Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 7185–7191 **7185**
DOI: 10.1021/ma101288w

High Proton Conductive and Low Gas Permeable Sulfonated Graft Copolyimide Membrane

Kota Yamazaki and Hiroyoshi Kawakami*

Department of Applied Chemistry, Tokyo Metropolitan University Hachioji, Tokyo 192-0397, Japan

Received June 9, 2010; Revised Manuscript Received July 29, 2010

ABSTRACT: We describe the syntheses of novel sulfonated graft copolyimides and investigate their proton conductivity and gas permeability properties. The graft copolyimide membrane showed significantly higher proton conductivity exceeding that of Nafion, and the proton conductivity at 90 °C and 98% RH was 1.2 S/cm, more than 7 times that of Nafion. Furthermore, the oxygen permeability of the membrane was approximately one-eighth the value of Nafion and had a very excellent gas barrier property. The selectivity ratio calculated from the proton and oxygen transports of the graft copolyimide membrane was 66 times that determined in Nafion. We first demonstrated that the graft copolymer membrane could realize a high proton conductivity and low gas permeability of the fuel. Consequently, this material proved to be promising as a proton exchange membrane and may have potential applications for use in fuel cells.

Introduction

Fuel cell vehicles, powered by hydrogen, have the potential to revolutionize our transportation system. Proton exchange membrane fuel cells (PEMFCs), which convert chemical energy efficiently into electrical energy via oxidation and reduction reactions, are receiving considerable attention as transport, stationary, and portable future power sources. They are more efficient than conventional internal combustion engine vehicles and produce no harmful tailpipe exhaust—their only emission is water. The important technical focus is on developing polymer electrolyte membranes that are able to achieve a high proton conductivity, low gas permeability of the fuel and oxidant, sufficient thermal stability, and long-term durability.[1,2] At present, the perfluorosulfonated membranes, such as Nafion, have been widely used because of their excellent oxidative and chemical stability as well as high proton conductivity.[3,4] They, however, have limitations such as a low thermal stability due to their low T_g and high gas permeability. Other recent studies have focused on the development of polymer electrolyte membranes based on the sulfonated aromatic hydrocarbon polymers due to their excellent chemical and thermal stabilities and good mechanical strength.[5−12] The proton conductivity of the membranes is well-known to increase with increasing sulfonic acid group. However, most of them containing a large number of sulfonic acid groups result in an unfavorable swelling of the membranes and a dramatic loss in their mechanical properties.[13,14] Some membranes have shown a reasonable thermal stability and long-term durability by optimization of their chemical structure or cross-linking of the polymers.[15,16] However, most of them have critical problems in realizing both a high proton conductivity and low gas permeability of the fuel; that is, the polymer electrolyte membranes with a high proton conductivity show a relatively high gas permeability. Hydrogen and oxygen crossovers through the membrane are an undesirable diffusion because their crossovers lead to at least three problems: fuel efficiency reduction, anode and cathode potential depression, and formation of reactive oxygen species.[17−19] More severely, the direct reaction between hydrogen and oxygen can produce hydrogen peroxide, and the decomposition of the hydrogen peroxide in the presence of various cationic impurities can further produce active hydroxy and peroxy radicals. These radicals are believed to attack not only the catalyst but also the membrane, causing significant catalyst-layer and membrane degradation.[20−22] Therefore, one of the important objectives for designing the polymer electrolyte membranes is the development of new polymer membranes combining high proton conductivity and low gas permeability of the fuel.

In this preliminary study, we describe the syntheses of novel sulfonated graft copolyimides and investigate their proton conductivities and gas permeability properties. We consider that the graft copolymers as model polymer systems are useful for gaining insights into aspects of polymer electrolyte membrane design and preferred polymer structures to lead to a good understanding of the relationships between the proton conductivity and the gas permeability.

