

Sulfonated Poly(arylene ether phosphine oxide ketone) Block Copolymers as Oxidatively Stable Proton Conductive Membranes

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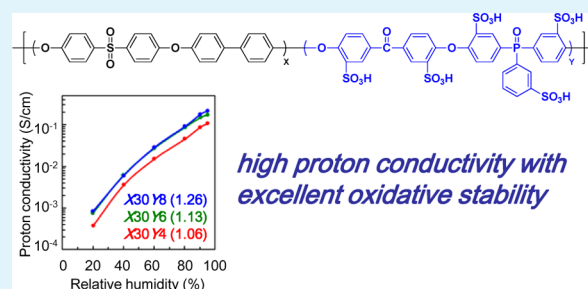
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Supporting Information

ABSTRACT: The introduction of triphenylphosphine oxide moiety into the hydrophilic segments of aromatic multiblock copolymers provided outstanding oxidative stability and high proton conductivity. Our designed multiblock copolymers are composed of highly sulfonated phenylene ether phosphine oxide ketone units as hydrophilic blocks and phenylene ether biphenylene sulfone units as hydrophobic blocks. High molecular weight block copolymers ($M_w = 204\text{--}309$ kDa and $M_n = 72\text{--}94$ kDa) with different copolymer compositions (number of repeat unit in the hydrophobic blocks, $X = 30$, and that of hydrophilic blocks, $Y = 4, 6, \text{ or } 8$) were synthesized, resulting in self-standing, transparent, and bendable membranes by solution-casting. The block copolymer membranes exhibited well-developed hydrophilic/hydrophobic phase separation, high proton conductivity, and excellent oxidative stability due to the highly sulfonated hydrophilic blocks, which contained phenylene rings with sulfonic acid groups and electron-withdrawing phosphine oxide or ketone groups.

KEYWORDS: proton conductive membranes, block copolymers, fuel cells, oxidative stability, phosphine oxide groups



Polymer electrolyte membrane fuel cells (PEMFCs) have attracted much attention as a promising energy converting system for electric vehicles and stationary use. Proton conductive membranes are one of the key materials of PEMFCs, which transport protons from the anode to the cathode and prevent the direct contact of hydrogen and oxygen. Perfluorosulfonic acid (PFSA) ionomer membranes such as Nafion (du Pont) are state-of-the-art; however, there have been a great demand for alternative proton conductive membranes free from fluorine atoms because of several disadvantages, including high production cost, low glass-transition temperature, high gas permeability, and environmental incompatibility.

One of the most attractive candidates as alternative proton conductive membranes is aromatic polymers with acidic function because of their easy synthesis and versatility in molecular design.^{1–3} Such aromatic polymers include sulfonated poly(arylene ether sulfone)s,⁴ poly(arylene ether ketone)s,⁵ polyimides,⁶ polyphenylenes,^{7,8} and their derivatives. Aromatic polymer electrolyte membranes have suffered from lower proton conductivity and less durability compared to the PFSA ionomers. Recent progress has revealed that multiblock copolymers composed of sulfonated hydrophilic segments and unsulfonated hydrophobic segments show much improved properties.⁹ We have reported that the dense sulfonation in the hydrophilic segments of multiblock poly(arylene ether)s resulted in comparable proton conductivity to the PFSA ionomer membranes even at low humidity (or low hydration).^{10–12} The unique hydrophilic–hydrophobic phase-separated morphology with interconnected ionic channels is

responsible for the high proton conductivity. Oxidative stability is another crucial factors for practical fuel cell operation. It has been suggested that the molecular structure of hydrophilic parts strongly affects the oxidative stability; the introduction of electron-withdrawing sulfone or ketone groups as well as sulfonic acid groups into the hydrophilic parts improved oxidative stability of the bulk membranes.¹³ In this paper, we report advanced version of our multiblock copolymer membranes from oxidative stability point of view. For this purpose, oligo(phenylene ether phosphine oxide ketone)s were chosen as a scaffold for sulfonic acid groups because of the low electron density and high oxidative stability of the phosphine oxide moiety.

