

Synthesis and Characterization of Block/block Sulfonated Co-polynaphthalimides for Polymer Electrolyte Fuel Cell (PEFC) Applications

Zhaoxia Hu¹, Yan Yin², Ken-ichi Okamoto¹

¹ Graduate School of Science & Engineering, Yamaguchi University, Ube, Yamaguchi, 755-8611, Japan; ² Tianjin University, Tianjin, China, 30072

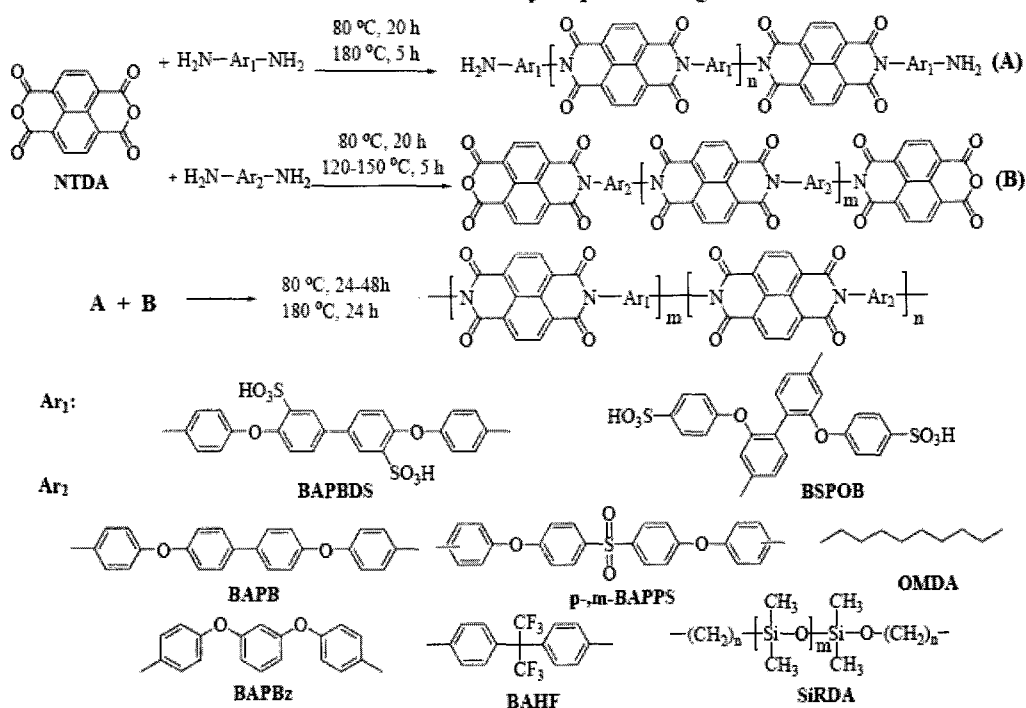
Introduction: Polymer electrolyte fuel cells (PEFCs) are regarded as a promising energy source in the applications for portable and stationary systems, i.e., automotives and small-scale power stations.[1] The need for high performance proton exchange membrane (PEM) materials, serving as the electrolytes and separator for PEFCs, has attracted increasing attention. So far, perfluorinated sulfonic acid polymers (i.e., Nafion of DuPont) are generally acknowledged as PEM materials for PEFCs, but their deteriorated mechanical property at elevated temperatures and high cost intrigued researches on sulfonated aromatic hydrocarbon alternative materials.[2] Among the reported hydrocarbon materials, naphthalene-based sulfonated polynaphthalimides (SPIs) are considered as one of the promising candidates because of their good film-forming ability, high thermal stability, and excellent mechanical properties.[3-9]