Experimental Section

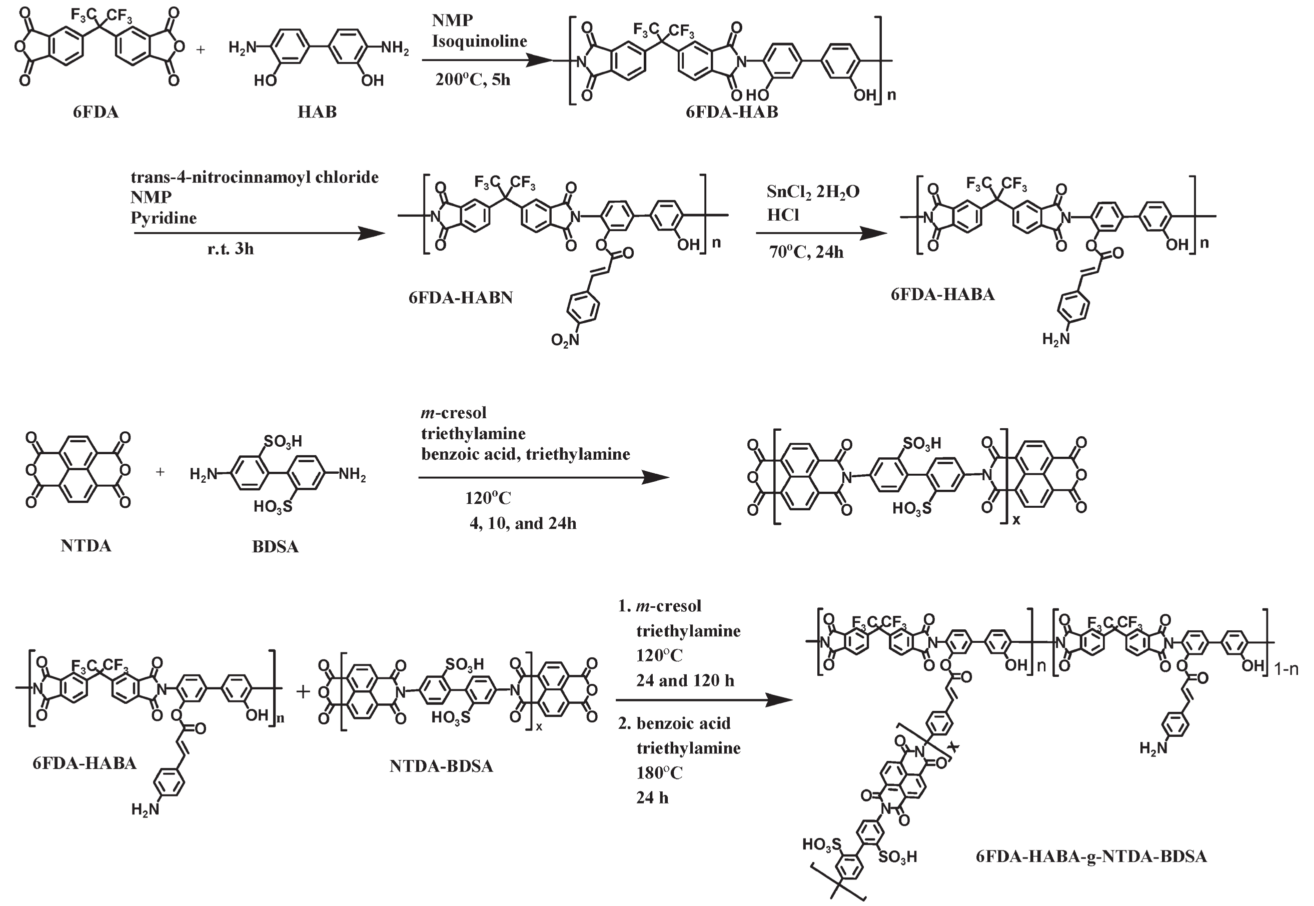
Materials. 2,2′-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) was purchased from Central Glass Co. (Tokyo, Japan) and was purified by sublimation. 3,3′-Hydroxy-4,4′-diaminobiphenyl (HAB) was purchased from Wako Chemical Ind. (Osaka, Japan) and was used as received. *trans*-4-Nitrocinnamoyl chloride (NCC) purchased from Aldrich Co. (Milwaukee, WI) was used as received. 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA) was purchased from the Sigma-Aldrich Co. (St. Louis, MO). 4,4′-Diaminobiphenyl-2,2′-disulfonic acid (BDSA) was purchased from the Tokyo Kasei Co. (Tokyo, Japan) and was purified by dissolution in a triethylamine aqueous solution and then precipitated in 1 N H_2SO_4. Finally, BDSA was dried in a vacuum oven at 70 °C for 12 h. 3,3′-Bis(3-sulfopropoxy)benzidine (BSPB) was prepared using the same method reported by Watanabe et al.[23] All other chemicals were purchased from Kanto Chemical Co. (Tokyo, Japan) and were used as received. Nafion 117 was used in this study as the control membrane. The membranes were obtained from the DuPont Co. Ltd. (Tokyo, Japan).

Syntheses of Sulfonated Graft Copolyimide. A novel sulfonated graft polyimide was synthesized as shown in Scheme 1. The 6FDA-HAB as the main-chain polymer was prepared using

---

*Corresponding author: Ph +81-426-77-1111 (ext) 4972; Fax +81-426-77-2821; e-mail kawakami-hiroyoshi@tmu.ac.jp.

Scheme 1. Syntheses of 6FDA-HABA-*g*-NTDA-BDSA



the same method reported by Lee et al.[24] Equivalent moles of 6FDA and HAB monomers were dissolved together with 2 mol equiv of isoquinoline catalyst in dry NMP. The solution was gently heated with stirring at 70 °C for 2 h and then refluxed with stirring for 5 h. 6FDA-HAB polyimide was precipitated in a mixture of methanol and water (6:4 volume ratio). Subsequently, the polyimide was dried in a vacuum oven at 150 °C for 15 h. In addition, the polyimide containing nitrocinnamate side groups, 6FDA-HABN, was synthesized from the obtained 6FDA-HAB and NCC. NCC was dissolved in NMP, followed by the addition of 1 mol equiv of the 6FDA-HAB and pyridine in excess. After stirring for 3 h at room temperature, 6FDA-HABN was precipitated in methanol. The precipitated polymer was filtered and dried at 150 °C under vacuum for 15 h.

The 6FDA-HABA containing aminocinnamate side groups was prepared from the tin(II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$) and hydrochloric acid. 6FDA-HABN was dissolved in NMP, followed by addition of excess $SnCl_2 \cdot 2H_2O$. After $SnCl_2 \cdot 2H_2O$ was dissolved, concentrated HCl was added dropwise in the polymer solution. After stirring for 24 h at 70 °C, 6FDA-HABA was precipitated in a mixture of methanol and water (5:5 volume ratio). The precipitated polymer was filtered and dried at 150 °C under vacuum for 15 h.

The sulfonated graft copolyimides, 6FDA-HABA-*g*-NTDA-BDSA, were synthesized from the 6FDA-HABA as the main-chain polymer and sulfonated dianhydride-terminated NTDA-BDSA as the side-chain polymer. The dianhydride-terminated polyimides, NTDA-BDSA, were prepared by the reaction of BDSA and the excess of NTDA in *m*-cresol for 4, 10, or 24 h at 120 °C.[5,12] The obtained sulfonated anhydride-terminated polyimides were NTDA-BDSA (1), (2), and (3), respectively. In addition, 6FDA-HABA was added in the NTDA-BDSA solution. The mixture was stirred at 120 °C for 24 h and at 180 °C for 24 h. The obtained sulfonated graft copolyimides were 6FDA-HABA-*g*-NTDA-BDSA (1), (2), and (3), respectively. After cooling to room temperature, the solution was poured into methanol several times to completely remove the residual sulfonated anhydride-terminated polyimide, NTDA-BDSA. In addition, 6FDA-HABA-*g*-NTDA-BDSA polyimides were precipitated in ethyl acetate. The sulfonated graft copolyimide, 6FDA-HABA-*g*-NTDA-BDSA (4), was synthesized using a different reaction time of 120 h between 6FDA-HABA and NTDA-BDSA (3). Finally, the sulfonated graft copolyimides were dried at 150 °C under vacuum for 15 h to remove the residual solvents.

