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Fuel-Cell Membranes

Proton-Conductive Aromatic Ionomers Containing Highly Sulfonated Blocks for High-Temperature-Operable Fuel Cells**

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The polymer electrolyte membrane fuel cell (PEMFC) has received considerable attention as a result of its high energy efficiency and lowered emissions of carbon dioxide and air pollutants. Perfluorosulfonic acid (PFSA) polymers, such as Nafion (DuPont), are state-of-the-art materials that have mostly been used as polymer electrolyte membranes. However, several problems, such as high production cost, environmental incompatibility (poor recyclability), high gas permeability, and insufficient thermomechanical properties above 80 °C, have been reported.[1] To overcome these drawbacks, aromatic (nonfluorinated) hydrocarbon polymers have been investigated as alternative membranes.[2] Most of these membranes showed low proton conductivity at low humidity ($<50\%$ relative humidity (RH)); however, low humidity is crucial for practical PEMFC operation.

Several approaches have been examined to improve proton conductivity under conditions of low humidity and high temperature. The strategies have included changes of the acidity and the position of sulfonic acid groups, and the control of membrane morphologies.[3] More recently, highly sulfonated moieties[4] or sequenced hydrophilic and hydrophobic groups as block copolymers[5] were claimed to be effective for this purpose. However, none of these alternative membranes could compete with Nafion membranes. We decided to combine both strategies in a single polymer architecture, in other words, to prepare a multiblock structure containing highly sulfonated hydrophilic blocks. Recently, we successfully synthesized a new series of multiblock poly(arylene ether sulfone)s (SPEs) containing sulfonated fluorenylidene biphenylene units. The well-controlled postsulfonation reaction of the precursor polymers enabled selective sulfonation on each aromatic ring of the fluorenylidene biphenylene groups with a degree of sulfonation up to 85 %.[6] Herein, we report advanced novel sulfonated poly(arylene ether sulfone ketone) (SPESK) multiblock membranes with precisely designed chemical structures. With a sulfone–ketone structure for the hydrophobic block, 100 % sulfonation of the hydrophilic block was observed (Figure 1 a). The thin membranes show unique morphology and proton conductivity comparable to ($<40\%$ RH) or higher than ($>40\%$ RH) that of Nafion membranes.

The block copolymers were synthesized from hydrophilic and hydrophobic oligomers by a nucleophilic aromatic substitution reaction. The degree of polymerization of the hydrophobic block (X) was controlled to 30 and 60, and that of the hydrophilic block (Y) to 8 and 12. All of the polymers had high molecular weights ($M_w > 125$ kDa), which supported the formation of a multiblock structure. Postsulfonation with chlorosulfonic acid yielded the targeted structure without detectable sulfonation of the hydrophobic block. Gel permeation chromatographic (GPC) analysis of the sulfonated polymers indicated that the main chain structure remained intact during the sulfonation reaction (Table 1). ^{1}H NMR analysis confirmed 100 % sulfonation (sulfonation on every phenylene ring in the fluorenylidene biphenylene unit). The ion-exchange capacities (IEC) of the SPESK block copolymers ranged from 1.07 to 1.62 meq g^{-1}. Details of the synthesis and polymer characterization are available in the Supporting Information.

Scanning transmission electron microscopic (STEM) images of lead-stained SPESK block membranes are shown in Figure 1 c–e; the dark areas correspond to hydrophilic blocks. An STEM image of the Nafion membrane is shown for comparison (Figure 1 b). The phase separation of the hydrophobic and hydrophilic blocks in the block copolymers was much improved with respect to that observed for previously reported random or block copolymers.[7] The high concentration of sulfonic acid groups within the hydrophilic blocks was expected to increase the hydrophilicity of these blocks and to result in enhanced phase separation between the hydrophilic and hydrophobic blocks. For example, 36 sulfonic acid groups are located in series in the hydrophilic block for $Y=8$, and 52 sulfonic acid groups for $Y=12$. In the case of X30Y8 SPESK, rodlike hydrophilic aggregates were observed, and the aggregates were well interconnected. This unique morphology was expected to provide an effective proton-transport pathway. The interconnectivity of hydrophilic aggregates appeared to be more pronounced for membranes with a higher IEC value (Figure 1 c,d). The results of small-angle X-ray scattering (SAXS) of the hydrated membranes are in agreement with the STEM results. The distance between hydrophilic or hydrophobic domains in the hydrated membrane was about 11 nm (see the