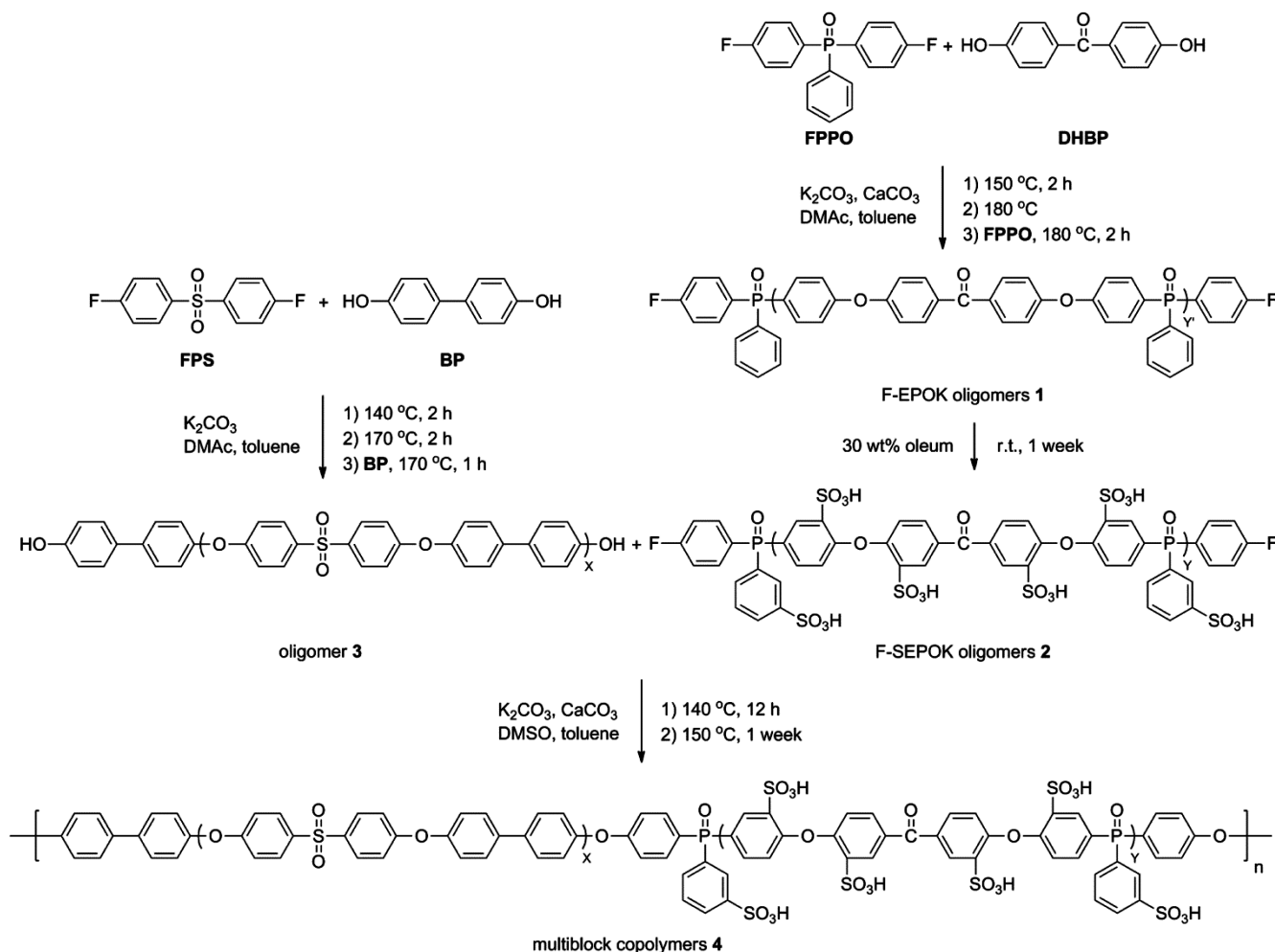
The targeted multiblock copolymers **4** were synthesized as shown in Scheme 1. Hydrophobic oligomer **3** was prepared by nucleophilic substitution polymerization of bis(4-fluorophenyl)sulfone (FPS) and 4,4'-biphenol (BP) under basic conditions. Slight excess of BP was used to obtain hydroxyl-terminated **3** with controlled number of repeat unit (X30). The structure of **3** was confirmed by ¹H NMR spectrum, in which all signals were well-assigned to the supposed structure (see Figure S1 in the Supporting Information). The X values obtained by ¹H NMR spectrum and GPC analysis were in fair agreement with that calculated from the feed monomer ratio (see Table S1 in the Supporting