Over the last few years, a considerable number of studies have been made on random co-SPIs. Recently, high performance SPI membranes based on sulfonated diamines, 4,4'-bis(4-aminophenoxy) biphenyl-3,3'-disulfonic acid (BAPBDS), 2,2'-bis(4-sulfophenoxy) benzidine (BSPOB) with 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) and non-sulfonated diamines were reported.[3-7] It was found the proton conductivity of the SPI membranes determined not only by their ion exchange capacity (IEC) and polymer's chemical structure, their morphology played a very important role. However, only few attempts have so far been made at block/block structure, which is considered favorable to form microphase-separated morphology. McGrath and his co-workers reported on sulfonated fluorinated block poly(arylene ether)s with well defined phase separation morphology and higher proton conductivity than Nafion at low relative humidity.[10] Taking their flexible and highly fluorine-contained structure into account, this type of polymers are promising alternatives. In regards to naphthalene SPIs, because of their rigid chemical structure, only a few researches on them have been reported by now. Kawakami et.al. reported the lower or similar water uptake and apparently higher proton conductivity of the block SPIs which increased with the increasing of block chain length.[8] Watanabe et.al. reported better proton conduction properties of block SPI membranes over random ones, because of the widespread and well-connected hydrophilic domains confirmed by TEM observations.[9] However, proton conductivity of the resulting b/b SPI membranes were not enhanced satisfactorily to be comparable to fluorinated polymers so far with long block length (>50).

胡朝霞¹, 尹燕², 岡本健一¹ (¹ 山口大院理工 (日本)、² 天津大学 (中国))

Herein, we report the synthesis and characterization of a series of novel block SPIs from BAPBDS or BSPOB with shorter block length. Various nonsulfonated diamines were chosen as the hydrophobic comonomer, and their effects on the morphology and proton conductivity were investigated.

Experimental: Block/block (b/b) co-SPIs were synthesized from traditional high temperature polycondensation by a two-pot method in *m*-cresol as shown in Scheme 1. Anhydride-terminated hydrophobic oligomer and amine-terminated hydrophilic oligomer were synthesized separately and then mixed to carry out copolymerization. The block length was controlled to be 5, 10 or 20 by varying the feed ratio of NTDA to diamines according to the following equation: $\{2l = (r + 1) / (r - 1)\}$, where $r (>1)$ refers to the molar ratio of sulfonated diamine to NTDA for hydrophilic oligomer, or the molar ratio of NTDA to nonsulfonated diamine for hydrophobic oligomer.



Scheme 1: Synthesis and chemical structures of b/b co-SPIs.

Results and discussion: Flexible and self-standing membranes with the thickness of 35-50 μm were obtained by *m*-cresol solution casting. Table 1 lists the IEC, reduced viscosity (η_r), water uptake (*WU*), size change in membrane plane (Δlc) and thickness (Δtc) direction, proton conductivity in membrane plane (σ_p).

Their reduced viscosity was in the range of 1.4-4.1 dL/g, indicating high molecular weight. All the SPI membranes showed anisotropic membrane swelling in water, with larger swelling in thickness direction than in plane direction. The swelling anisotropy was observed hardly changed for the b/b BAPBDS-based SPI membranes comparing to the random ones ($\Delta tc/\Delta lc \approx 3-4$). On the other hand, the BSPOB-based b/b membranes showed much greater anisotropy ($\Delta tc/\Delta lc > 20$) than the random ones ($\Delta tc/\Delta lc \approx 5-10$). The rigid benzidine structure in the BSPOB main-chain is considered the critical factor which leads to their high swelling anisotropy for the BSPOB-based SPI membranes.

Typical SEM image of the block SPI membranes **M1-M4** derived from hydrophobic nonsulfonated comonomers of BAPB, BAPBz, pBAPPS and OMDA showed heterogeneous structure. The

hydrophilic oligomer reaction system was clear through the whole polymerization process. However, the solution turned turbid in the hydrophobic reaction system when block length larger than 5 due to the poor solubility of the hydrophobic oligomers in *m*-cresol. After mixed together, the system still remained turbid. This gives a good account of the opaque appearance of the obtained membranes. On the other hand, b/b SPIs from BAHF, mBAPPS and SiRDA were transparent. TEM images of random (M11-r) and b/b BSPOB-based SPI membranes, (M11-b, M12-b1), are shown in Figure 1. In the TEM images, the bright areas represent hydrophilic (ionic) domains, and the darker areas represent the hydrophobic domains. For M11-r, no contrast was found, suggesting the uniform distribution of the hydrophilic and hydrophobic domains in the membrane. On the other hand, distinguishable contrast of the hydrophilic and hydrophobic domains was observed for M11-b. Hydrophilic domains were well connected and oriented in the membrane plane direction, which was reported for the first time for this type of polymers. For M12-b1, only slight contrast was found. It might due to difference in the hydrophobicity of nonsulfonated diamine moieties and block length.

