

## Preparation of Hyperbranched Aromatic Poly(ethersulfone)s Possessing Sulfonic Acid Terminal Groups for Polymer Electrolyte

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Hyperbranched poly(ethersulfone) (HPES) having terminal sulfonic acid group was synthesized from 2,6-bis(*p*-sodium sulfophenoxy)benzonitrile. These films of polymer blend of HPES and polyvinyl alcohol (PVA) exhibited the proton transportation ability.

New polymer film electrolytes such as sulfonated polymer films and strong acid doped or blend polymer films have been already reported as alternative materials to perfluorosulfonated polymer films,<sup>1</sup> which are the key electrolyte films generally used for the fuel cell. Because hyperbranched polymers, in contrast with the conventional linear polymers, have not only a low level of crystallinity and low viscosity, but also many terminals whose number increases with increasing the molecular weight, enormously sulfonated polymers can be prepared from  $AB_x$  type sulfonated monomers. On the other hand, polymer blend electrolyte films have excellent physical and chemical properties such as modulus, toughness, processability, and chemical resistance by selection of the ingenious pairing polymers. Thinking about the properties of the hyperbranched polymers, they seem to be an excellent candidate for polymer blend.<sup>2,3</sup>

In this paper, we report the preparation and properties of hyperbranched poly(ethersulfone) (HPES) having sulfonic acid terminal group by one step polymerization of a novel  $AB_2$  monomer. Polymer blend films of HPES and polyvinyl alcohol (PVA) were then prepared to measure the proton flux.<sup>4</sup>

As shown in Eq 1, HPES was prepared by self-polycondensation of 2,6-bis(*p*-sodium sulfophenoxy) benzonitrile **1**,<sup>5</sup> which was obtained by condensation of *p*-sodium hydroxybenzene sulfonic acid and 2,6-dichloro benzonitrile using of potassium carbonate as the base. The polycondensation was carried out in the presence of the mixture of phosphorus pentoxide and methane sulfonic acid (PPMA) as the condensing agent as well as solvent<sup>6</sup> at 140 °C for 24 h. The resulting reaction mixture was poured into water and the obtained aqueous solution was dialyzed to remove low molecular materials. HPES was isolated by the freeze-drying technique and then dried under vacuum at 100 °C for 8 h in the presence of  $P_2O_5$ . A brown powdery product was obtained in 92% yield (**2** in Table 1). Polymer **2** was soluble in DMSO and water.

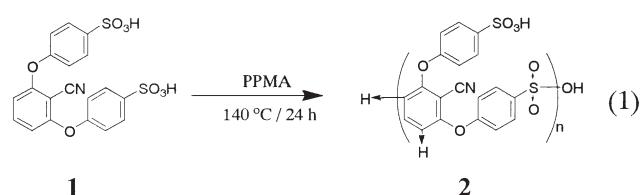
**Table 1.** Results of polycondensation

Run	Yield / %	$\eta_{inh}^a$ / dL/g	$M_w^b$ / $M_w/M_n$	$T_0/T_5$ / °C <sup>c</sup>	EW / g/mol
<b>2</b>	92	0.25	—	275/311	436
<b>3</b>	89	0.14	$4.4 \times 10^4$ (1.30)	285/325	—

<sup>a</sup>Measured at a concentration of 0.5 g/dL in NMP at 30 °C.

<sup>b</sup>Determined by GPC measurements in DMF containing lithium bromide (0.01 mol/L) as an eluent.

<sup>c</sup>Determined by TGA and DSC at a heating rate of 10 °C in  $N_2$ .



**1**

**2**

The structure of polymer **2** was elucidated using  $^1H$  NMR and IR measurements. In the  $^1H$  NMR spectrum, all peaks were appeared between 6.5–8.8 ppm, which didn't separate clearly. In the IR spectrum of polymer **2**, characteristic absorptions were observed at 1317 and 1225  $cm^{-1}$  assigned as sulfone in the main chain unit and the terminal sulfonic acid groups, respectively. It was worth to note that carbonyl group absorptions were observed at 1654  $cm^{-1}$  as well as the cyano absorption at 2233  $cm^{-1}$ . This fact suggested partial hydrolysis of the nitrile group under the polymerization condition. An equivalent weight of polymer **2** per one proton was calculated to be 436 g/mol by the titration using the aqueous sodium hydroxide solution. This value was almost the same as the calculated for polymer **2**.

