Available online at www.sciencedirect.com

ScienceDirect

Polymer 48 (2007) 5878–5883

polymer

www.elsevier.com/locate/polymer

Synthesis and properties of sulfonated poly(2,5-diphenethoxy-*p*-phenylene)

Kazuhiro Nakabayashi, Kazuya Matsumoto, Yuji Shibasaki, Mitsuru Ueda*

Department of Organic and Polymeric Materials, Graduate School of Science and Engineering,
Tokyo Institute of Technology, 2-12-1 H-120 O-okayama, Meguro-ku, Tokyo 152-8552, Japan

Received 23 April 2007; received in revised form 25 July 2007; accepted 6 August 2007
Available online 9 August 2007

Abstract

A novel regio-controlled poly(2,5-diphenethoxy-*p*-phenylene) partially functionalized with sulfonic acids has been developed for a proton exchange membrane. Poly(2,5-diphenethoxy-*p*-phenylene) was prepared via the oxidative-coupling polycondensation using iron(III) trichloride as an oxidant. A high molecular weight polymer over 270,000 in the weight-average molecular weight was quantitatively obtained in mild conditions. This polymer was then reacted with two and four equimolar trimethylsilylchlorosulfonate in dichloromethane to give the corresponding sulfonic acid-functionalized polymers, whose functionalities were 0.69 and 1.19 per a polymer unit, which were translated to be 1.73 and 2.49 mequiv/g in ion exchange capacity (IEC), respectively. These polymers showed excellent proton conductivity up to 2×10^{-1} S/cm at 80 °C and 95% relative humidity.

Keywords: Proton conductivity; Fuel cell; Sulfonic acid

1. Introduction

Proton-conductive polymers are one of the key materials in polymer electrolyte fuel cells (PEFCs). Because of their chemical and physical stabilities and high proton conductivity, perfluorinated polymers such as Nafion® or Flemion® are the state-of-the-art materials and have been extensively studied [1,2]. Despite of their advantages in the high conductivity, and good mechanical and chemical properties, some shortages exist that restrict their use in fuel cells, such as high cost, high methanol permeation property, and low conductivity at high temperatures over 80 °C.

Recently, there has been a great demand for alternative non-fluorinated polymeric materials that are more conductive, operable at high temperatures (>120 °C), environmentally benign, and inexpensive. One of the challenges is sulfonated aromatic hydrocarbon polymers [3–5], in which poly(phenylene)s [6–11], poly(ether ether ketone)s [6], poly(ether sulfone)s [12], poly(arylene ether)s [13–15], polyimide [16,17] are widely investigated as candidates of PEFC materials. However, to simplify the preparation process and enhance the performance of these materials, there are still some challenges, such as stereo-controllable chemical structures including easily controllable degree of sulfonation and sulfonation sites [18].

Among aromatic hydrocarbon polymers, poly(*p*-phenylene)s (PPs) [6–11] show excellent thermo-chemical stability, low water uptake, and low methanol permeation. PPs, however, show low solubility in common organic solvent, and thus difficult to obtain high molecular weight polymers to make robust films, which are necessary characteristics of a membrane electrode assembly to survive with PEFCs environments. In a previous work, Rikukawa et al. reported that sulfonated poly(*p*-phenylene)s with flexible polymer side chains were obtained via the nickel(0) catalyzed polymerization and showed higher and more stable proton conductivity

---

* Corresponding author. Tel./fax: +81 3 5734 2127.
E-mail address: ueda.m.ad@m.titech.ac.jp (M. Ueda).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.08.008

than sulfonated poly(ether ether ketone)s [6]. In this case, it is suggested that the flexible polymer side chain contributes to high proton conductivity because Nafion® also has the flexible polymer side chain. However, the Ni(0) catalyzed polymerization of the corresponding dihalobenzenes is generally very difficult to produce PPs with high-molecular weights [6,7,11]. Thus, the object of this paper is to show that an oxidative-coupling polymerization, which is an atom economical reaction, is an efficient method to prepare PPs with high-molecular weights, and the resulting PPs are easily sulfonated to give excellent proton-conductive membranes.