Table 1: Properties of NTDA-based block/block co-SPIs.

Code	NTDA-based SPIs	IEC ^a (meq/g)	η^b (dL/g)	WT ^c (%)	Size change ^c		σ_p^d (mS/cm)		
					Δt_c	Δl_c	50%	70%RH	in water
M1-r	BAPBDS/BAPB(2/1)-r	1.89(1.86)	4.4	57	0.14	0.05	5.4	29	127
M1-b	BAPBDS/BAPB(10/5)-b	1.89(1.66)	1.6	62	0.24	0.11	6.3	22	154
M2	BAPBDS/pBAPPS(10/5)-b	1.82(1.61)	1.4	55	0.15	0.08	6.2	28	125
M3	BAPBDS/BAPBz(10/6.7)-b	1.80	2.2	62	0.18	0.08	4.9	20	121
M4-r	BAPBDS/OMDA(1/1)-r	1.76	2.0	55	0.16	0.04	1.8	10	113
M4-b	BAPBDS/OMDA(10/10)-b	1.76	2.1	55	0.15	0.01	5.3	18	104
M5	BAPBDS/BAHF(20/10)-b	1.92(1.79)	2.7	79	0.34	0.10	11	36	179
M6	BAPBDS/BAHF(20/13.3)-b	1.76	1.6	65	0.24	0.07	7.3	22	139
M7	BAPBDS/BAHF(20/20)-b	1.51(1.44)	2.2	56	0.25	0.07	6.9	25	123
M8	BAPBDS/SiRDA(10/3.3)-b	1.79(2.37)	1.5	85	0.24	0.15	14	51	232
M9-b1	BAPBDS/SiRDA(20/10)-b	1.79(2.08)	1.9	95	0.21	0.16	11	41	208
M9-b2	BAPBDS/SiRDA(20/10)-b	1.55(2.35)	1.7	100	0.24	0.17	11	42	194
M10	BSPOB/BAPB(2/1)-r	1.88(1.94)	3.9	78	0.39	0.026	7	30	170
M11-r	BSPOB/BAHF(1/1)-r	1.51(1.42)	4.9	57	0.27	0.029	6	24	99
M11-b	BSPOB/BAHF(20/20)-b	1.51(1.42)	2.2	76	0.56	0.03	10	39	156
M12-r	BSPOB/mBAPPS(1/1)-r	1.40	3.0	45	0.16	0.03	3.4	16	75
M12-b1	BSPOB/mBAPPS(10/10)-b	1.40	4.1	60	0.32	0.01	8	31	118
M12-b2	BSPOB/mBAPPS(20/20)-b	1.40			0.34	0.01	5.6	31	145

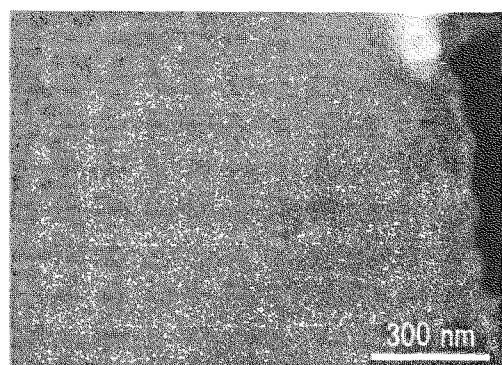
^a Calculated value, experimental value by titration in the parenthesis; ^b 5 wt% at 35 °C in *m*-cresol;

^c at 30 °C; ^d at 60 °C.

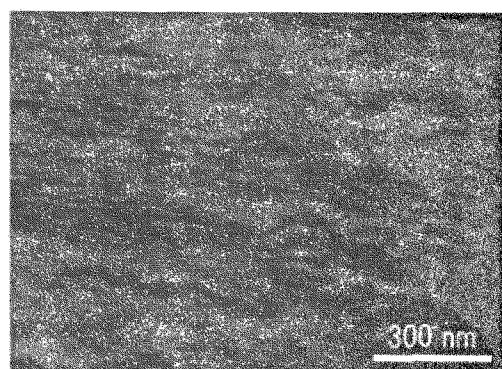
Proton conductivity in plane direction at various relative humidities (RHs) was investigated. (See Figure 2) Several random SPIs were cited for comparison. All turbid b/b SPI membranes showed no improvement in proton conductivity to the random ones. For the transparent ones, the BAPBDS-based b/b SPIs displayed slightly improved proton conductivity at low RHs (< 60 %RH). On the other hand, the BSPOB-based b/b SPIs showed fairly improved proton conductivities. For example, the membrane

of **M11-b** with IEC of 1.56 showed $\sigma_{//}$ values of 2 mS/cm and 10 mS/cm at 30 and 50 %RH, respectively, which are two times of the random one (**M11-r**), 0.7 mS/cm and 6 mS/cm, respectively.

