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Novel highly proton conductive sulfonated poly(*p*-phenylene) from 2,5-dichloro-4-(phenoxypropyl)benzophenone as proton exchange membranes for fuel cell applications†

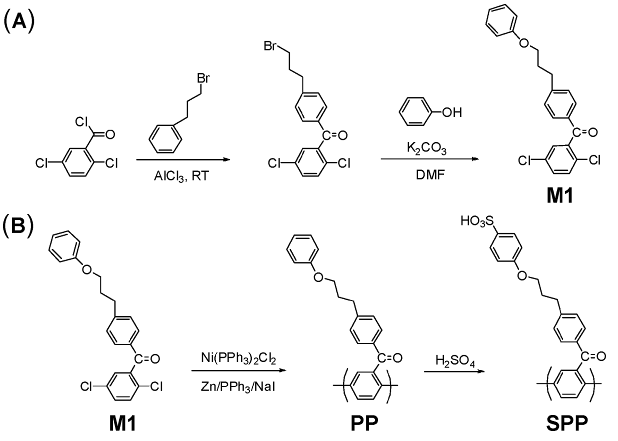
Surasak Seesukphronrarak and Akihiro Ohira*

Received (in Cambridge, UK) 23rd April 2009, Accepted 15th June 2009
First published as an Advance Article on the web 1st July 2009
DOI: 10.1039/b908140b

A novel sulfonated poly(4-phenoxypropylbenzoyl-1,4-phenylene) introducing a flexible alkyl chain was synthesized and achieved high proton conductivity even at low humidity (SPP: 0.077 S cm^{-1}, Nafion 112: 0.029 S cm^{-1} at 80 °C 50% RH).

The proton exchange membranes (PEM), the key material for the operation of a proton exchange membrane fuel cell (PEMFC), have received much attention as promising materials for clean power sources in portable and stationary electronic applications.[1] Currently, perfluorosulfonic acids (PFSA) such as Nafion® produced by DuPont are widely used as the PEM in PEMFC because of their good mechanical properties and high oxidative stability as well as their high proton conductivity compared to most hydrocarbon (HC) based membranes. However, high cost, loss of proton conductivity at high temperature and low humidity, and relatively high gas permeability have limited PFSA membranes for further commercial application.[2] Therefore, the development of an alternative non-perfluorinated polymeric materials such as sulfonated poly(arylene ether ketone),[3] sulfonated poly(ether sulfone),[4] sulfonated polyimide,[5] and sulfonated derivatives of poly(*p*-phenylene)[3a,6] have been extensively investigated by many research groups to achieve high proton conductivity and application at conditions of high temperatures with lower fuel crossover. Recently, sulfonated poly(*p*-phenylene) and their derivatives, with wholly aromatic structure throughout the backbone, have received much attraction as candidates for PEM due to their excellent thermal and hydrolytic stabilities. Unfortunately, some membranes composed of those polymers exhibit low solubility in organic solvents as well as poor flexibility (making it difficult to handle them) thereby it has still been difficult to apply these to PEMFC. Based on the significance of the development of novel polymers for PEMFC, here we developed a novel side chain type monomer, 2,5-dichloro-4-(phenoxypropyl)benzophenone, which contained an aliphatic group linked between a phenoxy unit and benzophenone in order to improve the flexibility of the polymer membrane and to increase the proton conductivity of the membrane. The flexible aliphatic group was expected to improve the hydrolytic stability and to increase the polymer chain mobility, which had a significant influence on proton transport resulting in an increase in proton conductivity. Therefore, in this communication, a novel side chain type sulfonated poly(*p*-phenylene) was prepared by Ni(0) catalyzed coupling polymerization from 2,5-dichloro-4-(phenoxypropyl)benzophenone. Preliminary results of proton conductivity, water uptake, thermal stability properties, and gas permeability were also obtained and compared with data for sulfonated poly(ether ether ketone), **S-PEEK**, and Nafion.

