Communications to the Editor

Bull. Korean Chem. Soc. **2012**, Vol. 33, No. 2   375

Tetrasulfonated Poly(arylene biphenylsulfone ether) Block Copolymer and Its Composite Membrane Containing Highly Sulfonated Blocks

Seung Hak Hyun,[†] Ae Rhan Kim,[†] Kee Suk Nahm,[†,‡] and Dong Jin Yoo[†,*]

[†]*Department of Hydrogen and Fuel Cells Engineering, Specialized Graduate School, Chonbuk National University, Jeollabuk-do 561-756, Korea.* *E-mail: djyoo@jbnu.ac.kr*
[‡]*School of Semiconductor and Chemical Engineering and Technology, Chonbuk National University, Jeollabuk-do 561-756, Korea*

Among different types of fuel cells, proton exchange membrane (PEM) fuel cells show the highest power density and have been actively investigated for automobile applications. Although Nafion has been typically considered as a PEM for practical applications, there are still some limitations such as the high cost and the degradation of proton conductivity at high temperature (> 80 °C).[1]

Several approaches have been examined to improve proton conductivity. The strategies have included changing the acidity and position of sulfonic acid groups and the control of membrane morphologies.[2] Recently, highly sulfonated moieties[3] or sequenced hydrophilic and hydrophobic groups as block copolymers[4] were claimed to improve proton conductivity under high temperature. However, none of these alternative membranes could compete with Nafion membranes. Related to these reports, we wish to study the thermal and electrochemical properties and morphological characteristic of a block membrane enhanceing the number of sulfonic acid groups in a repeat unit of a polymer. Here, we report on highly sulfonated poly(arylene biphenylsulfone ether) block copolymer (**5**) made using tetrasulfonated 4,4'-bis[(4-chloro-3-sulfonatophenyl)sulfony]biphenyl-2,2'-disulfonate (TsBCSBPD, **2**)[5] and its composite membrane using phosphotunstic acid (PWA).

In the previous paper,[6] we described the synthesis and characterization of tetrasulfonated poly(arylene biphenylsulfone ether) random copolymers made using TsBCSBPD (**2**). The block copolymer **4** was prepared as follows: First, hydrophobic oligomer **1** was made from 6F-BPA (4,4'-hexafluoroisopropylidene diphenol), DCDPS (4,4'-dichlorodiphenyl sulfone), and K_2CO_3 in dimethyl acetamide (DMAc).[7] Second, hydrophilic oligomer **3** was prepared from TsBCSBPD (**2**) and 6F-BPA in the same manner. Finally, we synthesized a block copolymer **4** from the hydrophobic **1** (Mw 10 kDa) and hydrophilic oligomer **3** (Mw 13 kDa) using a nuclephilic substitution reaction.[7] This was then followed by hydrolysis with sulfuric acid (Scheme 1). The polymer had a high molecular weight (Mw 57 kDa), which supported the formation of a block structure. The ^1H NMR spectrum of B37 copolymer is shown in Figure 1. ^1H NMR analysis confirmed 37% sulfonation (the degree of sulfonation on each phenylene

ring in the repeating unit).[8,9]

The B37 membrane was prepared by solution casting the acid form of the B37 copolymer in DMAc (10% w/v) and the B37-P30 (B37:PWA = 10:3, wt/wt) composite membrane was prepared by casting the acid form of the B37 and a commercial PWA (H_3PWO_{40}, Fluka Chemicals) in DMAc (10% wt/v). These castings were carried out onto a clean glass plate and then dried by a heat lamp at 80 °C for 24 h.

A summary of the thermal properties of the fabricated membranes is listed in Table 1. The TGA (thermogravimetric analysis) of B37, B37-P30, and Nafion N117 membranes
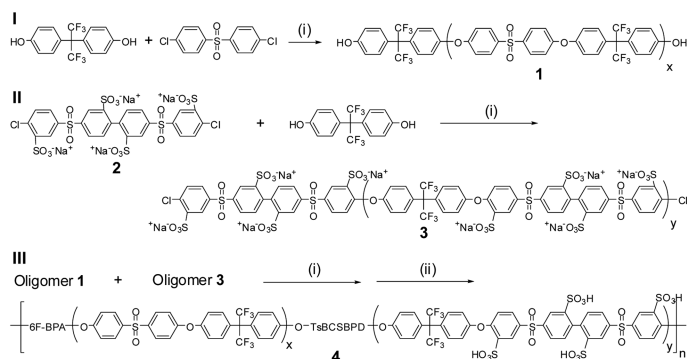
Scheme 1. Synthesis of highly sulfonated block copolymer **4**. (i) K_2CO_3, DMAc/toluene, 150 °C 4 h, 180 °C 16 h; (ii) 10% H_2SO_4, NMP.
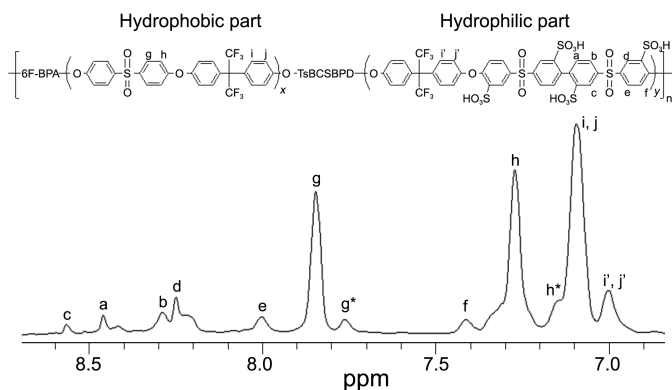
Figure 1. ^1H NMR spectrum (DMSO-d_6) of tetrasulfonated poly-(arylene biphenylsulfone ether) block (B37) copolymer **4**.