We now report a facile synthesis of novel high molecular weight sulfonated PPs via the oxidative regio-controlled polymerization and their properties such as proton conductivity, water uptake, thermal stability, and oxidative stability.

2. Experimental section

2.1. Materials

Hydroquinone (99%) and (2-bromoethyl)benzene (97%) were purchased from TCI. Trimethylsilylchlorosulfonate (99%) was purchased from Aldrich. Anhydrous $FeCl_3$, anhydrous K_2CO_3 (99.5%), anhydrous dichloroethane (99%), and nitrobenzene (99.5%) were purchased from Wako. Nitrobenzene was distilled before use. Other solvents and reagents were used as-received.

2.2. Measurements

The FT-IR spectra were measured on a Horiba FT-720 spectrometer. The ^1H (300 MHz) and ^{13}C NMR spectra (75 MHz) were recorded with a Bruker DPX300S spectrometer. Cyclic voltammogram was measured at room temperature in a typical three electrode with a working (Pt wire), a reference (Ag/AgCl), and a counter electrode (Pt spiral) under a nitrogen atmosphere at a sweeping rate of 10 mV/s (Hokuto Denko HSV-100). A 0.1 M solution of tetrabutylammonium perchlorate in anhydrous acetonitrile was used as an electrolyte. Number- and weight-average molecular weights (M_n and M_w) were measured by gel permeation chromatography (GPC) on a Hitachi LC-7000 system equipped with a polystyrene gel column (TSKgel GMHHR-M) eluted with tetrahydrofuran (THF) at a flow rate of $1.0\ \mathrm{mL\ min^{-1}}$ calibrated by standard polystyrene samples. Thermal analysis was performed using a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C/min for thermogravimetry (TG), differential thermal analysis (DTA), and Seiko EXSTAR 6000 DSC 6200 at a heating rate of 10 °C/min for differential scanning calorimetry (DSC) under nitrogen.

2.3. Synthesis of 1,4-diphenethoxybenzene (*1*)

The title compound was prepared from hydroquinone and 2-bromoethylbenzene by refluxing in acetone for 24 h under nitrogen. The solution was concentrated, and the resulting oil was dissolved in diethyl ether, washed with NaOH aq solution, and dried over $MgSO_4$. The solvent was distilled off, and the resulting oil solidified. Recrystallization from ethanol gave white needles in 23% yield. M.p. 57–58 °C (Ref. [19], 62 °C).

2.4. Synthesis of poly(2,5-diphenethoxy-p-phenylene) (*2*)

To a mixture of **1** (0.80 g, 2.5 mmol), potassium carbonate (0.35 g, 2.5 mmol), and nitrobenzene (10 mL), anhydrous $FeCl_3$ (2.0 g, 12.5 mmol) was added and stirred under nitrogen for 24 h. The solution was poured into methanol/1 N HCl aq. The precipitated polymer was collected by filtration, washed with methanol and water several times. The fibrous polymer was collected and dried in vacuum at 100 °C for 10 h. ^1H NMR ($CDCl_3$): 7.20–6.96 (12H, m), 4.04 (4H, s), and 2.88 ppm (4H, s). ^{13}C NMR ($CDCl_3$): 150.3, 138.8, 129.6, 128.6, 128.3, 126.5, 116.9, 70.4, and 36.5 ppm.

2.5. Synthesis of sulfonated poly(2,5-diphenethoxy-p-phenylene) (*3*)

To a solution of polymer **2** (0.64 g, 2.0 mmol) in 200 mL of dichloromethane, 1.0 M trimethylsilylchlorosulfonate in dichloromethane (4.0 mL) was added drop wise. The mixture was stirred at room temperature for 24 h and poured drop wise into hexane to precipitate a brown powder. The mixture of the resulting powder was stirred in 1 M H_2SO_4 aq at room temperature for 2 day for protonation. Then, the powder was washed thoroughly with water, and dried under vacuum at 60 °C for 10 h to obtain a brown powder **3** with $x = 0.69$ (which corresponds to 1.73 mequiv/g of the IEC).