A novel monomer **M1** having a propoxy linkage between the phenoxy unit and benzophenone group, 2,5-dichloro-4-(phenoxypropy)lbenzophenone, was designed and prepared in three steps as shown in Scheme 1. First, 2,5-dichlorobenzoyl chloride was prepared from 2,5-dichlorobenzoic acid with thionyl chloride. Then, 2,5-dichloro-4-(bromopropyl)benzophenone was obtained by Friedel–Crafts acylation of benzenepropylbromide with 2,5-dichlorobenzoyl chloride using $AlCl_3$ as catalyst. **M1** was obtained by reaction of 2,5-dichloro-4-(bromopropyl)benzophenone and phenol in the presence of K_2CO_3 and KI as a base and catalyst in acetone. The crude product was recrystallized from hexane twice to afford **M1** as white crystals in 60% yield. The structure of the final monomer **M1** was confirmed by FT-IR, ^{1}H-, ^{13}C-NMR, MS, and elemental analysis (see ESI† for details); all data supported the proposed chemical structure of **M1**. Homopolymer **PP** was synthesized by Ni(0) catalyzed coupling polymerization, generated *in situ* from $Ni(PPh_3)_2Cl_2$, PPh_3, Zn, and NaI in NMP.[7] Polymerization was carried out by heating at 75 °C for 3–4 h or until the polymer mixture



Scheme 1 Synthesis route of (A) monomer **M1** and (B) sulfonated homopolymer poly(*p*-phenylene) **SPP**.

FC-Cubic, National Institute of Advanced Industrial Science and Technology (AIST), Tokyo 135-0064, Japan.
E-mail: a-oohira@aist.go.jp; Fax: +81 3 3599 8554;
Tel: +81 3 3599 8550

† Electronic supplementary information (ESI) available: Monomer and polymer synthesis, experimental methods, measurement, results of TGA thermogram λ-relative humidity relationship and oxygen permeability. See DOI: 10.1039/b908140b

could no longer be stirred. The resulting polymer showed high viscosity. After purification and drying, the polymer was isolated in >90% yield. The molecular weight of the **PP** was determined by GPC using the polystyrene as standard. The number-average molecular weight (M_n) of **PP** was 3.79×10^4 with a polydispersity (M_w/M_n) value of 3.6. **PP** was then sulfonated using concentrated sulfuric acid at room temperature for 75 h. The successful introduction of the sulfonic groups was confirmed by FT-IR spectra which showed the characteristic bands for **SPP** at around 1160 and 1024 cm^{-1} due to the symmetric and asymmetric stretching of sulfonic groups. Although the IEC of **SPP** was rather high, we found that **SPP** was stable to water at room temperature, but was soluble in boiling water—similar to **S-PEEK**. **SPP** was readily soluble in dipolar aprotic solvents such as NMP, DMAc, DMSO, and DMF. **SPP** membranes were transparent, flexible, easier to handle even in the water-swelling form or in the dry form compared to that of some sulfonated poly(*p*-phenylene)s and their derivatives, which were rather brittle or showed difficulty in obtaining flexible membranes by casting.[4] This might be due to the presence of flexible aliphatic propyl on the monomer side group increasing the mobility of the polymer side chain.

The thermal stabilities of **PP** and **SPP** were determined at the heating rate of 10 °C min^{-1} by TGA under an air and a nitrogen atmosphere, respectively (see Fig. S1, ESI†). **PP** was a thermally stable polymer with a 10% weight loss temperature of about 384 °C. In the case of **SPP**, two step degradation patterns were observed as shown in Fig. S1 (see ESI†). Generally, the weight loss occurring below 150 °C is due to the evaporation of water absorbed in the polymers. There was no difference in the first stage weight loss in the TGA patterns under nitrogen and air atmospheres of SPP and decomposition occurred over the temperature range 220 to 400 °C caused by the decomposition of the sulfonic acid. This indicates that the degradation of **SPP** under air did not affect the significant thermal stability of the sulfonic group on the polymer side chain. However, the second weight loss step related to the degradation of the main chain under an air atmosphere, **SPP** degraded more quickly than those with nitrogen atmosphere in the temperature range 410–550 °C.