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Scheme 1. Synthesis of Oligomers 1, 2, and 3 and Multiblock Copolymers 4



Information). Precursor oligomers 1 for the hydrophilic segment were prepared from bis(4-fluorophenyl)phenylphosphine oxide (FPPO) and 4,4'-dihydroxybenzophenone (DHBP) under the reaction conditions similar to that for 3. Slight excess of FPPO was used to obtain fluorine-terminated oligomers 1.

The chemical structure of 1 was confirmed by 1H , ^{19}F and ^{31}P NMR spectra (see Figure S2 in the Supporting Information). ^{19}F NMR spectra showed a single signal at -107.4 ppm assignable to the terminal fluorine atoms, which is slightly different from that of FPPO (-107.3 ppm). ^{31}P NMR spectra showed two signals at 25.0 ppm and 24.9 ppm assignable to the phosphorus atoms in the main chain and at the terminal, respectively, which are both different from that of FPPO (24.8 ppm). While the Y' values in 1 obtained by 1H NMR spectra were in good agreement with those calculated from the feed monomer ratios, the ones obtained by GPC analyses were somewhat different (see Table S1 in the Supporting Information). This result may imply the possible interactions between the phosphine oxide moiety in 1 and the GPC columns. The sulfonation reaction of 1 was carried out in 30 wt % oleum at room temperature for 1 week. 1H NMR spectra and GPC profiles of the sulfonated oligomers 2 suggested complete sulfonation without detectable degradation (see Figure S3 in the Supporting Information). The sulfonic acid groups were substituted on each phenylene ring at the

position meta to the electron-withdrawing phosphine oxide or ketone groups, or ortho to the electron-donating ether groups. ^{19}F NMR spectra showed single signals at -107.2 ppm, which are almost the same as that of 1 (-107.4 ppm). It is suggested that no sulfonation occurred at the terminal fluoro-substituted phenylene rings probably because of the electron-withdrawing fluorine and phosphine oxide substituents.

Multiblock copolymerization of 2 and 3 was carried out under the reaction conditions similar to those for the above-mentioned oligomers. Long reaction time (1 week) and mild reaction temperature (150 °C) gave high molecular weight polymers 4 (Table 1). Multiblock copolymers 4 were soluble in polar organic solvents such as DMF, DMSO, and NMP, and were characterized by 1H and ^{31}P NMR spectra. In the comparison of the 1H NMR spectra of 4 with those of the starting oligomers 2 and 3, the signals assignable to the terminal groups (7 in Figure S4a and j in Figure S4b in the Supporting

Table 1. Molecular Weight and Ion Exchange Capacity (IEC) of Multiblock Copolymers 4

4	M_n (kDa)	M_w (kDa)	IEC (mequiv/g)		
			targeted	NMR	titration
X30Y4	90	204	1.30	1.06	0.92
X30Y6	94	309	1.85	1.13	0.99
X30Y8	72	268	2.22	1.26	1.09

