

# Synthesis and Properties of Novel Side-Chain-Type Sulfonated Polyimides

Zhaoxia Hu<sup>a</sup>, Yan Yin<sup>b</sup>, Shouwen Chen<sup>a</sup>, Otoo Yamada<sup>b</sup>, Kazuhiro Tanaka<sup>a</sup>,  
Hidetoshi Kita<sup>a</sup> and Kenichi Okamoto<sup>a\*</sup>

<sup>a</sup>*Department of Advanced Materials Science & Engineering, Faculty of Engineering, Yamaguchi University.* <sup>b</sup>*Venture Business Laboratory, Yamaguchi University, Tokiwadai 2-16-1, Ube, Yamaguchi 755-8611, Japan*  
Fax: +81-836-85-9660; E-mail: [okamotok@yamaguchi-u.ac.jp](mailto:okamotok@yamaguchi-u.ac.jp)

**Summary:** A series of novel sulfonated co-polyimides were synthesized from 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA), novel side-chain-type sulfonated diamines of 3,5-diamino-3'-sulfo-4'-(4-sulfophenoxy)benzophenone, 3,5-diamino-3'-sulfo-4'-(2,4-disulfo phenoxy) benzophenone and nonsulfonated diamines. The resulting copolyimide membranes showed high thermal stability and reasonably high proton conductivity even in the range of low relative humidity.

## Introduction

Polymer electrolyte fuel cells (PEFCs) are the most promising power sources in the future because of their high energy-efficiency and environmental friendship. Over the past decades, intensive researches have been focused on developing new materials as polymer electrolyte, especially sulfonated hydrocarbon polymers.<sup>[1-3]</sup> Sulfonated polyimides (SPIs) are one of the promising candidates for fuel cell applications because of their good mechanical properties, solvent durability and film forming ability. However, they have a drawback of poor water-stability especially at higher temperatures due to hydrolytic decomposition of imide rings. Therefore, it is essentially important to significantly improve the water-stability of SPI membranes by designing their primary structure and morphology.<sup>[3-10]</sup>

In this study, we report on the synthesis and characterization of novel side-chain-type SPIs based on novel diamines bearing sulfonated aromatic pendant groups, namely, 3,5-diamino-3'-sulfo-4'-(4-sulfophenoxy) benzophenone (DASSPB) and 3,5-diamino-3'-sulfo-4'-(2,4-disulfo phenoxy) benzophenone (DASDSPB).

## Experimental

**Monomer synthesis.** As shown in Scheme 1, the novel side-chain type sulfonated diamines were synthesized from 3,5-dinitrobenzoyl chloride as the starting material by means of Freidel-Crafts acylation, sulfonation, and reduction. The Freidel-Crafts acylation reaction was performed at -10 °C to 30 °C for 12 h. 3,5-dinitrobenzoyl phenyl ether (**1**) was obtained as white solid (yield: 66 %). Sulfonation was conformed at 40°C (6h) and 60°C (8h) for two

diamines, respectively. Reduction was conducted by stannous chloride and hydrochloric acid at 40°C. These diamines were purified by reprecipitation from water/ethanol.

**Polymer synthesis.** To a 100 mL completely dried 3-neck flask equipped with a condenser and nitrogen inlet was charged 1.878 g of DASDSPB (3.6 mmol), 24 mL of *m*-cresol, and 2.1 mL of triethylamine. After DASDSPB was completely dissolved, 1.287 g of NTDA (4.8 mmol) and 1.53 g of benzoic acid were added to the flask. The reaction solution was kept at 80 °C for 4 h and then 180 °C for 5 h. The reaction solution was cooled down to room temperature, and then 15 mL of *m*-cresol, 1.203 g of 2,2'-bis(4-aminophenyl)hexafluoro propane (3.6 mmol), 0.642 g of NTDA (2.4 mmol) and 0.51 g of benzoic acid were successively added to the flask. The reaction mixture was heated at 80 °C for 4 h and then at 180 °C for 15 h. After being cooled to room temperature, the viscous solution was poured into acetone. The precipitated polyimide was collected by filtration, washed with acetone and dried in *vacuo* at 100 °C for 10 h. The chemical structure of sequenced co-SPIs is shown in Fig. 1.