The humidity dependence of water uptake also was investigated at 80 °C and found that the water uptake is increased with increasing relative humidity and reached 61% at 95% RH, corresponding to an absorption of 10 water molecules per $-SO_3H$ group. In spite of the high ion exchange capacity (IEC: 3.39 mequiv g^{-1}), **SPP** membranes have acceptable water uptake of 61%, as shown in Fig. 1A. The λ values of **SPP** membranes increased as the relative humidity increased. Despite the increase in water content with IEC, there is no significant difference between **SPP** and Nafion. In the case of Nafion, continuous water channels can be formed even with small amounts of water, but for **S-PEEK**, a less phase-separated structure, enough water cannot be incorporated. Less chain mobility prevents the formation of large water domains in the membrane.[8] For **SPP**, however, λ values are similar to those of Nafion. This result implies that **SPP**, with a higher IEC value, is able to form larger water domains. Water uptake also results in dimensional stability in membrane thickness and in plane direction by comparing their hydrated state with dry state membranes. At room temperature, the results given in Table 1 show that the **SPP** membrane exhibited much larger swelling in the membrane thickness direction than in the plane direction. Although further improvement is needed, this property is promising because the low in-plane swelling may result in much lower stress at the interface and better stability of the MEA.[9]

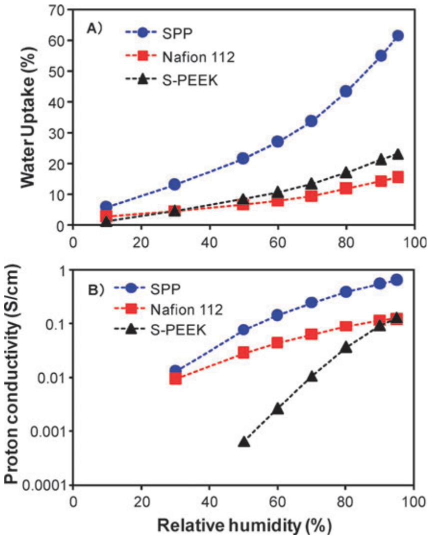


Fig. 1 Relative humidity dependence of (A) water uptake, (B) proton conductivity of the **SPP** membrane compared with Nafion 112 and **S-PEEK**.

In general, proton conductivity is known to have a significant role in the performance of fuel cells. Higher levels of proton conductivity allow higher power densities to be achieved. Generally, to achieve a high proton conductivity of PEMs composed of sulfonated random aromatic polymers, a high ion exchange capacity (IEC) is required.[10] The relative humidity dependence (10–95% RH) of the proton conductivities (σ) of **SPP** membrane, **S-PEEK**, and Nafion 112 (for comparison) were measured at 80 °C and are plotted in Fig. 1B. **SPP** exhibited higher conductivity than **S-PEEK** and Nafion 112, even in the low relative humidity range, and the proton conductivity increased with increasing relative humidity, eventually reaching the highest value of 0.657 S cm^{-1} at 80 °C and 95% RH, which is 4–5 times higher than Nafion 112 or **S-PEEK**. Even at lower humidity, the conductivity is 0.013 S cm^{-1} at 30% RH at 80 °C, which is comparable to that of Nafion. As far as we are aware, the proton conductivity of **SPP** was also higher than those of other sulfonated random aromatic polymer systems reported in the literature. The high conductivity is thought to be due to the higher water uptake at low relative humidity, an effect of the aliphatic propyl group that could increase the flexibility of the polymer chain resulting in a decrease of the distance between sulfonic acid groups on the same polymer backbone, which makes it possible to develop a hydrogen-bonded network for proton transport channels.[11]