Information) were absent in Figure S4c in the Supporting Information, suggesting the formation of the targeted multi-block copolymer. The molecular weight of **4** was $M_w = 204\text{--}309$ kDa and $M_n = 72\text{--}94$ kDa with reasonable polydispersity index ($M_w/M_n = 2.3\text{--}3.7$) for condensation polymers as estimated by GPC analyses (see Figure S5 in the Supporting Information). Casting from DMSO solutions provided transparent and bendable membranes. The ion exchange capacity (IEC) values obtained by ^1H NMR spectra (calculated from the integral ratios of hydrophilic moiety to hydrophobic moiety) and titration were considerably smaller than the targeted values (calculated from the multiblock copolymer compositions). The IEC values obtained by titration were similar among the three block copolymers despite of the large differences in the targeted values. In addition, the yields of the block copolymers were rather low (45–48%). These results suggest that the block copolymers **4** with IEC higher than 1.3 mequiv/g are soluble in water and were lost during the purification process.

The **4** membranes displayed well-developed hydrophilic/hydrophobic phase separation in the nanometer scale. Figure 1

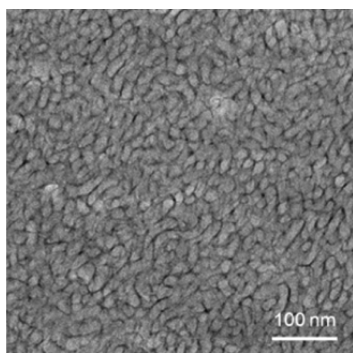


Figure 1. STEM image of **4** membrane (X30Y4) in lead ion form.

is a typical cross-sectional scanning transmission electron microscopy (STEM) image of **4** membrane (X30Y4) stained with lead ion, in which the dark areas represent hydrophilic domains with lead sulfonate groups. The hydrophilic domains were ca. 5 nm wide and interconnected throughout the image. Similar phase separated morphology was also observed for the **4** membranes (X30Y6) and (X30Y8).

Figure 2 displays water uptake and proton conductivity of **4** and Nafion membranes (in acid form) at 80 °C as a function of relative humidity (RH). As expected, **4** membranes with higher IEC values showed higher water uptake. Such tendency was more pronounced at higher RH. The **4** membranes showed slightly higher water uptake than that of Nafion because of the formers' higher IEC values. Proton conductivity of **4** membranes also increased with increasing IEC values. While the proton conductivity of **4** membranes were lower than that of Nafion at low RH, the conductivity of **4** membrane (X30Y8, IEC = 1.26 mequiv/g by ^1H NMR) was 216 mS/cm at 95% RH, which was 1.3 times higher than that of Nafion. Molecular design in the hydrophilic parts, i.e., densely and three dimensionally located sulfonic acid groups at the side chain as well as the main chain, would be responsible for relatively high proton conductivity of **4** membranes taking their low IEC values into account. The humidity dependence of the proton conductivity of **4** membranes was similar to that of our previous sulfonated block poly(arylene ether sulfone ketone) membranes.¹³

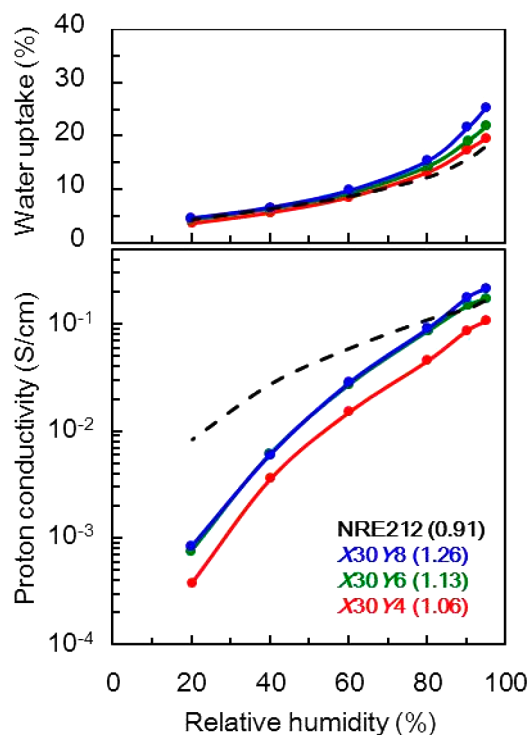


Figure 2. Water uptake and proton conductivity of **4** and Nafion NRE212 membranes (IEC values in parentheses) at 80 °C as a function of relative humidity (RH).