2.6. Membrane preparation and ion exchange capacity (IEC)

A solution of polymer **3** in *N*,*N*-dimethylacetamide (DMAc) was cast onto a flat glass plate. Drying under vacuum at 60 °C for 15 h gave a clear and flexible membrane. The thickness of the membranes was 30–70 μm. IEC was determined by titration with 0.02 M NaOH aq.

2.7. Proton conductivity

Proton conductivity in plane direction of membrane was determined using an electrochemical impedance spectroscopy technique over the frequency from 10 Hz to 100 KHz (Hioki 3532-80). A two-point-probe conductivity cell with two platinum plate electrodes was fabricated. Membrane samples were cut into strips that were 1.0 cm wide, 1.0 cm long, and 50 μm thick before being mounted in the cell. The cell was plated under a thermo-controlled humid chamber. Proton conductivity (σ) was calculated from:

$$\sigma = d/(L_s w_s R)$$

where d is the distance between the two electrodes, L_s and w_s are the thickness and width of the membrane at a standard condition of 80 °C, respectively, and R is the resistance value measured.

2.8. Water uptake and dimensional change

Water uptake was measured by immersing the membrane into water at room temperature for 8 h. Then the membrane was taken out, wiped with tissue paper, and quickly weighed on a microbalance. Water uptake was calculated from:

$$\mathrm{WU} = (W_\mathrm{s} - W_\mathrm{d})/W_\mathrm{d} \times 100 \quad \mathrm{wt\%}$$

where, W_s and W_d are the weights of hydrated and dried membranes, respectively.

Dimensional change was investigated by immersing the membrane into water at room temperature for 8 h, the changes of thickness and length were calculated from:

$$\Delta t_\mathrm{c} = (t - t_\mathrm{s})/t_\mathrm{s}$$

$$\Delta l_\mathrm{c} = (l - l_\mathrm{s})/l_\mathrm{s}$$

where t_s and l_s are the thickness and diameter of the dried membrane, respectively; t and l refer to those of the membrane in water for 8 h.

2.9. Oxidative stability

A small piece of a membrane sample was soaked in 3% H_2O_2 aq for 1 h at 25 °C. The stability was evaluated by changes in the weight and the appearance of the test samples.

3. Results and discussion

3.1. Polymerization

Table 1
Synthesis of poly(2,5-diphenethoxy-*p*-phenylene)[a]

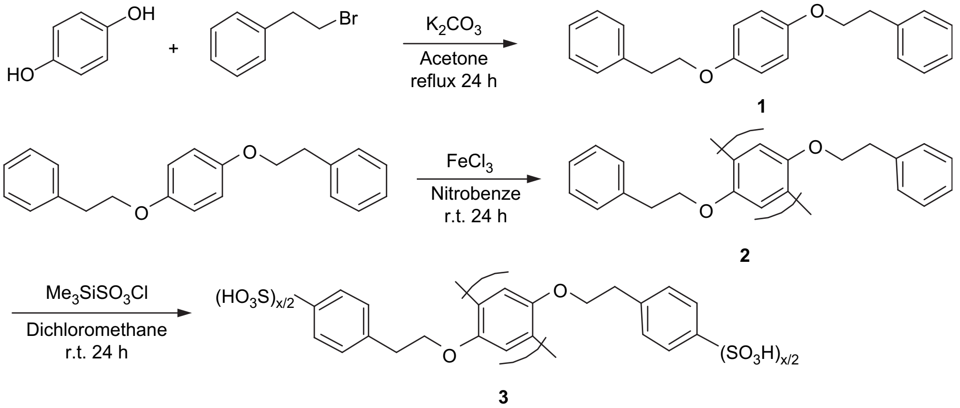
Run	$FeCl_3$ (equiv)	Yield (%)	M_n[b]	$M_\mathrm{w}/M_\mathrm{n}$[b]
1	4.0	83	8400	2.9
2	4.5	87	34,000	4.4
3	5.0	90	68,000	4.1

[a] Polymerization was carried out with 2.5 mmol of **1** in 10 mL of nitrobenzene for 24 h at room temperature in the presence of 1.0 mmol of K_2CO_3.