Since the crossover of hydrogen and oxygen between the anode and cathode in membrane electrode assembly (**MEA**) has a negative impact on the efficiency of PEMFC, the PEM should be a good gas barrier.[12] Fig. 2 shows the humidity

Table 1 IEC, water uptake, proton conductivity and dimension change of the **SPP** membrane

Samples	IEC[a]/mequiv g^{-1}	λ[b] (H_2O/SO_3H)	WU[b]/wt%	σ (80 °C)/S cm^{-1}		Dimensional change[c]	
				50% RH	95% RH	Δt	Δl
SPP	3.39	10.0	61.5	0.077	0.657	1.018	0.071
S-PEEK	2.07	7.7	28.8	0.001	0.13	0.351	0.160
Nafion112	0.91	8.2	13.3	0.029	0.127	0.008	0.07

[a] Measured by titration with 0.01M NaOH. [b] Measured at 80 °C, 95%RH. [c] Sample was measured in water at RT.

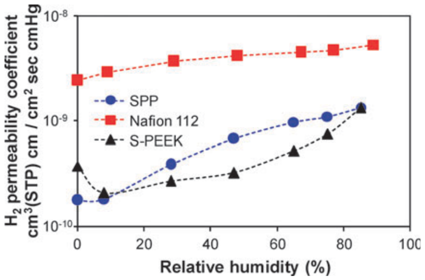


Fig. 2 Relative humidity dependence of hydrogen permeability of **SPP** membrane compared with Nafion 112 and **S-PEEK**.

dependence of hydrogen permeability of **the SPP** membrane at 80 °C. Permeabilities of **SPP** and **S-PEEK** are 10 times lower than that of Nafion in the dried state. With increasing relative humidity, permeabilities of all membranes increase, these increase particularly remarkably for **SPP** and **S-PEEK** at higher relative humidity, but the permeability of **SPP** is still significant lower than that of Nafion and almost the same as that of **S-PEEK** over 80% RH. Although **SPP** takes the largest amount of water in those membranes, the H_2 permeability of **SPP** was able to be suppressed almost equally with that of **S-PEEK**. Similar behavior was observed in oxygen permeability (see Fig. S3, ESI†). We would like to emphasize here that higher proton conduction can be achieved with lower gas permeation in the **SPP** membrane. Stronger intermolecular interaction between backbones may provide higher gas barrier properties, and the flexible side chain gives higher proton conductivity.

In summary, a novel side chain type sulfonated poly(*p*-phenylene) containing an aliphatic group was prepared by Ni(0) catalyzed coupling polymerization of 2,5-dichloro-4-(phenoxypropyl)benzophenone and sulfonated using concentrated sulfuric acid. The synthesized polymer showed good solubility and was easily turned into flexible and self-standing membranes. Although **SPP** possessed higher IEC value (3.39 mequiv g^{-1}), the membrane was stable to water at room temperature but dissolved in boiling water. The SPP membrane displayed an excellent proton conductivity even at low humidity (0.077 S cm^{-1}, 80 °C; 50% RH), while retaining acceptable water uptake. We have demonstrated that significant performance such as higher proton conductivity and gas barrier with dimensional stability can be optimized by the simple introduction of an aliphatic alkyl pendent chain. Further investigation and development of this class of polymer will be needed as a part of blends or copolymers to improve the solubility of the membrane in boiling water but still retain high proton conductivity. In our laboratory we are currently undertaking an investigation of the effect of flexible alkyl side groups on the physical properties such as water diffusion, mechanical properties and membrane morphology.

This work was financially supported by the Ministry of Economy, Trade and Industry (METI) and New Energy and Industrial Technology Development Organization (NEDO), Japan. We are grateful to Prof. Rikukawa of Sophia University for fruitful discussion.

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