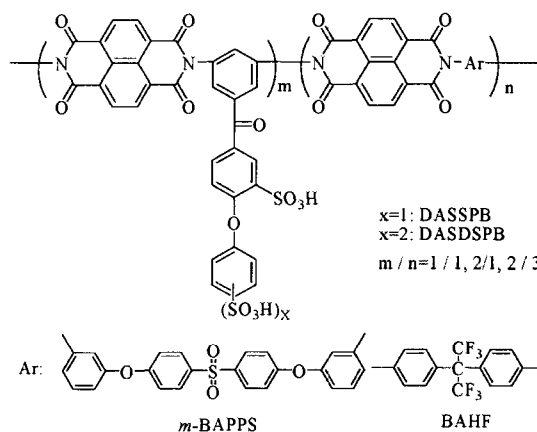
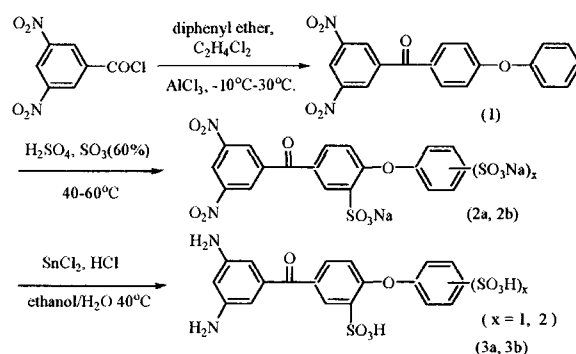


Figure 1. Structure of the sequenced co-SPIs.

**Membrane preparation and measurements.** Membranes were prepared by solution casting from DMSO and proton exchange with 0.5mol/L sulfuric acid, followed by drying in *vacuo* at 150°C for 10h. Thermogravimetry (TG) was measured with a Rigaku TG-8120 in Helium (flow rate: 100cm<sup>3</sup>/min) at a heating rate of 10°C/min. The water vapor sorption isotherms, water uptake (WU), dimensional change in membrane thickness ( $\Delta t_c$ ) and diameter ( $\Delta l_c$ ) were measured according to the method described in reference.<sup>[8]</sup> Proton conductivity was measured using a four-point-probe electrochemical impedance spectroscopy technique over the frequency range from 100Hz to 100KHz (Hioki 3552).

## Results and discussion

In the synthesis of sequenced co-SPIs, the anhydride terminated sulfonated polyimide oligomers were first prepared followed by formation of the nonsulfonated sequence at their both ends. The co-SPIs showed good solubility in



Scheme 1: Synthesis of novel sulfonated diamines with aromatic pendent groups.

common aprotic solvents such as DMSO. Their characterization results are shown in Table 1 and Figures 2 and 3. The first decomposition temperature ( $T_{d1}$ ) attributed to cleavage of sulfonic acid groups (or sulfo-alkoxy groups) was higher for the novel SPIs by more than 50 °C than for **M5**, suggesting much better stability against the cleavage of sulfonic acid groups in hot water for the novel SPIs than for the alkoxy side-chain type SPIs. The novel co-SPI membranes showed the isotropic membrane swelling, it is considered that the novel SPIs with large aromatic pendant groups have rigid molecular structure, which makes the orientation of polymer chains in plane direction somewhat difficult.<sup>19,10)</sup>

**Table 1 Properties of SPI membranes**

No.	SPIs	IEC <sup>a</sup> (meq/g)	WU <sup>c</sup> (%)	Dimensional change		$T_{d1}$ (°C)	$\sigma$ (S/cm) <sup>d</sup> (RH)		
				$\Delta t_c$	$\Delta l_c$		50%	70%	100 %
M1	NTDA-DASSPB/BAHF(2/1)	1.99	60	0.13	0.12	---	0.006 <sup>e</sup>	0.027 <sup>e</sup>	0.11 <sup>e</sup>
M2	NTDA-DASDSPB/BAPPS(1/1)	2.08	62	0.13	0.12	330	0.005	0.026	0.16
M3	NTDA-DASDSPB/BAPPS(2/3)	1.71	49	0.13	0.09	330	0.004	0.017	0.12
M4	NTDA-DASDSPB/BAHF(1/1)	2.24	76	0.12	0.13	305	0.012	0.035	0.19
M5	NTDA-3,3'-BSPB/BAPB(2/1)	2.02	64	0.48	0.03	255	0.001 <sup>e</sup>	0.007 <sup>e</sup>	0.14 <sup>e</sup>
M6	NTDA-BAPBDS/BAPB(2/1)	1.89	51	0.21	0.04	300	0.003 <sup>e</sup>	0.019 <sup>e</sup>	0.11 <sup>e</sup>

<sup>a</sup>Calculated data. <sup>b</sup>Measured at 35 °C in 0.5wt% DMSO solution with 1wt% LiCl. <sup>c</sup>at r.t. <sup>d</sup>at 60 °C. <sup>e</sup>at 50 °C.