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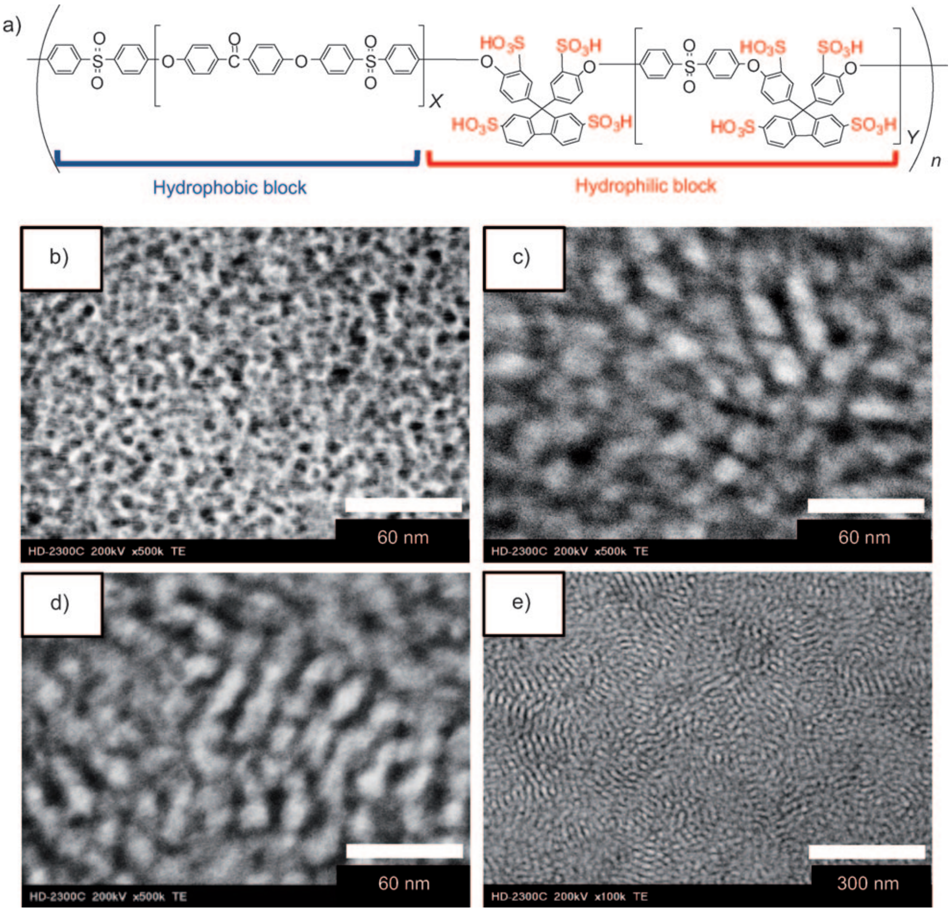

Figure 1. a) Structure of the SPESK block copolymer. b–e) Lead-stained STEM images of Nafion 112 (b), X60Y8 (c), X30Y8 (d), and X30Y8 (e).

Supporting Information), which is in good accordance with the images in Figure 1c,d. The SAXS data for the Nafion membrane gave a smaller distance of 5 nm, which correlates with the separation of water channels, as suggested by Kreuer et al.[8]

Figure 2a,b shows the dependence of water uptake and in-plane proton conductivity on RH at 80 and 110 °C. SPESKs showed higher water uptake than that of the Nafion 112 membrane as a result of their higher IEC values. Whereas X60Y8 SPESK (IEC = 1.07 meq g^{-1}) showed lower proton conductivity than that of Nafion, X30Y8 SPESK (IEC = 1.62 meq g^{-1}) showed higher or similar proton conductivity in comparison to that of Nafion over a wide humidity range at 80 °C. The SPESK retained its high proton conductivity even at 110 °C. The high proton conductivity is thought to originate from the highly developed phase separation of the block SPESK membranes. Although proton conductivities higher than that of Nafion have been reported previously for multiblock aromatic ionomer membranes, the fluorinated moieties included in their structures are partly responsible for the properties.[9] To the best of our knowledge, the proton conductivity reported herein is the highest for a fluorine-free polymer electrolyte membrane with an IEC value lower than 1.7 meq g^{-1}. If the densities of SPESK (1.48 g cm^{-3}) and Nafion (2.01 g cm^{-3}) are taken into account, the volumetric IEC values of these materials are rather closer (2.40 meq cm^{-3} for SPESK and 1.83 meq cm^{-3} for Nafion). The SPESK polymers also showed very high hydrolytic stability and moderate oxidative stability (Table 1). Oxidative degradation is likely to occur at phenylene carbon atoms *ortho* to the ether bonds by the attack of hydroxyl radicals (see Figure S3 1,3 in the Supporting Information) owing to the high electron density at these positions.[10] A test of long-term hydrolytic stability (1000 h at 100 °C) also confirmed negligible degradation for the X30Y8 and X60Y8 SPESK membranes.