[b] Determinded by GPC eluted with THF using polystyrene standard.

Monomer **1** was synthesized by the Williamson ether reaction of hydroquinone with (2-bromoethyl)benzene according the reported procedure (Scheme 1) [19]. It is important to measure the oxidation potentials of **1** for the selection of oxidants. The cyclic voltammogram of **1** was measured in acetonitrile solution containing 0.1 M tetrabutylammonium perchlorate in a glass cell equipped with a reference electrode (Ag/AgCl), a working electrode (Pt), and an auxiliary electrode (Pt). The cyclic voltammogram showed an oxidation peak at 1.37 V. From this oxidation potential, iron(III) chloride ($FeCl_3$) was selected as an oxidant. Then polymer **2** was prepared by the oxidative-coupling polymerization of **1** using $FeCl_3$. The results are summarized in Table 1. Polymerizations proceed smoothly at room temperature and a high molecular weight polymer of $M_\mathrm{w} = 279{,}000$, which is the highest value in the reported PPs, is obtained in the presence of 5.0 equiv of $FeCl_3$ to **1**. Polymer **2** showed good solubility in common organic solvents, such as THF, chloroform, and dichloromethane.

Polymer **2** was confirmed to be the regio-controlled poly(2,5-diphenethoxy-*p*-phenylene) by NMR spectroscopy (run 3 in Table 1). The aromatic regions of ^{13}C NMR and DEPT45 NMR spectra with the assignment of each peak are depicted in Fig. 1. There are seven signals at 150.2, 138.8, 129.3, 128.3, 128.0, 126.2, and 116.7 ppm due to the aromatic carbons. The DEPT45 spectrum shows the signal at 150.2, 138.8, and 128.0 ppm to be the quaternary carbons. These data support the regio-controlled structure of the resulting polymer. In the oxidative-coupling polymerization of 1,4-di-*n*-butoxybenzene using $FeCl_3$, a regio-irregular polymer was obtained [20]. On the other hand, the regio-controlled polymer can be prepared by an oxovanadium catalyzed polycondensation of 1,4-di-*n*-butoxybenzene, thanks to the catalyst property [21]. Although the reason why the regio-controlled polymerization of **2** proceeded is not clear, we tentatively think that the regio-selectivity in the polymerization of **2** results from the reactivity difference between 5 and 6 positions of monomer **1** after the reaction at 2 position.



Scheme 1. Synthesis of sulfonated poly(2,5-diphenethoxy-*p*-phenylene) **3**.

