Synthesis and Properties of Polyimides from Sulfonated Sulfonyl-Containing Diamine Monomer

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INTRODUCTION

Recently many six-membered ring sulfonated polyimides have been developed as promising electrolyte membrane materials for fuel cell application [1-3]. The problem often associated with sulfonated polyimide membranes is their poor hydrolysis stability and this could be solved by introducing flexible, highly basic and/or side chain-type diamine monomers [2-7]. On the other hand, the stability of the sulfonic acid groups has not been explored yet, and this problem can not be neglected when the fuel cells work at relatively high temperature (> 120 °C). Theoretically, the sulfonic acid groups are more stable toward hydrolysis when the phenyl rings to which the sulfonic acid groups are bonded have lower electron density. In this paper, a novel sulfonated diamine monomer, 4,4'-bis(4-aminophenoxy)diphenyl sulfone-3,3'-disulfonic acid (BAPPSDS), was synthesized, and the related polyimides were prepared. The central sulfonyl group of BAPPSDS is a strong electron-withdrawing group, and therefore, the sulfonic acid groups of BAPPDS are expected to be stable toward hydrolysis. The proton conductivity, water uptake, membrane stability toward water and methanol permeability of BAPPSDS-based polyimide membranes are also described.

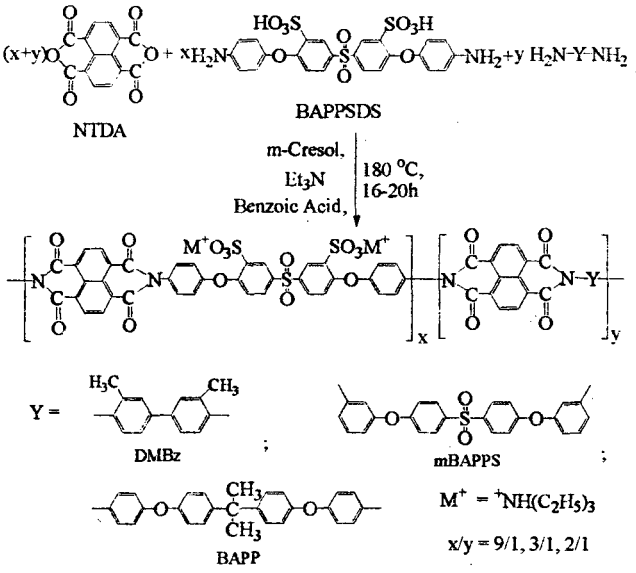
EXPERIMENTAL

BAPPSDS was synthesized by two-step reactions. BAPPSDS-based polyimides were prepared by polymerization of 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA), BAPPSDS and common nonsulfonated diamine monomers in m-cresol in the presence of triethylamine (Et_3N) and benzoic acid at 80 °C for 4 h and 180 °C for 16 h. The resulting highly viscous solutions were precipitated from acetone and the fiber-like precipitates were washed with acetone for three times and then dried in vacuo. Membranes were fabricated by conventional solution cast method. The as-cast membranes were in their triethylammonium salts form and were converted to the proton form by soaking in 1.0 N hydrochloric acid for one day. Proton conductivity was measured using a four-point-probe electrochemical impedance spectroscopy technique over the frequency range from 100 Hz to 100 KHz (Hioki 3552) [2].

RESULTS AND DISCUSSION

The new sulfonated diamine monomer, BAPPSDS, was synthesized by two-step reactions in a high yield. At first, 4,4'-dichlorodiphenyl sulfone was sulfonated by using fuming sulfuric acid as the sulfonating reagent to give 4,4'-dichlorodiphenyl sulfone-3,3'-disulfonic acid disodium salt. This intermediate product was then reacted with 4-aminophenol under basic condition to give bis[4-(4-aminophenoxy)phenyl] sulfone-3,3'-disulfonic acid disodium salt followed by treating with hydrochloric acid to give BAPPSDS. A series of sulfonated (co)polyimides were synthesized by (co)polymerization of NTDA, BAPPSDS, and common nonsulfonated diamines in the presence of triethylamine and benzoic acid (Scheme 1). The resulting copolyimides showed fairly high inherent viscosity (Table I). For all the copolyimides, tough films were obtained by solution cast method. TG-MS measurement revealed that the thermal decomposition temperature of the sulfofonic acid groups of BAPPSDS-based polyimides was higher than 250 °C indicating fairly high thermal stability of the polyimides.