Humidity dependence of storage modulus (E'), loss modulus (E''), and $\tan \delta$ of the **4** and Nafion membranes at 80 °C is shown in Figure 3. Under a wide range of relative humidity (ca. 0–90% RH), the storage moduli of the **4** membranes were as high as $10^8\text{--}10^9$ Pa and higher than that of Nafion membrane. In the E' , E'' , and $\tan \delta$ curves, transitions were observed at ca. 50–60% RH. These transitions could be glass transition. The transition RHs were approximately in the order of their IEC and water uptake values; 58% RH for (X30Y8, IEC = 1.26 mequiv/g), 56% RH for (X30Y6, IEC = 1.13 mequiv/g), and 54% RH for (X30Y4, IEC = 1.06 mequiv/g). Our previous multiblock copolymers with the same hydrophobic but different hydrophilic parts showed transitions at comparable RH (ca. 53% RH), meaning the transition is mainly dominated by the structure of hydrophobic components, whereas hydrophilic components do have some effects with the absorbed water as a plasticizer.¹³ This idea is not contradictory to the above-mentioned results on water uptake and proton conductivity measured under the same conditions. The water uptake and proton conductivity, which are more related to the hydrophilic components than the hydrophobic ones, did not show distinct transitions at 50–60% RH as shown in Figure 2.

Gas barrier property is another important parameter for fuel cell membranes, and those of hydrogen and oxygen were investigated. The hydrogen and oxygen permeability coefficients of the **4** membrane (X30Y8) were 1.2×10^{-9} cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹ and 5.8×10^{-10} cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹, respectively, at 80 °C, 95% RH. These values were lower than those of Nafion, 5.2×10^{-9} cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹ for hydrogen and 2.7×10^{-9} cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹ for oxygen, and comparable to those of our previous aromatic ionomer membranes with similar hydro-

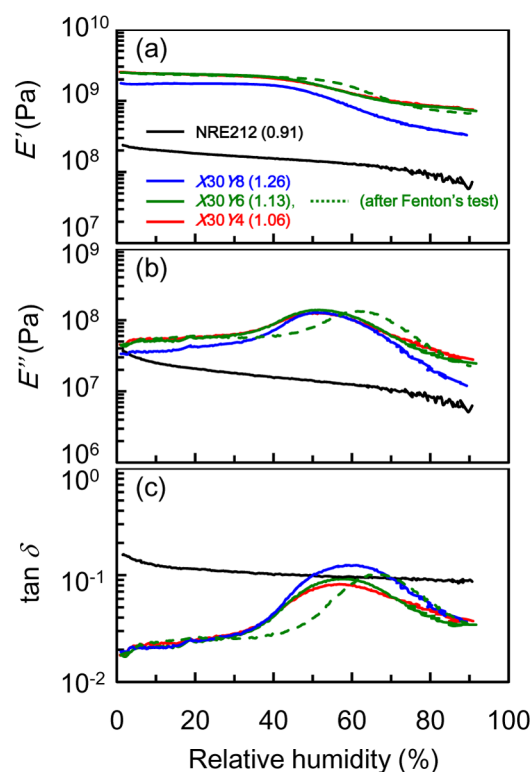


Figure 3. DMA analyses of **4** and Nafion NRE212 membranes; (a) E' (storage moduli), (b) E'' (loss moduli), and (c) $\tan \delta$ at 80 °C as a function of relative humidity (RH).

phobic blocks,¹¹ suggesting the **4** membrane exhibited good gas barrier property even under humidified conditions.