The sulfonated graft copolyimide with a different structure of the sulfonic acid group, 6FDA-HABA-*g*-NTDA-BSPB, was synthesized from the 6FDA-HABA as the main-chain polymer and sulfonated dianhydride-terminated NTDA-BSPB as the side-chain polymer. The NTDA-BSPB was prepared by the reaction of BSPB and the excess of NTDA in *m*-cresol at 120 °C for 24 h. Then, 6FDA-HABA polyimide was added in NTDA-BSPB solution. The mixture was stirred at 120 °C for 24 h and at 180 °C for 24 h. After cooling to room temperature, the solution was poured into methanol several times to remove the residual sulfonated anhydride-terminated polyimide. In addition, 6FDA-HABA-*g*-NTDA-BSPB was precipitated in ethyl acetate. Finally, the sulfonated graft copolyimides were dried at 150 °C under vacuum for 15 h to remove the residual solvents.

Preparation of Sulfonated Graft Copolyimide Membranes. The sulfonated graft copolyimide membranes were prepared using a solvent-cast method. The DMSO solution of the polyimide was cast on a glass plate, and the plate was then placed in a vacuum oven at 110 °C for 24 h. The membranes were immersed in ethanol and deionized water for 4 h each, then acidified with 0.1 M HCl solution for 4 h, and finally washed with deionized water for 4 h. The resulting membranes were dried in a vacuum oven at 80 °C for 24 h. The thickness of the membrane was ~50 μm.

Characterization of Sulfonated Graft Copolyimide Membranes. The molecular weights (M_w and M_n) of 6FDA-HABA as the main-chain polymer and NTDA-BDSA as the side-chain polymer were determined by gel-permeation chromatography (detector: Jasco 830-RI monitor, Tokyo, Japan) using two Shodex SB-806HQ and SB-804 HQ columns. Dimethylformamide containing 0.01 M lithium bromide was used as the eluent at the flow rate of 1.0 mL/min. The molecular weights were estimated by comparing the retention times on the columns to those of standard polystyrene.[5,12] The ionic-exchange capacity (IEC) was measured by classical titration using NaOH and HCl solutions.[5,12]

The water uptake of the sulfonated graft copolyimide membrane was gravimetrically measured from the dried and humidified membranes.[12] The polyimide membrane was dried in a vacuum oven at 80 °C for 10 h and then immersed in liquid water at room temperature. After 24 h, the membrane was then wiped dry and quickly weighed. The water uptake was calculated using eq 1

$$W = \frac{W_s - W_d}{W_d} \times 100\ (\%) \tag{1}$$

where W_s and W_d are the weights of the wet and dry membranes, respectively.

Low-temperature DSC experiments were performed using a Shimadzu DSC-60 (Tokyo, Japan). Fully hydrated membrane samples were carefully blotted to remove surface water and then transferred immediately to sealed aluminum pans. The samples were quickly placed in the calorimeter and cooled to −50 °C. The samples were then heated to 20 °C at a rate of 5 °C/min.

Size change in the sulfonated graft copolyimide membrane was measured in water at 80 °C for 5 h. The changes of the thickness and diameter were calculated from

$$\Delta T = \frac{T_s - T_d}{T_d} \times 100\ (\%) \tag{2}$$

$$\Delta L = \frac{L_s - L_d}{L_d} \times 100\ (\%) \tag{3}$$

where T_s and L_s are the thickness and diameter of the wet membranes, respectively, and T_d and L_d are the thickness and diameter of the dry membranes, respectively.

The thermal behavior of the polyimide membrane in a nitrogen atmosphere was evaluated by thermogravimetric analysis (TGA: Seiko TG/DTA300, SSC/5200H, Tokyo, Japan). The thickness of the membrane was ~50 μm. The oxidative stability to peroxide radical attack was investigated by measuring the elapsed times in which a membrane was dissolved completely after immersion of each membrane into Fenton's reagent of the 3% H_2O_2, 2 ppm $FeSO_4$ solution at 80 °C. The hydrolysis stability was investigated by measuring the elapsed times in which a membrane was dissolved completely after immersion of each membrane into water at 80 °C.

The proton conductivity in the plane direction of the membrane was measured by electrochemical impedance spectroscopy over the frequency range from 50 Hz to 50 kHz (Hioki 3532-50, Tokyo, Japan) as reported in previous papers.[5,12] The membranes (1.0 cm × 3.0 cm) and two blackened platinum plate electrodes were placed in a Teflon cell. The distance between the two electrodes was 1.0 cm. The cell was placed in a thermocontrolled humidity chamber to measure the temperature and humidity dependence of the proton conductivity.

The gas permeability coefficients of oxygen and nitrogen were measured with a high-vacuum apparatus (Rika Seiki, Inc., K-315-H, Tokyo, Japan).[25−27] The gas permeation measurements of the sulfonated copolyimide membranes were carried out from 25 up to 45 °C at 76 cmHg. The permeation parameters, D and S, of the sulfonated copolyimide membranes were calculated from

$$P = DS \tag{4}$$

$$D = \frac{L^2}{6\theta} \tag{5}$$

using the time lag, θ.

Results and Discussion

Proton Conductivity and Gas Permeability of 6FDA-HABA-*g*-NTDA-BDSA. Scheme 1 shows the chemical structure of the novel sulfonated graft copolyimide in which the sulfonated polyimide was graft-polymerized to the fluorinated polyimide as the main-chain polymer. Table 1 shows the molecular weight, ionic-exchange capacity (IEC), and grafting ratio of the sulfonated graft copolyimide. The molecular weights of the sulfonated copolyimides as the side-chain polymers were controlled by the polymerization times. The grafting ratio between the fluorinated polyimide and the sulfonated polyimide was controlled by changing the reaction time of the side-chain and main-chain polyimides; the reaction time to produce 6FDA-HABA-*g*-NTDA-BDSA (1), (2), and (3) was 24 h, while that for 6FDA-HABA-*g*-NTDA-BDSA (4) was 120 h. We synthesized the 6FDA-HABA-*g*-NTDA-BDSA (1), (2), and (3) with a similar IEC to elucidate the effect of the side chain length on the proton conductivity and gas permeability. On the other hand, the 6FDA-HABA-*g*-NTDA-BDSA (4) was prepared to elucidate the effects of the grafting ratio and IEC on the proton conductivity and gas permeability.