The proton conductivities (σ) of BAPPSDS-based polyimide membranes were strongly dependent on the relative humidity (RH). At low RH, the polyimide membranes displayed rather low σ. At high RH (>70%) or in water, the membranes showed reasonably high σ. Table 1 lists the proton conductivity and methanol permeability and their ratio ϕ (= σ/P_M) of a series of sulfonated polyimides and Nafion 117. The P_M values of NTDA-BAPPSDS/*m*BAPPS(2/1) were much smaller than those of other sulfonated polyimides and Nafion 117 membrane at 30 °C and 50 °C. As a result, the BAPPSDS-based membrane displayed much larger ϕ value than Nafion 117, but lower than other sulfonated polyimide membranes because of the lower proton conductivity.



The water stability test of BAPPSDS-based polyimide membranes was performed by immersing the membranes into distilled water at 80 °C or 100 °C and characterized by the time elapsed when the membranes became brittle in water. It was found that the stability was strongly dependent on temperature. NTDA-BAPPSDS/*m*BAPPS(3/1), for example, did not break into pieces after being soaked in deionized water at 80 °C for 600 h indicating fairly good water stability. However, at 100 °C the membrane dissolved in deionized water within 5 h. The water stability was significantly improved by reducing the IEC level. NTDA-BAPPSDS/*m*BAPPS(2/1), for example, was stable in deionized water at 100 °C for more than 200 h. which is much longer than that of NTDA-BAPPSDS/*m*BAPPS(3/1).

Table 1 Proton conductivity, methanol permeability and their ratios of sulfonated polymer membranes

Membranes	IEC	σ (S/cm) [a]		P_M (10^{-6} cm^2/s) [b]		$\phi = \sigma/P_M$ (10^4	Ref.
	[meq g^{-1}]	90%RH	In water	30°C	50°C	S.cm^{-3} s) (30°C)	
NTDA-BAPPSDS/*m*BAPPS(2/1)	1.73	0.071	0.07	0.84 [b]	1.64 [b]	8.3	c
NTDA-BAPBDS	2.63	0.031	0.19	1.14	-	18	4, 5
NTDA-2,2'-BSPB	2.89	0.11	0.18	1.05	2.06	13	5, 7
Nafion 117	0.91	0.085	0.12	2.21	3.32	4.8	5

[a] Measured at 50 °C; [b] Methanol concentration in feed: 8.6wt%, [bl] 10wt%; [c] This study.

References

(1) C. Genies, R. Mercier, B. Sillion, N. Cornet, G. Gebel, M. Pineri, *Polymer*, **42**, 359 (2001).
(2) X. Guo, J. Fang, T. Watari, K. Tanaka, H. Kita, K. Okamoto, *Macromolecules*, **35**, 6707 (2002).
(3) J. Fang, X. Guo, S. Harada, T. Watari, K. Tanaka, H. Kita, K. Okamoto, *Macromolecules*, **35**, 9022 (2002).
(4) T. Watari, J. Fang, K. Tanaka, H. Kita, K. Okamoto, *J. Membr. Sci.*, **230**, 111 (2004).
(5) K. Okamoto, *J. Photopolym. Sci. Technol.*, **16**, 247, (2003).
(6) Y. Yin, J. Fang, H. Kita, K. Okamoto, *Chem. Lett.*, **32**, 328 (2003).
(7) Y. Yin, J. Fang, T. Watari, K. Tanaka, H. Kita, K. Okamoto, *J. Mater. Chem*, **14**, 1062 (2004).