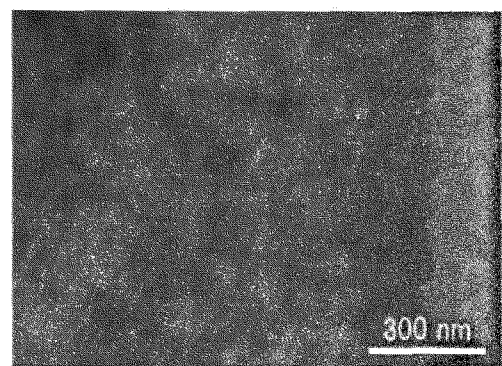
Proton conductivity in water under various temperatures in both directions was investigated for the BSPOB-based SPI membranes. (See Figure 3) Anisotropic proton conduction was observed for all the SPI membranes ($\sigma_{//} > \sigma_{\perp}$). The ratio of $\sigma_{\perp}/\sigma_{//}$ for the b/b SPI membranes was smaller (0.11-0.44) than the random one (0.64), indicating the greater anisotropy of proton conduction for the b/b SPI membranes. Given that microphase-separated structure was observed for the b/b SPI membranes, it seems reasonable to argue that the membrane morphology plays an important role on the proton conduction process. The connective hydrophilic domains oriented in the plane direction for the b/b SPI membranes leads to the better proton conduction in the plane direction, but not in thickness direction.



(A)



(B)



(C)

Figure 1: TEM images of (A) **M11-r**, (B) **M11-b**, and (C) **M12-b1** stained by Cs^+ .

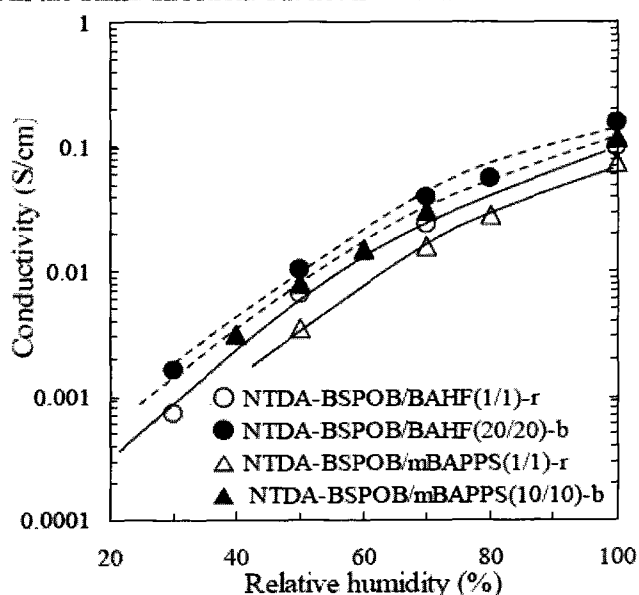


Figure 2: Relative humidity dependence of proton conductivity ($\sigma_{//}$) for SPI membranes at 60 °C.

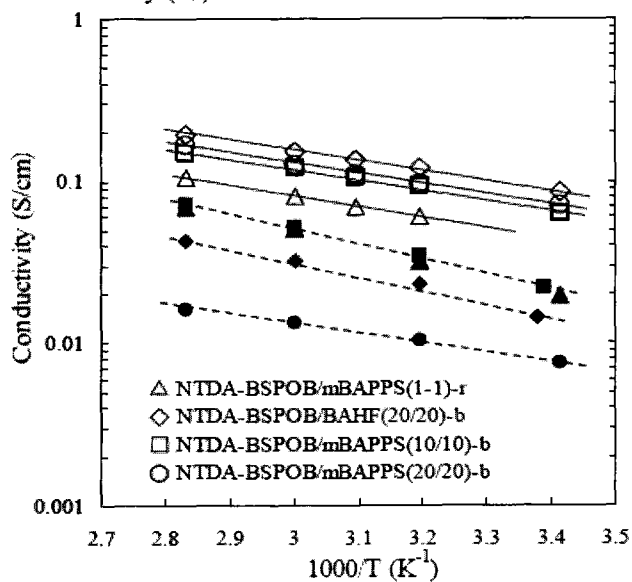


Figure 3: Temperature dependence of proton conductivity for SPI membranes in water. ($\sigma_{//}$: open keys; σ_{\perp} : closed key)