The **4** membranes were hydrolytically and oxidatively stable even under harsh conditions. Hydrolytic stability of **4** membranes was investigated in pressurized H₂O at 140 °C for 24 h, resulting in negligible changes in weight, apparent molecular weight, and chemical structures (see Figure S8 in the Supporting Information). Oxidative stability tested in Fenton's reagent at 80 °C for 1 h is summarized in Table 2. Most

Table 2. Results of Oxidative Stability Tests

4	residual weight (%)	residual M_w (%)	IEC ^a (mequiv/g)	IEC ^b (mequiv/g)
X30Y4	96	94	0.82	0.92
X30Y6	100	81	0.90	0.99
X30Y8	100	100	0.91	1.09

^aAfter Fenton's test. ^bBefore Fenton's test.

nonfluorinated hydrocarbon ionomers do not survive under such severe conditions with considerable losses in weight, molecular weight, and mechanical strength. Our previous sulfonated multiblock copolymers without phosphine oxide moiety degraded to certain extent, and some membranes broke into pieces with considerable weight (ca. 10–90%) and molecular weight (ca. 40–60%) losses, depending on the IEC values (0.91–1.69 mequiv/g).¹³ In contrast, **4** membranes showed negligible changes in weight, apparent molecular weight, and chemical structure (Table 2 and Figure S9 in the Supporting Information). Because they share the same hydrophobic components, it is concluded that the phosphine oxide moiety incorporated in the hydrophilic components has contributed to the outstanding oxidative stability of **4**

membranes. The post-test membranes retained strength and flexibility, and IEC values, further confirming their oxidative stability. The post-test **4** (X30Y6) membrane showed similar storage moduli (green dashed lines in Figure 3) compared with those of the pristine membrane. The peaks in loss modulus and $\tan \delta$ curves were observed at slightly higher RH for the post-test sample.

Previous study suggested the possibility that the phosphine oxide groups chelate the ferrous ions in Fenton's reagent and passivate the radicals resulting in the suppression of the oxidative degradation.¹⁴ The phosphine oxide groups in the present multiblock copolymers **4** may have some interactions with the ferrous ions as implied by very minor chemical shifts in the ³¹P NMR spectra after the oxidative stability test (see Figure S9 in the Supporting Information). However, the ferrous ions (ca. 1×10^{-4} mol) exist 2 orders of magnitude more than the phosphine oxide groups (ca. 1×10^{-6} mol) in our experiment, indicating that the most ferrous ions still function as catalysts and generate radical species. Therefore, we assume that the phosphine oxide moiety promotes the decomposition of H₂O₂ and the derived oxidative radical species and suppresses the degradation of the polymer main chains and sulfonic acid groups. Control experiments were carried out in Fenton's reagent for hydrophilic oligomer **2** and a similar oligomer with no phosphine oxide groups. Although both oligomers decomposed significantly in the solution, phosphine oxide moieties were intact as suggested by ³¹P NMR spectrum.

In conclusion, we have designed and synthesized a novel series of sulfonated poly(arylene ether phosphine oxide ketone) multiblock copolymers **4**. The **4** membranes showed well-developed hydrophilic/hydrophobic phase separation, reasonable water uptake, high proton conductivity, and excellent oxidative and hydrolytic stability because of the introduction of phosphine oxide moiety as well as dense sulfonic acid groups in the hydrophilic blocks. The **4** membranes kept high mechanical strength under a wide range of humidity at 80 °C. These properties seem promising for practical fuel cell applications.

■ ASSOCIATED CONTENT

📄 Supporting Information

Detailed synthesis and characterization of oligomers **1**, **2**, and **3** and multiblock copolymers **4**. Photographs and STEM images of **4** membranes in lead ion form. Results of hydrolytic and oxidative stability tests. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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