The structure of the obtained sulfonated graft copolyimide was determined by ^{1}H NMR and FT-IR. Figure 1 shows the ^{1}H NMR spectrum of sulfonated graft copolyimide (3). The proton peak of the hydroxyl side group appears at 10.0 ppm, and the vinyl proton peaks introduced by NCC reaction appear at 6.5 and 7.6 ppm. The conversion yield of the NCC incorporation reaction calculated from ^{1}H NMR was estimated to be ~50% (data not shown). The peaks of aromatic protons in NTDA-BDSA could be well assigned to the supposed chemical structure, and there was no peak of poly(amic acid) at around 11 ppm. These results of the ^{1}H NMR spectroscopy showed that novel sulfonated graft copolyimides were synthesized and were completely imidized.

Figure 2 shows the FT-IR spectra of the sulfonated graft copolyimide membranes. The absorption bands at 1669 and 1711 cm^{-1} correspond to the C=O stretching vibration in NTDA-based polyimide. The peak at 1346 cm^{-1} was considered as typical of the C−N group vibration in NTDA-BDSA. The peaks at 1030 and 1177 cm^{-1} correspond to the stretching vibration of the SO_2.

The thermal stability of the sulfonated graft polyimides was investigated by TGA measurements. Figure 3 shows the TGA curves of 6FDA-HABA-*g*-NTDA-BDSA (4) and NTDA-BDSA. The curve of 6FDA-HABA-*g*-NTDA-BDSA (4) was similar to that measured in NTDA-BDSA. The weight loss above 290 °C was due to the desulfonation of the 6FDA-HABA-*g*-NTDA-BDSA (4) and NTDA-BDSA. The loss above 550 °C was ascribed to the decomposition of the polymer main chain. The TGA curves of 6FDA-HABA-*g*-NTDA-BDSA (1), (2), and (3) also displayed thermal stability similar to that of 6FDA-HABA-*g*-NTDA-BDSA (4) (data not shown).

Figure 4 shows the temperature dependence of the proton conductivity of the sulfonated graft copolyimide membranes

Table 1. Molecular Weight, Ionic-Exchange Capacity (IEC), and Grafting Ratio of Sulfonated Graft Copolyimide

polymer	M_w of side-chain polymer	IEC (mequiv/g)	grafting ratio (%)
6FDA-HABA-*g*-NTDA-BDSA (1)[a]	5.6×10^4	2.47	4.1
6FDA-HABA-*g*-NTDA-BDSA (2)[a]	1.1×10^5	2.46	2.1
6FDA-HABA-*g*-NTDA-BDSA (3)[a]	1.4×10^5	2.43	1.5
6FDA-HABA-*g*-NTDA-BDSA (4)[a]	1.4×10^5	3.14	14

[a] Molecular weight of 6FDA-HABA (main-chain polymer): 7.0×10^4.

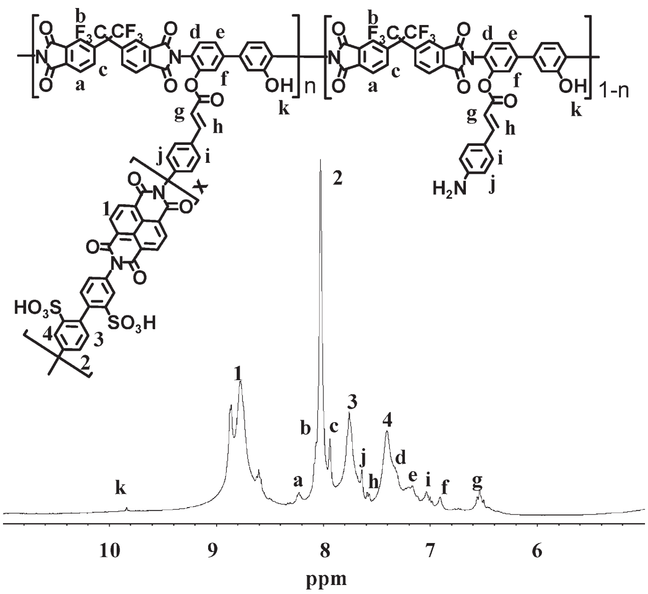


Figure 1. ^{1}H NMR spectrum of 6FDA-HABA-*g*-NTDA-BDSA (3).

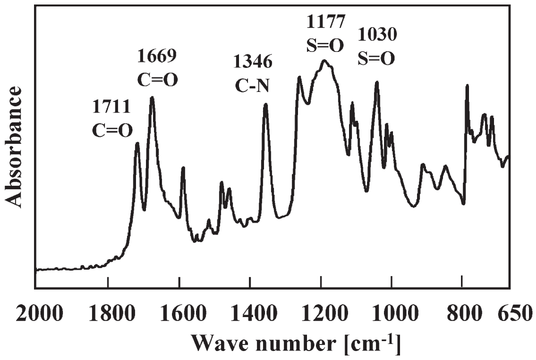


Figure 2. FT-IR spectrum of 6FDA-HABA-*g*-NTDA-BDSA (3).

at a 98% relative humidity. Their proton conductivities in 6FDA-HABA-*g*-NTDA-BDSA (1), (2), and (3) with the same IEC values were dependent upon the molecular weight of the side-chain polyimide and increased with increasing molecular weight. In addition, 6FDA-HABA-*g*-NTDA-BDSA (3) and (4) showed higher proton conductivities exceeding that of Nafion at all temperatures and their proton conductivities at 90 °C and 98% RH were 1.1 and 1.2 S/cm, respectively, more than 7 times that of Nafion. Especially, it should be noted that 6FDA-HABA-*g*-NTDA-BDSA (3) with an IEC value of 2.43 showed a significantly superior proton conductivity compared to that determined for other sulfonated aromatic hydrocarbon polymers as a linear polymer with a similar IEC[28−30] and that 6FDA-HABA-*g*-NTDA-BDSA (4) at low temperature showed significantly superior proton conductivity. We found that the molecular weight and grafting ratio of the side-chain polymer in the sulfonated graft copolyimide had a significant influence on the proton conductivity of the 6FDA-HABA-*g*-NTDA-BDSA.