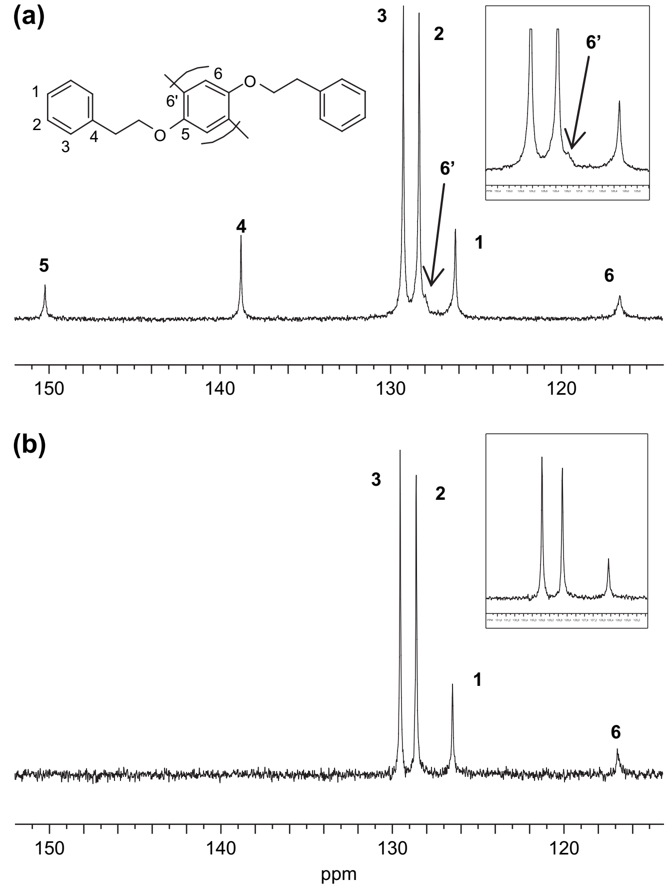


Fig. 1. Expanded (a) ^{13}C NMR spectra of **2** and (b) its DEPT45 NMR in $CDCl_3$.

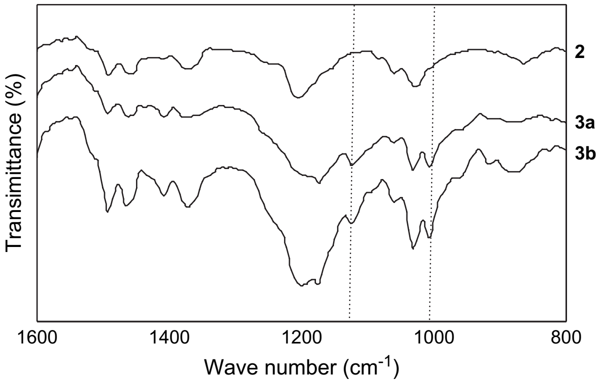


Fig. 2. FT-IR spectra of **2**, **3a**, and **3b**.

3.2. Sulfonation of polymer 2

Polymer **2** was treated with trimethylsilylchlorosulfonate in dichloromethane to afford sulfonated polymer **3** (Table 2). The degree of sulfonation (x) per a repeating unit was determined by titration. The value x could be easily controlled by changing the amount of trimethylsilylchlorosulfonate used in the reaction. When two and four equimolar trimethylsilylchlorosulfonate to **2** was used, sulfonated polymers **3a** with $x = 0.69$ (which corresponds to 1.73 mequiv/g of the IEC) and **3b** with $x = 1.19$ (2.49 mequiv/g of the IEC) are obtained, respectively. Polymer **3** showed good solubility in DMAc, dimethyl sulfoxide (DMSO), and *N*,*N*-dimethylformamide (DMF). The introduction of sulfonic acid groups was confirmed by IR spectroscopy. The IR spectrum of **3** exhibits the characteristic absorptions at 1007 cm^{-1} and 1184 cm^{-1} due to the SO_2 stretching (Fig. 2).

Table 2
Synthesis of polymer **3**[a]

Run	Me_3SiSO_3Cl (equiv)	Sulfonation degree (x)[b]	IEC (mequiv/g)[c]
3a	2.0	0.69	1.73
3b	4.0	1.19	2.49

[a] The equivalent of Me_3SiSO_3Cl was added to moles of a repeat unit in the reaction.

[b] Average number of sulfonic acid groups per a repeat unit.

[c] Measured by titration.

3.3. Thermal stability

Fig. 3 shows the TG curves of polymer **3**. A two-step weight loss is observed from 50 °C to 130 °C and above 180 °C. The first weight loss is due to the evaporation of hydrated water, and the second weight loss is attributable to the decomposition of the sulfonic acid groups and polymer side chains. T_g of polymer **3** was not observed. These results suggest that polymer **3** is stable under the PEFC operating environment.

3.4. Oxidative stability

Oxidative stability was investigated for polymer **3** by soaking them in a H_2O_2 aq solution. The weight losses of **3a** and **3b** membranes are observed about 10 and 17 wt%, respectively (Table 3), which are comparable to the reported values of other side-chain sulfonated polyimides [22–24]. These membranes still remained a self-supporting film. The IR spectra of **3a** and **3b** membranes after this experiment exhibited the characteristic absorption at 1650 cm^{-1} due to the C=O stretching, which indicates that the weight loss of **3** membranes is due to the partial decomposition (about 12%) of polymer side chain.

