Synthesis and Properties of Sulfonated Polyimides from Sulfophenoxy Benzidines

Yoshiki Suto, Yan Yin, Hidetoshi Kita and Ken-ichi Okamoto

Department of Advanced Materials Science & Engineering, Faculty of Engineering, Yamaguchi University, Tokiwadai 2-16-1, Ube, Yamaguchi 755-8611, Japan

Novel sulfonated diamine isomers, 2,2'-bis(4-sulfophenoxy)benzidine (2,2'-BSPOB) and 3,3'-bis(4-sulfophenoxy)benzidine (3,3'-BSPOB), were prepared by direct sulfonation with fuming sulfuric acid from corresponding diamines of 2,2'(or 3,3')-bisphenoxybenzidin. Sulfonated polyimides (SPIs) were synthesized from these sulfonated diamines of BSPOB and 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) via polycondensation. Tough and ductile membranes were obtained by solution casting method. The SPI membranes with reasonable ion exchange capacities (IECs) displayed high proton conductivity and excellent water stability.

Keywords: sulfonated polyimides, proton conductivity, water stability

1. Introduction
In recent years, polymer electrolyte fuel cells (PEFCs) and direct methanol fuel cells (DMFCs) have been attracting great attention as a clean energy technology. Proton-conducting polymer membranes are one of the key materials in fuel cell applications. As alternatives to Nafion, a perfluorinated ionic membrane with high cost and high methanol permeation, many nonfluorinated proton exchange membranes have been studied [1, 2]. Sulfonated polyimides (SPIs) are one of the most promising hydrocarbon polymers suitable for fuel cell applications and have been declared to show high performance [3–5]. In this paper, we report novel SPIs derived from novel sulfonated diamines bearing sulfophenoxy side chains.

2. Method
The novel sulfonated diamine monomers having sulfophenoxy side groups, 2,2'-bis(4-sulfophenoxy)benzidine (2,2'-BSPOB) and 3,3'-bis(4-sulfophenoxy)benzidine (3,3'-BSPOB) were synthesized by direct sulfonation using fuming sulfuric acid at 40 °C for 2 h. The corresponding SPIs were synthesized from these sulfonated diamines and 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) and nonsulfonated diamines via traditional one-step polycondensation method [4]. The chemical structure of the resulting SPIs is shown in Fig. 1.

3. Results
The SPIs had viscosities in the range of 2.1–3.9 dL/g, indicating high molecular weight. The SPI membranes displayed anisotropic dimensional change in water with much larger swelling in thickness than in plane.

Fig. 2 shows relative humidity (RH) dependence of proton conductivity for NTDA-based SPI membranes at 60 °C. The data of Nafion 112 and other SPI membranes, with similar ion exchange capacity (IEC), from sulfonated diamines such as 2,2'-BSPB and BAPBDS are also cited for comparison [4]. It was found that the proton conductivities of all the SPI membranes showed more significant RH dependence than that of Nafion 112. Most of the SPI membranes showed similar or higher conducting performance than Nafion 112 at higher RHs. The co-SPI membrane
of NTDA-2,2’-BSPOB/BAPB (2/1) displayed slightly higher proton conductivity than other co-SPIs, with similar IEC values. This membrane also exhibited high conductivity values of 0.4–0.5 S/cm in water at 130–140 °C, indicating high potential for PEFCs at high temperature.

To investigate the membrane stability under fuel cell condition, the SPI membranes were subject to aging experiment at high temperature in water. Table 1 lists the mechanical properties against the aging at 130 °C. It can be seen that after the aging treatment, the proton conductivity of the co-SPI membranes almost did not change under various moisture condition.

All the SPI membranes displayed decreases in elongation-at-break (EB) at the first stage of aging, for example, after aging for 24 h. This was due to the reduced effect of polymer chain entanglement as a result of polymer chain scission. However, the EB values did not decrease much more with the further aging. After aging for 200–300 h, the maximum stress (MS) of the 2,2′-BSPOB-based co-SPI membrane maintained reasonable high values above 60 MPa, which was about twice that of the BAPBDS-based one, suggesting good mechanical properties and excellent water stability which is favorable for fuel cell applications.

**Table 1** Properties of NTDA-based SPI membranes before and after aging in water at 130 °C.

<table>
<thead>
<tr>
<th>NTDA-based SPIs</th>
<th>(η)* (DL/g)</th>
<th>Aging time (h)</th>
<th>90% RH (σ) (mS/cm)</th>
<th>70% RH (σ) (mS/cm)</th>
<th>50% RH (σ) (mS/cm)</th>
<th>YM* (GPa)</th>
<th>MS* (MPa)</th>
<th>EB (EB%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2′-BSPOB/BAPB (2/1)</td>
<td>3.9</td>
<td>0</td>
<td>168 128</td>
<td>128 30</td>
<td>2.9 122 45</td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td></td>
<td>192</td>
<td>167 128</td>
<td>128 28</td>
<td>2.4 69 9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2′-BSPOB/BAPBz (1/1)-s</td>
<td>2.9</td>
<td>0</td>
<td>118 14</td>
<td>14 2.2</td>
<td>2.3 94 37</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>300</td>
<td>120 10</td>
<td>10 3.0</td>
<td>2.2 64 11</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>3,3′-BSPOB/BAPB (2/1)</td>
<td>2.1</td>
<td>0</td>
<td>143 104</td>
<td>17 2.0</td>
<td>2.5 111 35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>192</td>
<td>142 92</td>
<td>22 2.6</td>
<td>2.1 60 8</td>
<td></td>
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<tr>
<td>BAPBDS/BAPB (2/1)</td>
<td>2.7</td>
<td>0</td>
<td>117 94</td>
<td>18 2.3</td>
<td>1.2 100 120</td>
<td>0.81 40</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>48</td>
<td>91 86</td>
<td>16 2.1</td>
<td>0.81 40 6</td>
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<tr>
<td></td>
<td></td>
<td>96</td>
<td>–</td>
<td>–</td>
<td>0.61 34 6</td>
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</tbody>
</table>

*At 35 °C with 0.5 g/dL in m-Cresol. bAt 50 °C. bYM, MS, EB refer to Young’s modulus, maximum stress and elongation at break, respectively.

4. Conclusion

Novel SPI membranes containing sulfophenoxy side chains were successfully synthesized. They displayed high proton conducting performance and good water stability.

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**References**