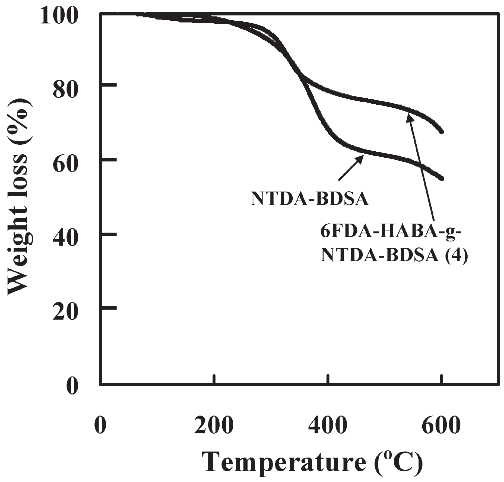


Figure 3. TGA curves of NTDA-BDSA and 6FDA-HABA-*g*-NTDA-BDSA (4).

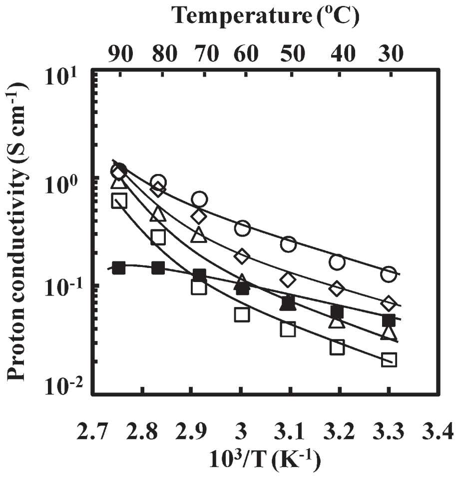


Figure 4. Temperature dependence of proton conductivity for sulfonated graft copolyimide membrane at 98% RH: (□) 6FDA-HABA-*g*-NTDA-BDSA (1), (△) 6FDA-HABA-*g*-NTDA-BDSA (2), (◇) 6FDA-HABA-*g*-NTDA-BDSA (3), (○) 6FDA-HABA-*g*-NTDA-BDSA (4), (■) Nafion 117.

The water uptake has been expressed as the number of water molecules per sulfonic group (λ).[31]

$$\lambda = \frac{n(\mathrm{H_2O})}{n(\mathrm{SO_3}^-)} = \frac{\mathrm{WS}}{18\mathrm{IEC}} \qquad (6)$$

where $n(\mathrm{H_2O})$ is the H_2O mole number, $n(\mathrm{SO_3})$ is the SO_3 group mole number, WS is the water uptake value by weight, IEC is the ion exchange capacity, and 18 corresponds to the water molecular weight. The hydrated state of the membrane was estimated from the endothermic peaks corresponding to the water melting measured by DSC.[32]

$$\lambda = \lambda_f + \lambda_b \qquad (7)$$

Table 2. Water Uptake and Number of Water Molecules per Sulfonic Group (λ) of Sulfonated Copolyimide Membrane

polymer	IEC (mequiv/g)	water uptake[a] (%)	λ[b]	λ_f[c]	λ_b[d]
6FDA-HABA-*g*-NTDA-BDSA (1)	2.47	68	15	1	14
6FDA-HABA-*g*-NTDA-BDSA (2)	2.46	84	19	4	15
6FDA-HABA-*g*-NTDA-BDSA (3)	2.43	104	24	9	15
6FDA-HABA-*g*-NTDA-BDSA (4)	3.14	137	24	12	12

[a] At 25 °C in water. [b] $\lambda = \lambda_f + \lambda_b$, where λ is the the number of water molecules per sulfonic group. [c] λ_f: the number of free water molecules per sulfonic group. [d] λ_b: the number of bound water molecules per sulfonic group.

Table 3. Oxygen Permeability Coefficient (P_{O_2}), Diffusivity Coefficient (D_{O_2}), and Solubility Coefficient (S_{O_2}) of Sulfonated Copolyimide Membrane at 35 °C and 76 cmHg

polymer	proton conductivity[a] (S cm^{-1})	P_{O_2}[b]	D_{O_2}[c]	S_{O_2}[d]	selectivity ratio[e]
6FDA-HABA		1.0	1.6	0.63	
NTDA-BDSA	0.35	0.31	0.21	1.5	8.9
6FDA-HABA-*g*-NTDA-BDSA (1)	0.61	0.28	0.16	1.7	17
6FDA-HABA-*g*-NTDA-BDSA (2)	0.94	0.33	0.18	1.8	22
6FDA-HABA-*g*-NTDA-BDSA (3)	1.1	0.35	0.21	1.7	25
6FDA-HABA-*g*-NTDA-BDSA (4)	1.2	0.14	0.12	1.2	66
NTDA-BDSA-*b*-6FAP	0.51	1.8	1.2	1.6	2.2
Nafion 117	0.14	1.1	4.6	0.23	1.0

[a] At 90 °C and 98% RH. [b] P_{O_2}: 10^{-10} (cm^3(STP) cm/(cm^2 s cmHg)). [c] D_{O_2}: 10^{-8} (cm^2/s). [d] S_{O_2}: 10^{-2} (cm^3(STP)/(cm^3 cmHg)). [e] Selectivity ratio = [selectivity (polymer)/selectivity (Nafion)] and selectivity = proton conductivity/P_{O_2}.

where λ is the total hydration number calculated from eq 6, λ_f is the number of free water molecules per sulfonic group measured by DSC, and λ_b is the number of bound waters per sulfonic group calculated from eq 7. Although the IEC values of 6FDA-HABA-*g*-NTDA-BDSA (1), (2), and (3) were very similar, their λ values increased with the increasing molecular weight of the side-chain polymer. In addition, their λ_f values were enhanced by the molecular weight of the side-chain polyimide, while their λ_b values indicated no significant difference among 6FDA-HABA-*g*-NTDA-BDSA (1), (2), and (3). The λ_f of 6FDA-HABA-*g*-NTDA-BDSA (4) also significantly increased, as is apparent from Table 2. We believe that the high proton conductivities of 6FDA-HABA-*g*-NTDA-BDSA (3) and (4) are responsible for the amount of the free water and that the proton transport in their membranes is mainly dominated by the vehicle mechanism.[33-36]