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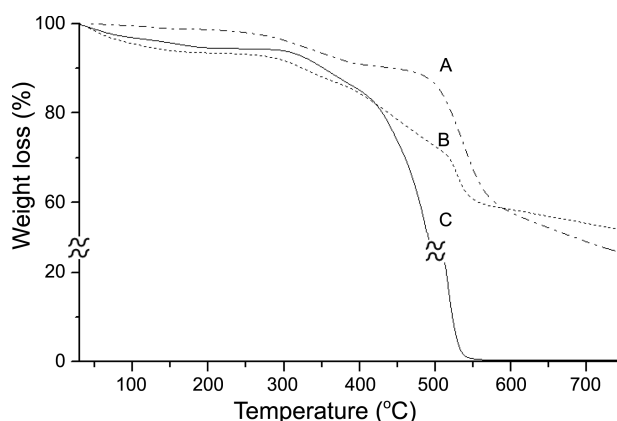
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Figure 2. Comparison of thermogravimetric curves: (A) B37, (B) B37-P30, and (C) Nafion 117.

Table 1. Comparison of T_d, T_g, water uptake, and conductivity of Nafion 117 and copolymers

Polymers	$T_{5wt\% loss}$ [°C]	$T_{10wt\% loss}$ [°C]	T_g [°C]	Water uptake	Conductivity[a] [mS cm^{-1}]
Nafion 117	117	352	108	17	91
B37	323	445	213	24	37
B37-P30	110	325	191	21	69

[a]Measured at 90 °C and 100% RH.

exhibited two distinct weight-loss profiles (Figure 2). The weight loss of sulfonated polymers in the range 35-200 °C is attributed to the desorption of water bonded to sulfonic groups.[10] In B37 block copolymer, the degradation in the first step at around 250 °C is attributed to the sulfonic acid decomposition, while the degradation in the second step at around 500 °C is primarily due to main chain decomposition.[11] TGA behaviour of the composite B37-P30 block membrane shows that it also undergoes a two-step degradation, although the degradation temperatures were somewhat lower than the pure B37 block copolymer.[10] The glass transition temperature, T_g, of each membrane is also reported in Table 1. The T_g of the composite membrane has a very broad range and is noted to decrease somewhat with 30% PWA. Thus, the PWA incorporation in B37 affected the T_g much for the corresponding B37 polymer. These thermal behaviours suggest that B37 and B37-P30 membranes have adequate thermal properties for PEMFC applications because their thermal decomposition can be detected above 200 °C.

Tapping mode AFM (atomic force microscopy) phase images of the (A) Nafion 117 and (B) B37-P30 membranes are shown in Figure 3. The high concentration of sulfonic acid groups within the hydrophilic blocks increased the hydrophilicity of these blocks and resulted in enhanced phase separation between the hydrophilic and hydrophobic blocks.[12] In the case of the (B) B37-P30 membrane, rod-like hydrophilic aggregates were observed, and the aggregates were interconnected well. This unique morphology was
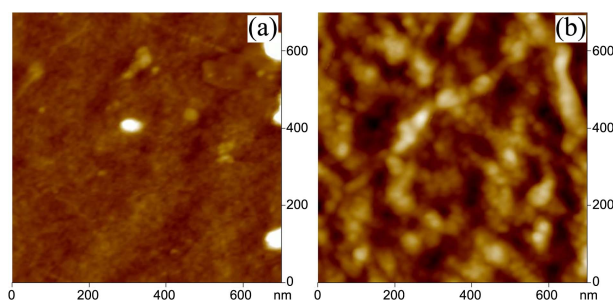

Figure 3. AFM surface images (700 × 700 nm scale): (A) Nafion 117 and (B) B37-P30 membranes.

expected to provide an effective cation-transport pathway. The interconnectivity of the hydrophilic aggregates appeared to be more pronounced for membrane with a higher conductivity. In this study, the B37-P30 composite membrane has a proton conductivity of 69 mS cm^{-1} at 100%RH and 90 °C , while the conductivity of the Nafion 117 is 91 mS cm^{-1} under the same conditions.[6,9]

In summary, we have synthesized thermally stable block copolymers with highly sulfonated hydrophilic domain using a tetrasulfonated monomer. They have shown enhanced phase separation and resulted in improved proton conductivity. Further research works including an electrochemical study will be reported elsewhere.

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