Water vapor sorption isotherms of SPI membranes are shown as the plots of the number of water molecules per sulfonic acid group ( $\lambda$ ) vs. water vapor activity ( $a_w$ ) in Fig.2. The  $\lambda$ - $a_w$  isotherms of the novel co-SPIs were similar to that of **M6** rather than **M5**. In the range of  $a_w$  less than 0.8, the  $\lambda$  values were much smaller for **M5** than for the other SPIs. On the other hand, in the range of  $a_w$  above 0.9, the  $\lambda$  values were similar among these three types of SPIs.

Fig. 3 shows the RH dependence of proton conductivity ( $\sigma$ ) for SPI membranes and Nafion 117 at 50 °C. These four membranes had the similar  $\sigma$  values at 100 %RH (in water) but largely different ones at a lower RH, which were in the order of Nafion 117 > **M1** > **M5** > **M6**. In general, a membrane with the well microphase-separated structure tends to have the well-connected hydrophilic domains or proton conducting channels, leading to higher proton conductivity even at a lower RH.<sup>12)</sup> Nafion 117 is a typical example. In spite of the well microphase-separated structure, the alkoxy side-chain-type SPI membranes including **M6** displayed lower proton conductivity in the low RH range, probably because the connection of hydrophilic domain might be less pronounced due to the smaller water sorption. In contrast to **M6**, the novel SPIs including **M1** displayed higher proton conductivity even in the low RH range, which might be due to their favorable morphology.

The proton conductivity was also measured at high temperatures. It was found that the resulting novel SPI membranes showed high  $\sigma$  values at 120 °C and 50-100% RH. For example, M4 displayed  $\sigma$  values of 0.05S/cm and 0.3 S/cm at 50 % and 100 % RH, respectively, at 120 °C, suggesting a potential feasibility for PEFC applications at high temperature.

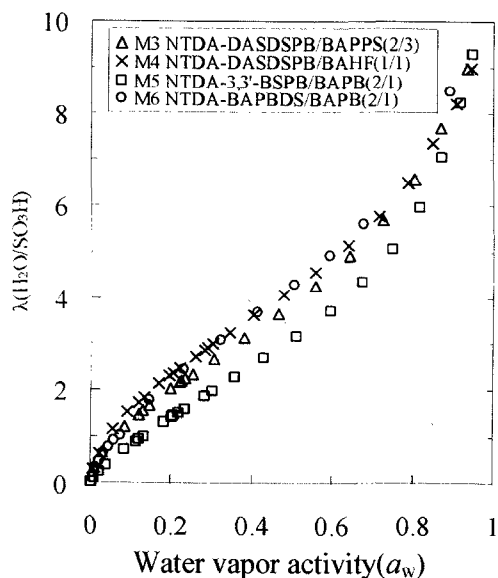


Figure 2. Water vapor sorption isotherms of SPI membranes at 50°C.

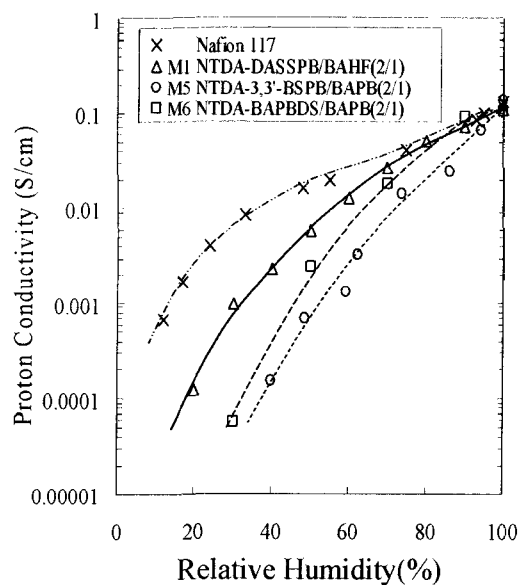


Figure 3. RH dependence of proton conductivity of SPI membranes at 50°C.

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