The polymer electrolyte membrane is required to have an excellent membrane stability and low gas permeability of the fuel and oxidant as well as high proton conductivity. Cross-linking between polymers or hybridization of the membrane by the addition of inorganic particles is reported to be an effective method for improving the membrane stability.[15,16] However, the basic idea of the polymer development for reducing the gas permeability of the polymer electrolyte membrane without decreasing proton conductivity is not necessarily definite. Table 3 shows the oxygen permeability coefficients of the sulfonated graft copolyimide membranes and the sulfonated block copolyimide membrane as control of the linear polymer in the dry state at 35 °C and 76 cmHg. Although the block copolyimide membrane with high proton conductivity showed higher oxygen permeability than Nafion, the oxygen permeabilities of the sulfonated graft copolyimide membranes were approximately one-third that of Nafion. Furthermore, the oxygen permeability of 6FDA-HABA-*g*-NTDA-BDSA (4) was approximately one-eighth the value of Nafion, and the membrane had a very excellent gas barrier property. The low gas permeability of the sulfonated graft copolyimide membranes is responsible for the reduced DO_2 as is apparent from Table 2, and their DO_2 values were very similar to that measured in NTDA-BDSA as the side-chain polymer. In addition, the high gas barrier characteristic of 6FDA-HABA-*g*-NTDA-BDSA (4) is due to the remarkable reduction of the oxygen diffusivity when compared to other sulfonated graft copolyimides. We consider that the strong intermolecular interaction induced by sulfonic acid groups suppresses the gas diffusivity through the sulfonated graft copolyimide membrane. On the other hand, the oxygen permeability for the NTDA-BDSA-*b*-6FAP membrane as the linear polymer indicated a high DO_2 value. The selectivity ratio calculated from the proton and oxygen transports of the 6FDA-HABA-*g*-NTDA-BDSA (4) was 66 times larger than that determined in Nafion. Off course, it is necessary to measure the humidity dependence of the oxygen permeability coefficient for the NTDA-BDSA-*b*-6FAP membrane. In general, the gas permeability through the polymer membrane is known to increase with increasing humidity, and the oxygen permeability for the NTDA-BDSA-*b*-6FAP membrane also enhances with humidity. However, as reported by Watanabe,[37] the increase ratio of the gas permeability coefficient for the sulfonated polyimide membrane under high humidity is almost similar to that measured in Nafion; therefore, we consider that the oxygen permeability coefficient of 6FDA-HABA-*g*-NTDA-BDSA significantly suppresses when compared to that in Nafion.

In general, the operating temperature for fuel cell application is required to be high temperature over 100 °C for reducing of carbon monoxide poisoning at the anode from an impure hydrogen feed, providing easy heat rejection, producing more usable waste heat to increase system efficiency, and accelerating the electrochemical reaction kinetics. However, the gas permeability generally increases with operating temperature. Therefore, the polymer electrolyte membrane is required to suppress the gas crossover at high temperature ranges. Table 4 shows the gas permeability coefficients of sulfonated graft copolyimide membranes and Nafion at 80 and 120 °C simulated from the activation energy for their gas permeability coefficients (ΔE_a). Nafion indicated a high ΔE_a value, and the oxygen permeability coefficients calculated at 80 and 120 °C were 13 and 70 barrer [cm^3 (STP)/(cm^2 s cmHg)], respectively, and were almost similar to the experimental values as reported by Watanabe et al.[38] On the other hand, the oxygen permeability coefficients calculated at 80 and 120 °C for the sulfonated graft copolyimide membranes were much smaller than those determined in Nafion. Especially, 6FDA-HABA-*g*-NTDA-BDSA (4) indicated significantly low gas permeability compared to other sulfonated graft copolyimides.

Proton Conductivity and Gas Permeability of 6FDA-HABA-*g*-NTDA-BSPB. It was found that the 6FDA-HABA-*g*-NTDA-BDSA membrane shows a high proton conductivity of ~1 S cm^{-1} and significantly low gas permeability due to the graft structure. These properties of the membrane provide many advantages for realizing high-performance PEMFCs. However, 6FDA-HABA-*g*-NTDA-BDSA has drawbacks due to lower membrane stability as one of the important elements for polymer electrolyte membranes. The reason for the low membrane stability of the sulfonated graft copolyimide is attributed to lower stability of the sulfonated diamine, BDSA, reported by other researchers.[39] To improve the membrane stability of the sulfonated graft copolyimide, a novel sulfonated graft copolyimide, 6FDA-HABA-*g*-NTDA-BSPB, composed of the side-chain-type sulfonated diamine has been synthesized. In general, the polyimides prepared from diamine monomers having side-chain-type sulfonic acid show better membrane stability than those from a diamine having main-chain-type sulfonic acid.[40−42] This may partly come from the higher basicity of the diamine moieties due to the electron-donating effect. The chemical structure of 6FDA-HABA-*g*-NTDA-BSPB is shown in Figure 5.

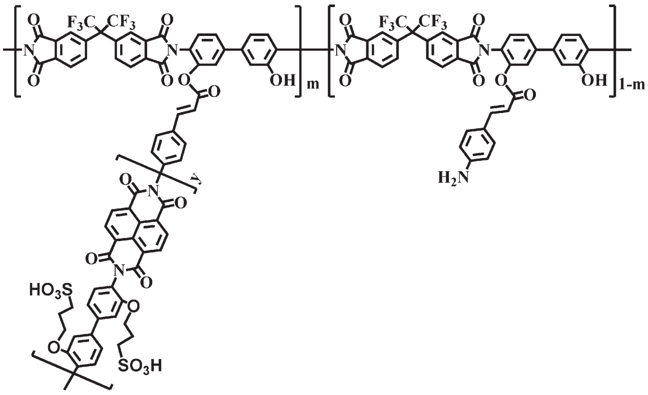


Figure 5. Chemical structure of 6FDA-HABA-*g*-NTDA-BDSA.

Table 5 shows the oxidative and hydrolytic stabilities and dimensional change of sulfonated graft copolyimide membranes. Both sulfonated graft copolyimides, 6FDA-HABA-*g*-NTDA-BDSA and 6FDA-HABA-*g*-NTDA-BSPB, showed a similar IEC due to the control of the molecular weight of side-chain polyimide and the grafting ratio. Although the dimensional change in 6FDA-HABA-*g*-NTDA-BSPB was similar to that in 6FDA-HABA-*g*-NTDA-BDSA, the oxidative and the hydrolytic stabilities of 6FDA-HABA-*g*-NTDA-BSPB exhibited 4.5 and 80 times larger values than those determined in 6FDA-HABA-*g*-NTDA-BDSA, indicating that the 6FDA-HABA-*g*-NTDA-BSPB membrane has good membrane stability. However, when compared to the perfluorosulfonated membranes, such as Nafion, the membrane stabilities of sulfonated copolyimide membranes having main-chain-type sulfonic acid are also insufficient for use as fuel cell applications yet, and the more improvements of the membranes are required for fuel cell electrolytes.