Anisole-terminated HPES **3** was prepared by addition of anisole in the end of the self-polymerization of **1** to measure the molecular weight of the polymer. The molecular weight ( $M_w$ ) and the molecular weight distribution ( $M_w/M_n$ ) of polymer **3** were determined as  $4.4 \times 10^4$  and 1.30.

The TG curve of polymer **2** showed the weight loss for hydrated water between 100 °C and 160 °C, the terminal decomposition at 275 °C, and the 5% weight loss at 310 °C. The glass transition temperature was not clearly observed.

As the self-standing film of polymer **2** could not be obtained, that of polymer **2** and PVA ( $DP = 1750 \pm 50$ ) blend was prepared by casting the aqueous solution of them onto a glass plate in the presence of glutaraldehyde as a cross-linking agent for PVA. The films containing polymer **2** of 10–50% were prepared as shown in Table 2. The blend films were transparent and brown with highly swollen nature. Although, in general, water content increases with increasing the number of sulfonic acid, PVA-50 showed lower amount of the water content compared with PVA-33. In the case of PVA-50, as the more number of sulfonic acid catalyzed the cross-linking reaction more effectively, water in the film might be squeezed because of the higher number of cross-linked points. The ion exchange capacities (IEC) of the blend films were calculated to be the range of 0.3–1.2 by titration, where the values increased with increasing the proportion of polymer **2**.

To measure the proton fluxes<sup>4</sup> the blend films were set as a separator between two cell compartments filled with the deionized water and the hydrochloric acid aqueous solution (0.01 mol/L), respectively. The proton fluxes between two cells by the concentration difference diffusion were measured by mon-

**Table 2.** Characterization of the films composed of Polymer **2** and PVA

Film	PVA/g	Polymer <b>2</b> /g	Glutaraldehyde/g	Thickness/ $\mu$ m	Water content <sup>a</sup>	IEC <sup>b</sup>
PVA-10	0.04	0.005	0.01	70	0.59	0.31
PVA-25	0.04	0.017	0.01	80	0.92	0.65
PVA-33	0.04	0.025	0.01	75	1.01	0.80
PVA-50	0.04	0.05	0.01	100	0.67	1.2

<sup>a</sup>Water content was calculated from the following equation,  $W_c = (W_{\text{wet}} - W_{\text{dry}})/W_{\text{wet}}$ .

<sup>b</sup>Ion exchange capacity was calculated by titration.

itoring the pH value of the deionized water. As shown in Figure 1, the proton fluxes of the blend films increased with increasing the polymer **2** content, showing  $2.5 \times 10^{-9}$  mol/s·cm<sup>2</sup> in the case of PVA-50. This value was one digit smaller than the commercially available proton transport membrane.<sup>7</sup> It is thought that the value of the fluxes may be improved by using less water content polymers instead of PVA. On the other hand, the proton flux of

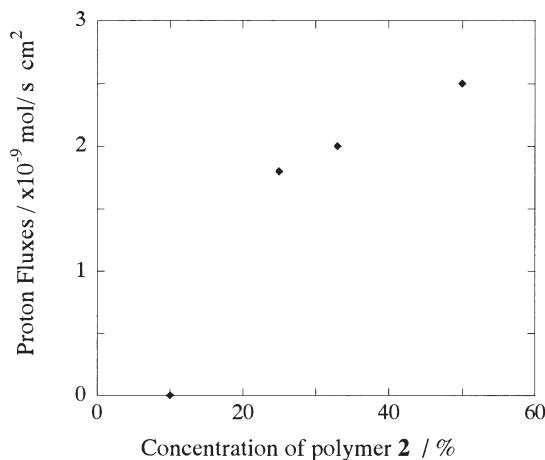
PVA-10 was too small to measure the variation of pH, because the effective proton conduction passing was not formed in the film of PVA-10.

In summary, the novel HPES having terminal sulfonic acid group was newly synthesized. It was applied to prepare the complex electrolyte film by blending with PVA and glutaraldehyde to measure proton fluxes.

We are indebted to Professor Akihiko Tanioka for the performance of the proton flux experiments.

#### References and Notes

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- 5 Resulting product was washed by methanol and recrystallized by water. Yield: 86%. <sup>1</sup>H NMR (DMSO)  $\delta$ : 7.70(4H, d), 7.54(1H, t), 7.15(4H, d), 6.63(2H, d).
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**Figure 1.** Proton fluxes vs concentration of polymer **2**.