Table 2: Anisotropy of membrane swelling and proton conductivity for SPI membranes.

Code	IEC ^a (meq/g)	Thickness (mm)	WU ^b (g/100g)	Size change ^b		Δt_c	σ (mS/cm) ^c		
				Δt_c	Δl_c		Δl_c	σ_{\perp}	σ_{\parallel}
M1-r	1.89	60	57	0.14	0.05	2.9	74	102	0.73
M1-b	1.89	71	62	0.24	0.11	2.2	97	142	0.68
M5	1.92	64	79	0.34	0.10	3.4	97	179	0.54
M10	1.89	35	78	0.39	0.03	13	118	152	0.78
M11-r	1.51	33	57	0.27	0.03	9.0	—	99	—
M11-b	1.51	58	76	0.56	0.03	19	32	150	0.22
M12-r	1.40	54	45	0.16	0.03	5.3	51	80	0.64
M12-b1	1.40	55	60	0.32	0.01	25	52	120	0.44
M12-b2	1.40	60	—	0.34	0.004	94	14	125	0.11
Nafion 112	0.91	55	39	0.13	0.12	1.1	136	139	0.98

^a Calculated data; ^b At 30 °C; ^c At 60 °C.

Conclusion: B/b NTDA-based SPIs were successfully prepared by a two-pot polymerization method. Morphology of the membranes depended largely on the hydrophobic moieties. Tough and transparent membranes were obtained from the SPIs based on BAHF, mBAPPS and SiRDA nonsulfonated comonomers, while unclear membranes obtained from BAPB, BAPBz, pBAPPS or OMDA. They all showed high thermal stability and good mechanical properties. The b/b SPI membrane of NTDA-BSPOB-BAHF(20/20)-b showed a well defined microphase-separated morphology, where the hydrophilic domains were connected and oriented in the plane direction. Transparent b/b SPI membranes showed improved proton conductivity. Stronger anisotropic proton conduct behavior was found for the b/b SPI membranes compared to the random one, with higher proton conductivity in plane direction than in thickness direction.

Acknowledgement: Parts of this work were financially supported by NEDO, Fuel cell and hydrogen energy development department.

References:

- [1] O. Savadogo, *New Mater. Electrochem. Syst.*, 1, 1998, 47-66.
- [2] K. Mauritz, R. Moore, *Chem. Rev.*, 104, 2004, 5435-4585.
- [3] X. Guo, J. Fang, S. Harada, T. Watari, K. Tanaka, H. Kita, K. Okamoto, *Macromolecules*, 35, 2002, 6707-6713 and 9022-9028.
- [4] T. Watari, J. Fang, X. Guo, K. Tanaka, H. Kita, K. Okamoto, T. Hirano, *J. Membr. Sci.*, 230, 2004, 111-120.
- [5] Y. Suro, Y. Yin, H. Kita, K. Okamoto, *J. Photopolym. Sci. Technol.*, 19, 2006, 273-274.
- [6] Y. Yin, O. Yamada, K. Tanaka, K. Okamoto, *Polym. J.*, 38, 2006, 197-219.
- [7] N. Asano, M. Aoki, S. Suzuki, K. Miyatake, H. Uehida, M. Watanabe, *J. Am. Chem. Soc.*, 128, 2006, 1762-1769.
- [8] T. Nakano, S. Nagaoka, H. Kawakami, *Polym. Adv. Technol.*, 16, 2005, 753-757.
- [9] N. Asano, K. Miyatake, M. Watanabe, *J. Polym. Sci., Part A: Polym. Chem.*, 44, 2006, 2744-2748.
- [10] Ghassemi, J.E. McGrath, T.A. Zawodzinski Jr, *Polymer*, 47, 2006, 4132-4139.