Table 6 shows the proton conductivity and oxygen permeability coefficient of sulfonated graft copolyimide membranes. Although the proton conductivity of 6FDA-HABA-*g*-NTDA-BSPB exhibited a 4.6 times larger value than that determined in Nafion, the former decreased compared to 6FDA-HABA-*g*-NTDA-BDSA (3). In addition, the oxygen permeability of 6FDA-HABA-*g*-NTDA-BSPB increased compared to 6FDA-HABA-*g*-NTDA-BDSA (3) due to the enhanced oxygen diffusivity of the 6FDA-HABA-*g*-NTDA-BSPB. However, we believe that 6FDA-HABA-*g*-NTDA-BSPB is desirable for the development of proton exchange membranes, considering the balance between the proton conductivity and membrane stability of the proton exchange membranes.

Conclusions

A series of sulfonated graft copolyimides were successfully synthesized by controlling the grafting ratio between the fluorinated polyimide as the main-chain polymer and the sulfonated

Table 4. Oxygen Permeability Coefficient (P_{O_2}) of Sulfonated Copolyimide Membrane at 35, 80, and 120 °C and at 76 cmHg

polymer	ΔE_a (kJ/mol)	P_{O_2} (35 °C)	P_{O_2}[a] (80 °C)	P_{O_2}[a] (120 °C)
6FDA-HABA		1.0		
NTDA-BDSA		0.31		
6FDA-HABA-*g*-NTDA-BDSA (1)	9	0.28	0.43	0.58
6FDA-HABA-*g*-NTDA-BDSA (2)	10	0.33	0.54	0.76
6FDA-HABA-*g*-NTDA-BDSA (3)	9	0.35	0.55	0.76
6FDA-HABA-*g*-NTDA-BDSA (4)	11	0.14	0.25	0.37
Nafion 117	49	1.1	13	70

[a] Oxygen permeability coefficient estimated from activation energy (ΔE_a). P_{O_2}: 10^{-10} (cm^3(STP) cm/(cm^2 s cmHg)).

Table 5. Oxidative and Hydrolysis Stabilities and Dimensional Change in Sulfonated Graft Copolyimide

polymer	M_w of side chain polymer	grafting ratio (%)	IEC (mequiv/g)	oxidative[a] stability (h)	hydrolysis[b] stability (h)	ref
6FDA-HABA-*g*-NTDA-BDSA (3)	1.4×10^5	1.5	2.43	1.0	16	this study
6FDA-HABA-*g*-NTDA-BSPB	1.3×10^5	3.8	2.41	4.5	1300	this study
NTDA-type sulfonated polyimide			2.04	1.7	293	43

[a] The oxidative stability was characterized by the time that the membranes completely dissolved in 3% H_2O_2, 2 ppm $FeSO_4$ at 80 °C. [b] The hydrolysis stability was characterized by the time that the membranes completely dissolved in water at 80 °C.

Table 6. Oxygen Permeability Coefficient (P_{O_2}), Diffusivity Coefficient (D_{O_2}), and Solubility Coefficient (S_{O_2}) of Sulfonated Copolyimide Membrane at 35 °C and 76 cmHg

polymer	proton conductivity[a] (S cm^{-1})	P_{O_2}[b]	D_{O_2}[c]	S_{O_2}[d]	selectivity ratio[e]
6FDA-HABA-*g*-NTDA-BDSA (3)	1.1	0.35	0.21	1.7	25
6FDA-HABA-*g*-NTDA-BSPB	0.69	0.45	0.25	1.8	12
Nafion 117	0.14	1.1	4.6	0.23	1.0

[a] At 90 °C and 98% RH. [b] P_{O_2}: 10^{-10} (cm^3(STP) cm/(cm^2 s cmHg)). [c] D_{O_2}: 10^{-8} (cm^2/s). [d] S_{O_2}: 10^{-2} (cm^3(STP)/(cm^3 cmHg)). [e] Selectivity ratio = [selectivity (polymer)/selectivity (Nafion)] and selectivity = (proton conductivity/P_{O_2}).

polyimide as the side-chain polymer. This paper showed that the proton and oxygen transport properties of the graft copolyimide membranes were greatly dependent on the molecular weight of the side-chain polymer and the grafting ratio. In particular, the graft copolyimides, 6FDA-HABA-*g*-NTDA-BDSA (3) and (4), showed higher proton conductivities exceeding that of Nafion at all temperatures, and their proton conductivities at 90 °C and 98% RH were 1.1 and 1.2 S/cm, respectively, more than 7 times that of Nafion. In addition, the oxygen permeability of 6FDA-HABA-*g*-NTDA-BDSA (4) was approximately one-eighth the value of Nafion due to significantly low oxygen diffusivity, and the membrane had a very excellent gas barrier property. However, 6FDA-HABA-*g*-NTDA-BDSA has drawbacks of lower membrane stability as one of the important elements for polymer electrolyte membranes. To improve the membrane stability of the sulfonated graft copolyimide, a novel sulfonated graft copolyimide, 6FDA-HABA-*g*-NTDA-BSPB, composed of different sulfonated diamines was synthesized. The 6FDA-HABA-*g*-NTDA-BSPB was desirable for the development of proton exchange membranes, considering the balance between the proton conductivity, gas permeability, and membrane stability of the proton exchange membranes. In this study, we have proved that the sulfonated graft copolymer is a promising candidate for optimizing the polymer structure for fuel cell applications.

Acknowledgment. This work was supported by a grant from NEDO, Japan.

