange membrane fuel cells (AEMFCs) have been receiving considerable attentions from both academic and industrial communities in recent decades. High performance anion exchange membranes (AEMs) are the key components in the development of AEMFCs.<sup>[1-5]</sup> Here we report the synthesis and characterization of AEMs by bromination of benzylmethyl-containing poly (fluorenyl ether sulfone)s. Poly(sulfone)s with a variety of benzylmethyl content were synthesized by polycondensation of 4-fluorophenyl sulfone, 4, 4'-biphenol, and 9, 9-bis (3, 5-dimethyl-4-hydroxyphenyl) fluorene (DMHPF). Benzyltrimethyl ammonium functionality was then introduced by bromination of benzylmethyl group, followed by amination using trimethylamine. The properties of fluorene-containing AEMs were varied by adjusting the ratio of 4, 4'-biphenol and DMHPF, as well as the amount of brominating reagent. The properties of these AEMs were fully characterized, and the structure-property relationship for this series of AEMs was elucidated.

### 2. Results and discussion

As depicted in Scheme 1, benzylmethyl-containing poly (fluorenyl ether sulfone)s (PFES) were synthesized by polycondensing 4-fluorophenyl sulfone with varied molar ratios (1:0, 0.8:0.2, and 0.6:0.4) of DMHPF and 4, 4'-biphenol. The representative <sup>1</sup>H NMR spectra of plain PFES and brominated FPES (BrPFES) were compared in Figure 1. The bulk water uptake as a function of IEC is plotted in Figure 2. As expected, the water uptakes of PFES-based AEMs increased with the increase of IEC in a non-monotonic style. Figure 4 shows the temperature dependence of water uptakes for QPFES-60-based AEMs. The water uptakes for all AEMs increased linearly with the increasing temperatures. The slopes strongly correlated with IEC and the hydrophobicity of the backbones. For AEMs with similar IEC but different backbone composition, the bicarbonate conductivity followed the trend of QPFES-100>QPFES-80>QPFES-60 in Figure 4. Generally, the trend of conductivity for all AEMs was similar to that of water uptake, which indicated that the bicarbonate conduction in these AEMs was strongly correlated to the bulk water uptakes. The temperature dependence of bicarbonate conductivities of QPFES-60-based AEMs is illustrated in Figure 5. The conductivities increased gradually with increasing temperatures in an Arrhenius mechanism.

### 3. Conclusions

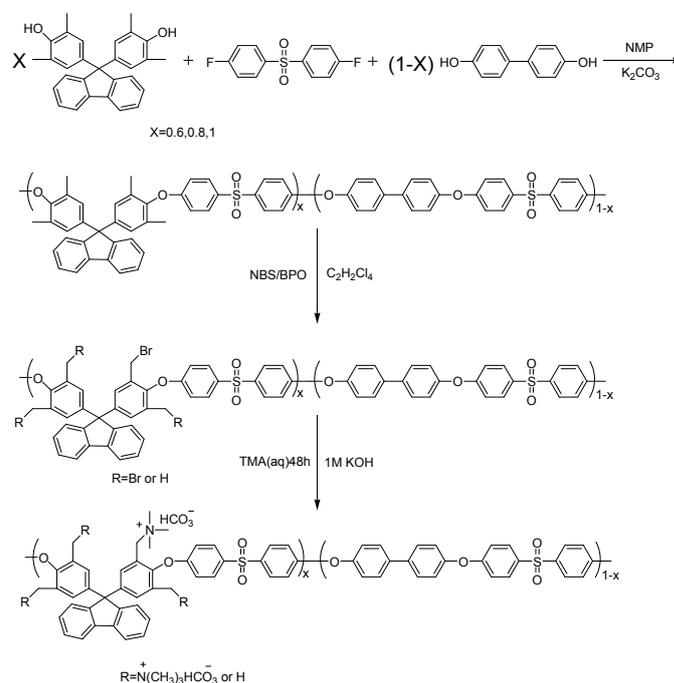
In this work, a series of fluorene-containing AEMs were prepared by bromination of benzylmethyl-containing poly(fluorene ether sulfone)s, followed by quaternization with trimethylamine, and ion exchange. Bromination showed several advantages over chloromethylation such as relatively shorter reaction time, higher efficiency, and higher selectivity. Consequently, the properties of QPFES-based AEMs, such as water uptake and conductivity, can be easily controlled by the amounts of bromination reagent and the ratios of 9, 9-bis (3, 5-dimethyl-4-hydroxyphenyl) fluorene to 4, 4'-biphenol. For a given polymer backbone, water uptakes and ion conductivities increased with the