A 25 μm thick X30Y8 SPESK membrane was tested in fuel-cell operation. Carbon-supported platinum was used as the catalyst for the anode and the cathode (Pt loading: 0.45 mg cm^{-2}). Performance in an H_2/air fuel cell was tested at 100 °C with humidification at 53 or 30 % RH for both electrodes. The X30Y8 membrane showed acceptable cell performance (Figure 3). At a cell voltage of 0.6 V, the current density was 250 mA cm^{-2} at 30 % RH and 410 mA cm^{-2} at

Table 1: Properties and stability of SPESK block copolymers.

Polymer	IEC [meq g^{-1}][a]	Degree of sulfonation [%][b]	Molecular weight [kDa][c] (MWD)[d] before sulfonation	Molecular weight [kDa][c] (MWD)[d] after sulfonation	Residual weight after stability test [%] oxidative test[e]	Residual weight after stability test [%] hydrolytic test[f]
X60Y8	1.07	100	150 (1.9)	192 (2.4)	49	100
X60Y12	1.41	100	170 (2.3)	360 (3.0)	45	100
X30Y8	1.62	100	125 (1.7)	252 (3.2)	40	100
Nafion 112	0.91	–	–	–	100	100

[a] The IEC values were determined by titration. [b] The degree of sulfonation was determined by NMR spectroscopy. [c] Weight-averaged molecular weight. [d] Molecular-weight distribution. [e] The polymer was heated in the Fenton reagent ($FeSO_4$ (2 ppm) in 3 % H_2O_2) at 80 °C for 1 h. [f] In an accelerated hydrolytic test, the polymer was heated in water at 140 °C for 24 h.

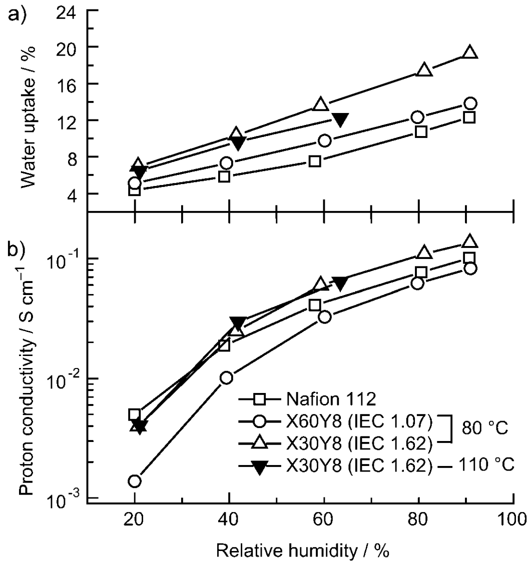

Figure 2. a) Water uptake and b) in-plane proton conductivity of Nafion 112 and block SPESKs as a function of relative humidity at 80 and 110 °C. The IEC values are given in meq g^{-1}.

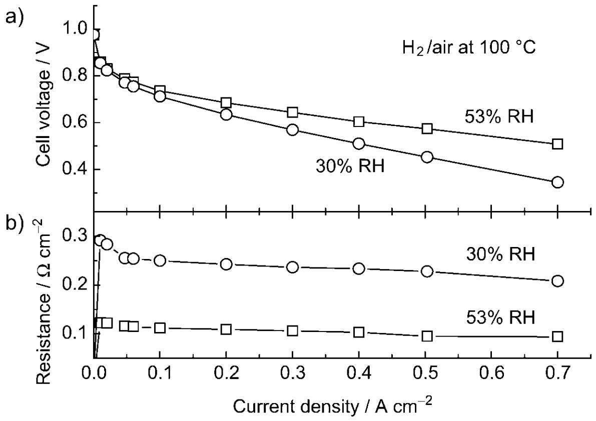

Figure 3. H_2/air PEMFC performance of SPESK X30Y8 (IEC = 1.62 meq g^{-1}) at 100 °C with humidification at 53 and 30 % RH (the same humidification was applied to both electrodes): a) cell voltage including ohmic resistance; b) ohmic resistance.