References and Notes

(1) Dhar, H. P. *J. Electroanal. Chem.* **1993**, *357*, 237.
(2) Steele, B. C. H.; Heinzel, A. *Nature* **2001**, *414*, 345.
(3) Shoesmith, J. P.; Collins, R. D.; Oakley, M. J.; Stevenson, D. K. *J. Power Sources* **1994**, *49*, 129.
(4) Kreuer, K. D. *J. Membr. Sci.* **2001**, *185*, 29.
(5) Nakano, T.; Nagaoka, S.; Kawakami, H. *Polym. Adv. Technol.* **2005**, *16*, 753.
(6) Fujimoto, C. H.; Hickner, M. A.; Cornelius, C. J.; Loy, D. A. *Macromolecules* **2005**, *38*, 5010.
(7) Lee, C. H.; Park, H. B.; Chung, Y. S.; Lee, Y. M.; Freeman, B. D. *Macromolecules* **2006**, *39*, 755.
(8) Li, Y.; Roy, A.; Badami, A. S.; Hill, M.; Yang, J.; Dunn, S.; McGrath, J. E. *J. Power Sources* **2007**, *172*, 30.
(9) Gao, Y.; Robertson, G. P.; Kim, D. S.; Guiver, M. D.; Mikhailenko, S. D.; Li, X.; Kaliaguine, S. *Macromolecules* **2007**, *40*, 1512.
(10) Li, N.; Zhang, S.; Liu, J.; Zhang, F. *Macromolecules* **2008**, *41*, 4165.
(11) Sekhon, S. S.; Park, J. S.; Cho, E. K.; Yoon, Y. G.; Kim, C. S.; Lee, W. Y. *Macromolecules* **2009**, *42*, 2054.
(12) Suda, T.; Yamazaki, K.; Kawakami, H. *J. Power Sources* **2010**, *195*, 4641.
(13) Einsla, B. R.; Kim, Y. S.; Hickner, M. A.; Hong, Y. T.; Hill, M. L.; Pivovar, B. S.; McGrath, J. E. *J. Membr. Sci.* **2005**, *255*, 141.
(14) Pang, J.; Zhang, H.; Li, X.; Jiang, Z. *Macromolecules* **2007**, *40*, 9435.
(15) Lee, C. H.; Hwang, S. Y.; Sohn, J. Y.; Park, H. B.; Kim, J. Y.; Lee, Y. M. *J. Power Sources* **2006**, *163*, 339.
(16) Lee, K. S.; Jeong, M. P.; Lee, J. P.; Lee, J. S. *Macromolecules* **2009**, *42*, 584.
(17) Liu, F.; Yi, B.; Xing, D.; Yu, J.; Zhang, H. *J. Membr. Sci.* **2003**, *212*, 213.
(18) Cheng, X.; Zhang, J.; Tang, Y.; Song, C.; Shen, J.; Song, D.; Zhang., J. *J. Power Sources* **2007**, *167*, 25.
(19) Inaba, M.; Kinumoto, T.; Kiriake, M.; Umebayashi, R.; Tasaka, A.; Ogumi, Z. *Electrochim. Acta* **2009**, *54*, 1076.
(20) Wang, H.; Capuano, G. A. *J. Electrochem. Soc.* **1998**, *145*, 780.
(21) Panchenko, A. *J. Membr. Sci.* **2006**, *278*, 269.
(22) Zhang, S.; Yuan, X. Z.; Hin, J. N. C.; Wang, H.; Friedrich, K. A.; Schulze., M. *J. Power Sources* **2009**, *194*, 588.
(23) Asano, N.; Miyatake, K.; Watanabe, M. *Chem. Mater.* **2004**, *16*, 2841.
(24) Lee, S. W.; Kim, S. I.; Lee, B.; Choi, W.; Chae, B.; Kim, S. B.; Ree, M. *Macromolecules* **2003**, *36*, 6527.
(25) Mikawa, M.; Nagaoka, S.; Kawakami, H. *J. Membr. Sci.* **1999**, *163*, 167.
(26) Kawakami, H.; Nakajima, K.; Nagaoka, S. *J. Membr. Sci.* **2003**, *211*, 291.
(27) Sannomiya, A.; Nagaoka, S.; Suzuki, Y.; Iwaki, M.; Kawakami, H. *Polymer* **2006**, *47*, 6585.
(28) Gao, Y.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Li, X.; Kaliaguine, S. *Macromolecules* **2005**, *38*, 3237.
(29) Kim, D. S.; Robertson, G. P.; Kim, Y. S.; Guiver, M. D. *Macromolecules* **2009**, *42*, 957.
(30) Zhang, G.; Fu, T.; Shao, K.; Li, X.; Zhao, C.; Na, H.; Zhang, H. *J. Power Sources* **2009**, *189*, 875.
(31) Zawodzinski, T. A., Jr.; Neeman, M.; Sillerud, L. O.; Gottesfeld, S. *J. Phys. Chem.* **1991**, *95*, 6040.
(32) Lin, J.; Wu, P. H.; Wycisk, R.; Pintauro, P. N.; Shi, Z. *Macromolecules* **2008**, *41*, 4284.
(33) Kreuer, K. D.; Rabenau, A.; Weppner, W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 208.
(34) Finsterwalder, F.; Hambitzer, G. *J. Membr. Sci.* **2001**, *185*, 105.
(35) Su, Y. H.; Liu, Y. L.; Sun, Y. M.; Lai, J. Y.; Wang, D. M.; Gao, Y.; Liu, B.; Guiver, M. D. *J. Membr. Sci.* **2007**, *296*, 21.
(36) So, S. Y.; Hong, Y. T.; Kim, S. C.; Lee, S. Y. *J. Membr. Sci.* **2010**, *346*, 131.
(37) Saito, J.; Miyatake, K.; Watanabe, M. *Macromolecules* **2008**, *41*, 2415.
(38) Bae, B.; Miyatake, K.; Watanabe, M. *Macromolecules* **2009**, *42*, 1873.
(39) Watari, T.; Fang, J.; Tanaka, K.; Kita, H.; Okamoto, K.; Hirano, T. *J. Membr. Sci.* **2004**, *230*, 111.
(40) Yin, Y.; Fang, J.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. *J. Mater. Chem.* **2004**, *14*, 1062.
(41) Asano, N.; Aoki, M.; Suzuki, S.; Miyatake, K.; Uchida, H.; Watanabe, M. *J. Am. Chem. Soc.* **2006**, *128*, 1762.
(42) Savard, O.; Peckham, T. J.; Yang, Y.; Holdcroft, S. *Polymer* **2008**, *49*, 4949.
(43) Zhai, F.; Guo, X.; Fang, J.; Xu, H. *J. Membr. Sci.* **2007**, *296*, 102.