increasing IEC. AEMs based on copolymer showed better potentials for alkaline fuel cell applications due to a combination of reasonably high conductivities and improved dimensional stability.

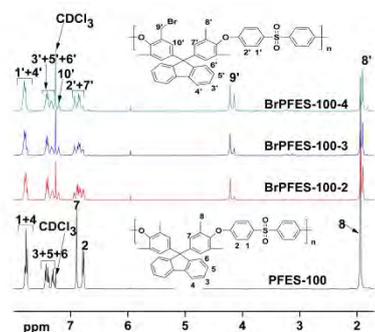
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## References

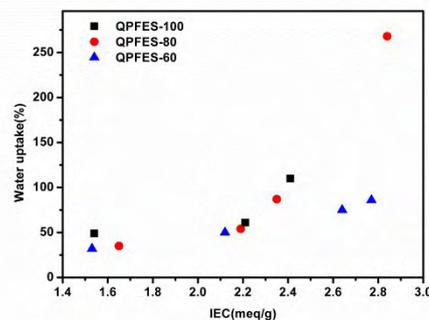
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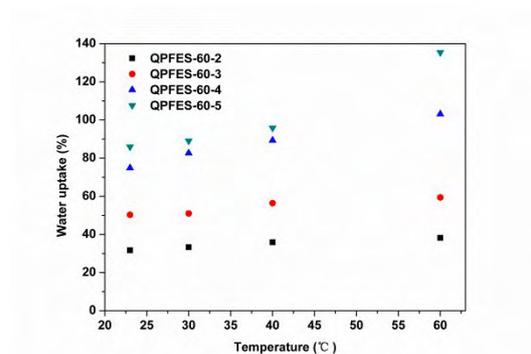
**Scheme 1.** Synthetic routes to PFES-based anion exchange membranes.



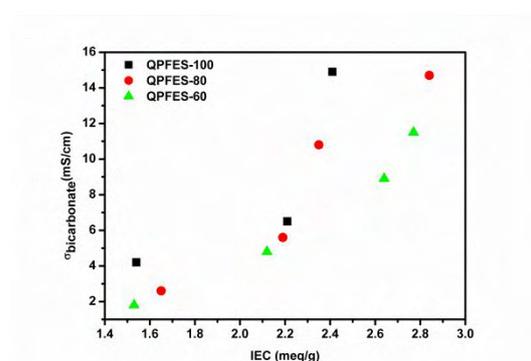
**Figure 1.** The  $^1\text{H}$  NMR spectra of PFES-100 and BrPFES-100.



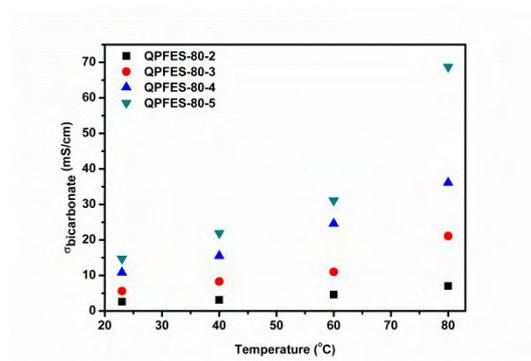
**Figure 2.** Water uptakes as a function of ion exchange capacity (IEC) for PFES-based AEMs.



**Figure 3.** Water uptakes of AEMs based on QPFES-60 as a function of temperature.



**Figure 4.** Bicarbonate conductivities as a function of ion exchange capacity (IEC) for PFES-based AEMs.



**Figure 5.** Bicarbonate conductivities of AEMs based on QPFES-60 as a function of temperature.