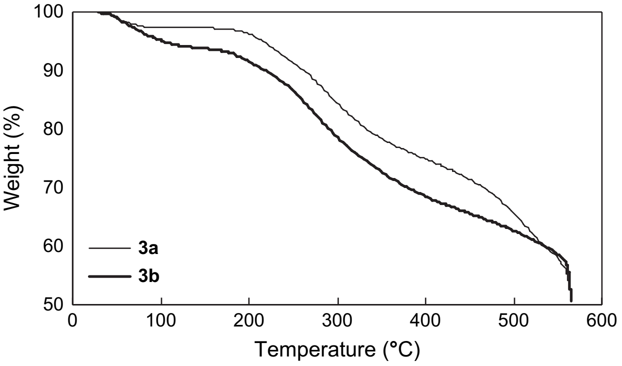


Fig. 3. TG curves of **3a** (thin line) and **3b** (thick line).

Table 3
Water uptake, dimensional change, and oxidative stability of polymer **3**

Run	WU (wt%)	Δt	Δl	Weight loss (%)[a]
3a	194	0.28	0.35	10
3b	222	0.58	0.67	17

[a] Weight loss of membranes after treating H_2O_2 aq for 1 h.

Table 4
Comparison of the state of water of **3a**, **3b**, and Nafion 117 membranes

Sample	IEC (mequiv/mg)	Free water (%)	Bound water (%)
3a	1.73	86.7	13.3
3b	2.49	85.7	14.3
Nafion 117	0.90	62.1	38.6

3.5. DSC analysis

The water around **3** was analyzed with a DSC [25] as shown in Fig. 4. In DSC curves, a single peak around 0 °C stands for an endothermic peak corresponding to the heat of fusion of free water – the same transition temperature as that of bulk water. The amount of free water in **3a** and **3b** was obtained from an integration of the endothermic peak area. Then, the amount of bound water was calculated from the difference between the total water and free water. Bound water is classified into freezing bound water and non-freezing bound water, which is due to the degree of interaction between the water molecules and the polymeric matrix with polar and ionic groups [25]. The amount of free water and bound water is summarized in Table 4. The amount of bound water of **3a**, **3b**, and Nafion 117 is 13.3, 14.3, and 38.6 wt%, respectively. In addition, another endothermic peak at around 100 °C is observed, indicating the heat of vaporization of the water. The existence of more bound water content causes an increase of the vaporization temperature, which indicates stronger water–polymer interactions.

3.6. Water uptake and dimensional change

Water uptake and dimensional change are closely related to the properties like IEC, proton conductivity, and dimensional stability. The water within the membranes' provides a carrier for the proton and maintains high proton conductivity. However, excessive water uptake induces unacceptable dimensional change. Water uptakes of **3a** and **3b** membranes were measured at 80 °C under various humidity conditions. The results are summarized in Table 3 and Fig. 5(a), in comparison with those of Nafion 117. Membranes **3a** and **3b** show considerably high water uptake; **3a** membrane with IEC = 1.73 mequiv/g absorbs 30 wt% of water at 95% RH, **3b** membrane with IEC = 2.49 mequiv/g absorbs 54 wt% of water at 95% RH, which corresponds to 12 and 9.2 water molecules per a sulfonic acid group, respectively. These are comparable to the reported value for PPs [6], and higher than that of Nafion 117 (7.7 H_2O/SO_3H) under the similar conditions. Water uptakes of **3a** and **3b** membranes decrease rapidly with decreasing RH, which is also similar to the reported phenomena [6].