含砜基的磺化二胺单体及相应的磺化聚酰亚胺的合成与性能

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引言：

近几年，六元环的磺化聚酰亚胺由于其在燃料电池质子交换膜中的应用前景而得到迅速的发展 [1-3]。磺化聚酰亚胺存在的主要问题是其耐水性比较差，目前这一问题可以通过引入柔性结构，碱性较强或侧链型结构的磺化二胺单体而得到初步解决[2-7]。另一方面，磺酸基的稳定性也是一个问题，在燃料电池的工作温度（> 120 °C）较高时尤其不能忽略。理论上来说，降低磺酸基所在的苯环上的电子云密度有利于提高磺酸基的稳定性。本文合成了一种新型的含有砜基的磺化二胺单体（4,4'-双(4-氨基苯氧基)二苯砜-3,3'-二磺酸 (BAPPSDS)）以及相应的磺化聚酰亚胺。BAPPSDS 中的砜基是一个强吸电子基团，因此有望提高所在苯环上的磺酸基的稳定性。本文还对这些磺化聚酰亚胺的质子导电率，吸水性，膜的耐水性以及甲醇透过率等作了研究。

实验：

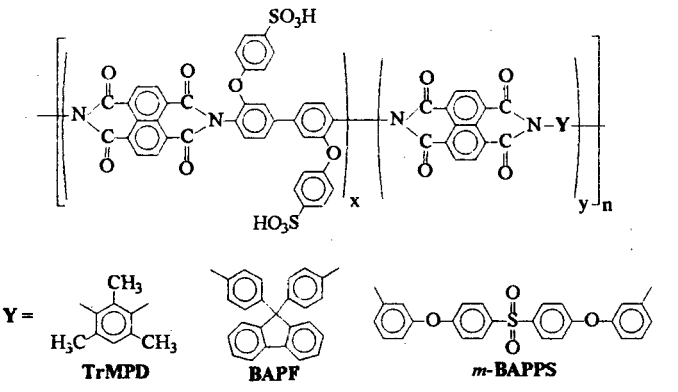
BAPPSDS 通过两步反应制备而得。相应的磺化聚酰亚胺通过 1,4,5,8-萘四酸二酐 (NTDA), BAPPSDS 和一些非磺化二胺单体，以间甲酚作溶剂，在三乙胺以及苯甲酸的存在下先在 80 °C 反应 4 小时然后在 180 °C 反应 16 小时聚合制备而得。所得到的粘稠液体倒入丙酮中，将沉析出的纤维状固体用丙酮反复洗涤 3 次，然后置于真空烘箱中干燥。干燥后的磺化聚酰亚胺通过传统的溶液浇注法制得膜。将所得的三乙胺型膜在 1.0 N 的盐酸溶液中浸泡一天进行质子交换。质子导电率是用四点法测得的，所用频率从 100 Hz 到 100 KHz (Hioki 3552) [2]。

结果与讨论：

BAPPSDS 是通过两步反应制备而得的。首先，将原料 4,4'-对氯二苯砜用发烟硫酸进行磺化得到 4,4'-对氯二苯砜-3,3'-二磺酸二钠盐 。然后将这一中间产物与对氨基苯酚在碱性条件下进行反应得到双[4-(4-氨基苯氧基)苯基] 砜-3,3'-二磺酸二钠盐 。二钠盐用盐酸进行处理后即可得到最终 BAPPSDS。一系列不同磺酸基含量的磺化聚酰亚胺通过 1,4,5,8-萘四酸二酐（NTDA），与 BAPPSDS 以及一些非磺化二胺单体，以间甲酚作溶剂，在三乙胺以及苯甲酸的存在下通过一步法聚合而得（见 Scheme 1）。所得到的磺化聚酰亚胺具有较高的特性粘度（见 表 1），通过溶液浇注法都能够得到力学强度较好的膜。TG-MS 测试得到基于 BAPPSDS 的磺化聚酰亚胺中的磺酸基的分解温度高于 250 °C，这就表明了该类磺酸聚酰亚胺具有较好的热稳定性。

磺化聚酰亚胺由传统的溶液浇注法制成膜。所得的三乙胺型磺化聚酰亚胺膜在搅拌条件下，用 1.0 N 的盐酸溶液中浸泡两天进行质子交换，得到质子型膜。质子交换的完全通过 ^{1}HNMR 进行确认。