53 % RH. Better performance was observed upon operation with an H_2/O_2 system (see the Supporting Information). The high proton conductivity of SPESK at low RH and high temperature was verified through practical fuel-cell operation (which also confirmed that in-plane and through-plane proton conductivity were consistent). Such conditions are crucial, especially for electric-vehicle applications, which are considered to be too severe for nonfluorinated membranes.

In summary, we have designed and synthesized fluorine-free hydrocarbon multiblock copolymers with highly sulfonated hydrophilic blocks by a postsulfonation method. Enhanced phase separation was observed and resulted in improved proton conductivity at low humidity and high temperature. A fuel cell was successfully operated with the membranes at 30 and 53 % RH and 100 °C.

Experimental Section

Typical synthesis of hydroxy-terminated telechelic oligomers **1** (for $Y = 8$): 9,9-bis(4-hydroxyphenyl)fluorene (BHF; 4.00 g, 11.42 mmol), bis(4-fluorophenyl)sulfone (FPS; 2.58 g, 10.15 mmol), potassium carbonate (3.16 g, 22.84 mmol), *N,N*-dimethylacetamide (DMAc; 20 mL), and toluene (10 mL) were placed in a 100 mL round-bottomed flask, and the reaction mixture was heated with a Dean–Stark trap at 140 °C for 3 h, and then at 165 °C for a further 12 h. The resulting slightly viscous mixture was diluted with DMAc (20 mL) and poured dropwise into water (1 L). The crude product was washed with deionized water and methanol several times and dried in a vacuum oven overnight.

Typical synthesis of fluorine-terminated telechelic oligomers **2** (for $X = 30$): FPS (1.00 g, 3.93 mmol), 4,4′-dihydroxybenzophenone (DHBP; 0.81 g, 3.81 mmol), potassium carbonate (1.09 g, 7.86 mmol), calcium carbonate (7.87 g, 78.6 mmol), DMAc (20 mL), and toluene (10 mL) were placed in a 100 mL round-bottomed flask, and the reaction mixture was heated with a Dean–Stark trap at 140 °C for 1.5 h, and then at 165 °C for another 1.5 h. The resulting mixture was slightly viscous. The temperature was then decreased to room temperature, and the oligomer **2** was mixed with a hydroxy-terminated telechelic oligomer **1** for block copolymerization.

Block copolymerization: The above mixture of hydroxy-terminated hydrophilic and fluorine-terminated hydrophobic oligomers (**1** and **2**) was copolymerized at 165 °C for 3 h (see Scheme S1 in the Supporting Information). After the polymerization, additional DMAc (ca. 20 mL) was added to lower the viscosity of the mixture. The mixture was poured into a large excess of dilute hydrochloric acid (10 mL of concentrated HCl in 1 L of water) to precipitate the product. The crude product was washed with dilute hydrochloric acid and hot methanol several times. The obtained polymer was dissolved in DMAc and reprecipitated by the addition of acetone. A white fiber of the product **3** was dried at 80 °C in a vacuum oven overnight.

Sulfonation of block copolymers and membrane preparation: A solution of chlorosulfonic acid (1.07 g) in dichloromethane (50 mL) was placed in a round-bottomed flask. A solution of the X30Y8 block copolymer **3** (0.8 g) in dichloromethane (50 mL) was added dropwise to the solution of chlorosulfonic acid in dichloromethane with stirring. Chlorosulfonic acid was calculated to be present in fivefold excess with respect to the fluorenylide diphenylene unit of the X30Y8 block copolymer **3**. The sulfonation reaction was allowed to proceed for 24 h until all of the sulfonated polymer had precipitated from the reaction mixture. The product was poured into cold water (500 mL) and filtered. It was then washed with hot water several times and dried under vacuum at 80 °C overnight to give a sulfonated block copolymer (SPESK) **4**.

A solution of the SPESK **4** (1 g) in DMAc (10 mL) was cast onto a flat glass plate. Drying of the solution at 60 °C overnight gave a (50 ± 5) μm thick, transparent, tough film. The film was dried further in a vacuum oven at 80 °C for at least 6 h. The resulting membrane was treated with a 1 M aqueous solution of H_2SO_4 for 4 h, washed with water several times, and dried at room temperature.

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