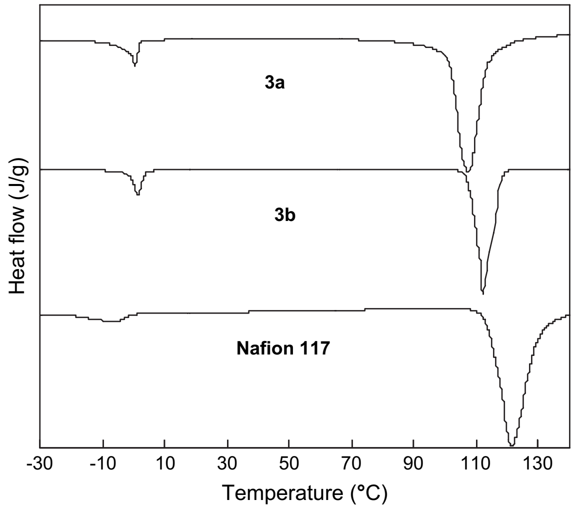


Fig. 4. DSC thermo-diagram of **3a**, **3b**, and Nafion 117.

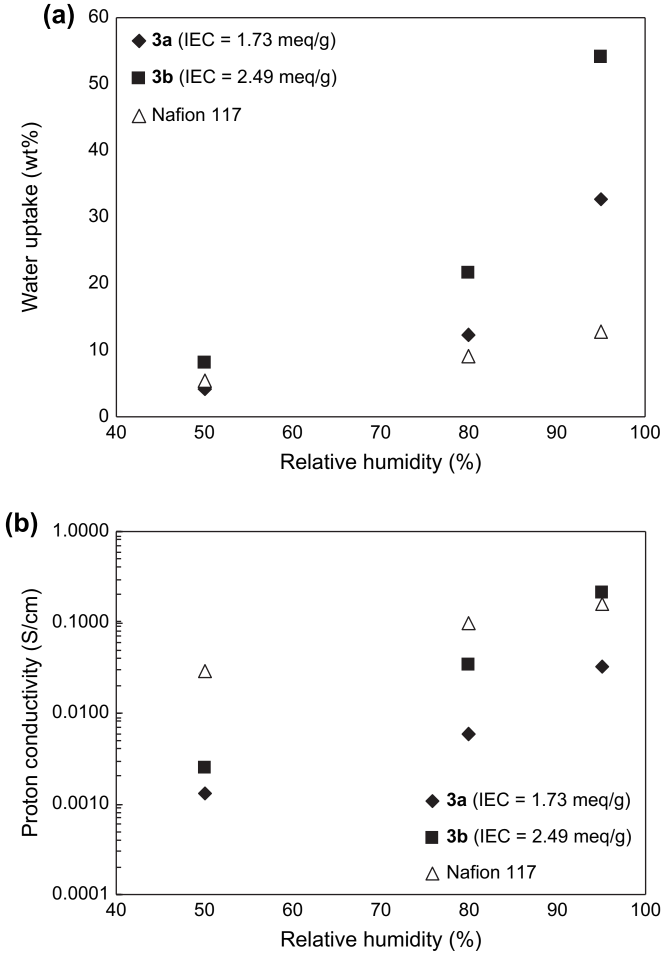


Fig. 5. Humidity dependence of (a) water uptake and (b) proton conductivity of **3a**, **3b**, and Nafion 117 membranes at 80 °C.

3.7. Proton conductivity

The proton conductivity of **3a** and **3b** membranes was measured at 80 °C under various humidity conditions. Proton conductivity through the membranes is considerably affected by the water state and water uptake. The results are summarized in Fig. 5(b), in comparison with those of Nafion 117. While lower proton conductivity is observed for **3a** membrane, **3b** membrane has a high proton conductivity of 2×10^{-1} S/cm at 95% RH, which is higher than those of reported PPs and Nafion 117. The proton conductivities of **3a** and **3b** membranes decrease under 50% and 80% RH, respectively. These behavior is similar to that of reported PPs and other sulfonated aromatic polymers, and is explained with the decrease of water uptake of these membranes under 50% and 80% RH and a low content of bound water of **3a**, **3b** membranes.