Scheme 1



基于 BSPOB 的磺化聚酰亚胺膜的质子导电率存在湿度依赖性。对于 NTDA-BSPOB/TrMPD(9/1)而言，在高相对湿度下（RH > 70%），膜的质子导电率（> 10^{-2} S/cm）较高，然而在低相对湿度下（RH= 20%）膜的质子导电率相当低（约 10^{-4} S/cm）。在整个湿度范围内，随着温度的升高（最高达 160 °C），质子导电率没有明显的降低，这一性能将有利于应用于中温(120 – 150 °C)燃料电池中。在水中，NTDA-BSPOB/*m*BAPPS(9/1)具有很高的得质子导电率，在 25 °C 时为 0.18 S/cm，随着温度升至 70 °C，质子导电率增加至 0.31 S/cm，这些值都要高于 Nafion 117。

耐水性的测试是将磺化聚酰亚胺膜浸入去离子水中，分别在不同温度下（80 °C 或 100 °C）进行测量，将膜在热水中开始变脆的时间作为衡量膜的耐水性的依据。表 1 列出了磺化聚酰亚胺的吸水性，耐水性和尺寸变化。从表中可以看出，虽然 NTDA-BSPOB/*m*BAPPS(9/1)具有很高的离子交换容量（IEC），但依然能在 100 °C 的去离子水中 3000 小时保持不变形，体现了优异的耐水性。而且，在 100 °C 的去离子水中浸泡后在膜平面方向其尺寸变化小于 7 %，这远远小于其它磺化聚合物。

Table 1 Water uptake, water stability, and dimensional changes of sulfonated polyimide membranes at 100 °C.

Polyimide[a]	IEC [meq/g]	Water uptake [g/100g polymer]	Water stability [h]	Dimensional changes [%]		Ref
				ΔL	ΔA	
NTDA-BSPOB/*m*BAPPS(9/1)	2.40	160	>3000	150	7	e
NTDA-BSPOB/TrMPD(9/1)	2.49	143	600	110	32	e
NTDA-BSPOB/TrMPD(2/1)	2.10	72[b]	>720[b]	22[b]	32[b]	e
NTDA-BAPBDS	2.63	107[b]	1000	16[f]	15[d]	9
NTDA-3,3'-BSPB	2.89	250[c]	700	180[f]	11[d]	6
NTDA-2,2'-BSPB	2.89	222[c]	2500	220[f]	0[d]	6

[a]BAPBDS, 3,3'-BSPB and 2,2'-BSPB refer to 4,4'-bis(4-aminophenoxy)biphenyl-3,3'-disulfonic acid, 3,3'-bis(3-sulfopropoxy)benzidine and 2,2'-bis(3-sulfopropoxy)benzidine, respectively.
[b]80 °C; [c]50 °C; [d]measured at room temperature. e: This study.

参考文献:

1) O. Savadogo, *J. New Mat. Electrochem. Systems*, **1**, 47 (1998).
2) M. Rikukawa and K. Sanui, *Prog. Polym. Sci.*, **25**, 1463 (2000).
3) Guo, X.; Fang, J.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. *Macromolecules*, **35**, 6707 (2002)
4) J. Fang, X. Guo, S. Harada, T. Watari, K. Tanaka, H. Kita, K. Okamoto, *Macromolecules*, **35**, 9022 (2002).
5) Y. Yin, J. Fang, H. Kita, K. Okamoto, *Chem. Lett.*, **32**, 328 (2003).
6) Y. Yin, J. Fang, T. Watari, K. Tanaka, H. Kita, K. Okamoto, *J. Mater. Chem*, **14**, 1062 (2004).
7) Y. Yin, J. Fang, Y. Cui, K. Tanaka, H. Kita, K. Okamoto, *Polymer*, **44**, 4509 (2003).
8) K. Okamoto, *J. Photopolym. Sci. Technol.*, **16**, 247 (2003).
9) T. Watari, J. Fang, K. Tanaka, H. Kita, K. Okamoto, *J. Membr. Sci.*, **230**, 111 (2004).