4. Conclusions

We have demonstrated the facile synthesis and properties of a novel sulfonated poly(2,5-diphenethoxy-*p*-phenylene) **3** via the oxidative-coupling polymerization, followed by sulfonation. Poly(2,5-diphenethoxy-*p*-phenylene) **2** with high a molecular weight was easily obtained. The polymer structure of **2** was confirmed by ^{13}C and ^{13}C DEPT45 NMR spectra, and identified to be the regio-controlled poly(2,5-diphenethoxy-*p*-phenylene). Polymer **2** showed good solubility in common organic solvent, such as THF, chloroform, and dichloromethane. Changing the amount of trimethylsilylchlorosulfonate used in the reaction could easily control the degree of sulfonation. Under dry conditions, the robust film of polymer **3** was stable up to 180 °C without any decomposition. Polymer **3b** membrane (IEC = 2.49 mequiv/g) showed a high proton conductivity of 2×10^{-1} S/cm at 95% RH, which was higher than that of Nafion 117. This new synthetic method provides an efficient route in comparison with conventional routes for sulfonated PPs.

References

[1] Mauritz KA, Moore RB. Chem Rev 2004;104:4537.
[2] Savadoga O. J New Mater Electrochem Syst 1998;1:47.
[3] Hickner AH, Ghassemi H, Kim YS, Einsla BR, McGrath JE. Chem Rev 2004;104:4587.
[4] Rikukawa M, Sanui K. Prog Polym Sci 2000;25:1463.
[5] Yin Y, Yamada O, Tanaka K, Okamoto K. Polym J 2006;38:197.
[6] Kobayashi T, Rikukawa M, Sanui K, Ogata N. Solid State Ionics 1998; 106:219.
[7] Ghassemi H, McGrath JE. Polymer 2004;45:5847.
[8] Fujimoto CH, Hickner MA, Cornelius CJ, Loy DA. Macromolecules 2005;38:5010.
[9] Ninivin CL, Balland-Longeau A, Demattei D, Palmas P, Saillard J, Coutanceau C, et al. J Appl Polym Sci 2006;101:944.
[10] Hickner MA, Fujimoto CH, Cornelius CJ. Polymer 2006;47:4238.
[11] Ninivin CL, Balland-Longeau A, Demattei D, Coutanceau C, Lamy C, Léger JM. J Appl Electrochem 2004;34:1159.
[12] Kerres JA. J Membr Sci 2001;185:3.
[13] Miyatake K, Chikashige Y, Watanabe M. Macromolecules 2003;36: 9691.
[14] Chikashige Y, Chikyu Y, Miyatake K, Watanabe M. Macromolecules 2005;38:7121.
[15] Miyatake K, Chikashige Y, Higuchi E, Watanabe M. J Am Chem Soc 2007;129:3879.
[16] Fang JH, Guo XX, Harada S, Watari T, Tanaka K, Kita H, et al. Macromolecules 2002;35:9022.
[17] Miyatake K, Yasuda T, Hirai M, Nanasawa M, Watanabe M. J Polym Sci Part A Polym Chem 2007;45:157.
[18] Liu B, Robertson GP, Kim DS, Guiver MD, Hu W, Jiang Z. Macromolecules 2007;40:1934.
[19] Vande Velde CML, Baeke JK, Geise HJ, Blockhuys F. Acta Crystallogr 2003;E59:823.
[20] Okada T, Ogata T, Ueda M. Macromolecules 1996;29:7645.
[21] Ueda M, Abe T, Awano H. Macromolecules 1992;25:5125.
[22] Asano N, Miyatake K, Watanabe M. Chem Mater 2004;16: 2841.
[23] Yasuda T, Miyatake K, Hirai M, Nanasawa M, Watanabe M. J Polym Sci Part A Polym Chem 2005;43:4439.
[24] Asano N, Aoki M, Suzuki S, Miyatake K, Uchida H, Watanabe M. J Am Chem Soc 2006;128:1762.
[25] Lee CH, Park HB, Chung YS, Lee YM, Freeman BD. Macromolecules 2006;39:755.