



La Science à l'œuvre pour le
at work for Canada

NRC Publications Archive (NPArc) Archives des publications du CNRC (NPArc)

Enhancement of Proton Transport by Nanochannels in Comb-Shaped Copoly(arylene ether sulfone)s

Li, Nanwen; Wang, Chenyi; Lee, So Young; Park, Chi Hoon; Lee, Young Moo; Guiver, Michael D.

Publisher's version / la version de l'éditeur:

Angewandte Chemie, 123, 39, pp. 9324-9327

Web page / page Web

<http://dx.doi.org/10.1002/ange.201102057>

<http://nparc.cisti-icist.nrc-cnrc.gc.ca/npsi/ctrl?action=rtdoc&an=18724093&lang=en>

<http://nparc.cisti-icist.nrc-cnrc.gc.ca/npsi/ctrl?action=rtdoc&an=18724093&lang=fr>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

http://nparc.cisti-icist.nrc-cnrc.gc.ca/npsi/jsp/nparc_cp.jsp?lang=en

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

http://nparc.cisti-icist.nrc-cnrc.gc.ca/npsi/jsp/nparc_cp.jsp?lang=fr

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Contact us / Contactez nous: nparc.cisti@nrc-cnrc.gc.ca.



National Research
Council Canada

Conseil national
de recherches Canada

Canada

Enhancement of Proton Transport by Nanochannels in Comb Copoly(arylene ether sulfone)s

Nanwen Li, Chenyi Wang, So Young Lee, Young Moo Lee*, Michael D. Guiver*

Efficient and selective transport of protons is critical both in biological contexts and in materials for renewable energy.^[1] In hydrogen fuel cells, for example, after oxidation of molecular hydrogen at the anode, the resulting protons must be transported across a proton selective membrane to reach the cathode. This membrane, often referred to as the proton exchange membrane (PEM), has been one of the bottlenecks to achieving affordable fuel-cell technology.^[2] Among the various types of proton exchange membranes, arylene-based polymers are attracting much attention as alternatives to perfluorinated polymer membranes, such as Nafion[®], because arylene-based PEMs have advantages over the perfluorinated membranes in terms of cost, monomer safety, and structural diversity.^[3] However, a critical issue that severely hampers FC performance is PEMs that simultaneously provide high proton conductivity that does not decline precipitously with decreasing relative humidity. In the case of automotive application, the U.S. Department of Energy has established a target of about 10^{-1} S/cm for the proton conductivity of the membrane at 120 °C and 50% relative humidity (RH) operating conditions.^[3a] In a low-humidity environment, dehydration of the PEMs typically occurs and the collapse of the physical architecture of the membrane leads to a significant loss of conductivity.^[4] As a consequence, the performance of current PEM-based devices is critically dependent on the operating humidity of the membranes.^[5]

The key to proton transport in PEMs is believed to be nanochannels of sulfonic acid groups, through which 'hydrated' protons can pass efficiently.^[6] Several approaches have been examined to form nanochannels for arylene-based PEMs, and thus improve proton conductivity under conditions of reduced humidity

and elevated temperature. These strategies have included changes in the acidity and the position of sulfonic acid groups, and the control of membrane morphologies.^[6,7] More recently, highly sulfonated moieties^[8] or sequenced hydrophilic and hydrophobic groups as block copolymers were claimed to be effective for this purpose.^[9] However, research on this class of copolymers is still in the initial stages, and the precise control of nanoscale morphology of multiblock copolymers may be restricted due to the polydispersity of each block.^[10] Therefore, a remaining challenge in the materials science of membranes lies in the molecular design of proton-conducting channels with optimized properties similar to the well-known perfluorinated polyelectrolytes. We and others have demonstrated that graft or comb copolymer architecture results in valuable properties for PEMs,^[11] but their fuel cell performance rapidly declined due to the chemical instability of the aliphatic sites of the polystyrene graft chain.^[12] Herein, we report promising results on the facile molecular design of materials that display high stability and proton conductivity over a wide range of humidity. Our approach is centered on a novel class of fully aromatic comb polymers with highly sulfonated flexible graft chains that can self-assemble into nanoscale-organized structures (Figure 1).

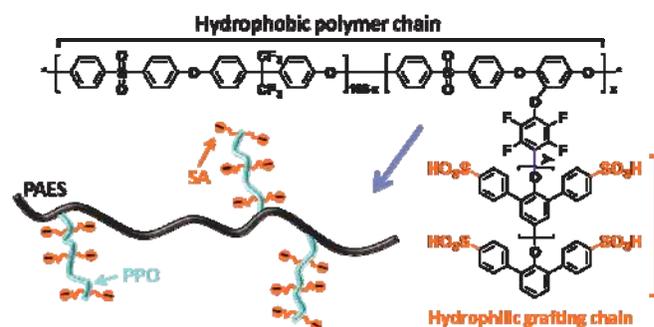


Figure 1. Structure and simplified illustration of fully aromatic comb copolymers 4.

The synthesis of the fully aromatic comb copolymers used in this study involves the combination of an –OH functionalized polymer main-chain with the mono-functional terminus of an aromatic oligomer. The conversion of methoxyl groups to reactive phenoxide groups using BBr_3 has been demonstrated to be an effective strategy to graft onto poly(arylene ether sulfone)s.^[12d] Firstly, quantitative yields of functional polymer main chain **2** (PAES-*x*-OH) (Scheme S1) were readily obtained containing different amounts –OH groups (*X*), as confirmed by ¹H NMR (Figure S1).

To avoid the instability of aliphatic graft chains, fully aromatic graft oligomers were incorporated into the molecular design, to improve the chemical stability of the PEM. Poly(phenylene oxide) (PPO) derivatives are unique among aromatic polymers. Different from polycondensation, PPOs are synthesized by catalyzed oxidative coupling of substituted phenols, resulting in single

[*] Dr. N. Li, Dr. C. Wang, Dr. M. D. Guiver, Prof. Y. M. Lee
WCU Department of Energy Engineering,
Hanyang University
Seoul 133-791, (Republic of Korea)
E-mail: Michael.Guiver@nrc-cnrc.gc.ca
ymlee@hanyang.ac.kr

S.Y. Lee, Prof. Y. M. Lee
School of Chemical Engineering, College of Engineering
Hanyang University
Seoul 133-791, (Republic of Korea)

Dr. M. D. Guiver
Institute for Chemical Process and Environmental
Technology
National Research Council
Ottawa, Ont, KIA OR6 (Canada)

[**] This research was supported by the WCU (World Class University) program, National Research Foundation (NRF) of the Korean Ministry of Science and Technology (No. R31-2008-000-10092-0), which we gratefully acknowledge.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

phenoxide-terminated chain ends.^[13] We identified mono-phenol-terminated PPO oligomers as ideal candidates for use as aromatic graft chains. Our work builds upon that of Hay et al.,^[14] who used Cu-catalyzed coupling to synthesize poly(2,6-diphenyl phenylene oxide) with low viscosity, Percec and Mühlbach^[15] who prepared poly(2,6-dimethyl phenylene oxide) with molecular weights of 1000 to 27000 g/mol, and Nishide et al.,^[16] who synthesized poly(2,6-dimethyl phenylene oxide) with molecular weights of 2000 to 7000 g/mol.

In the present work, poly(2,6-diphenyl phenylene oxide) (DPh-PPO) oligomers with M_n in the range of 1750 to 3500 g/mol, depending on the reaction temperature, were synthesized via Cu(I)-catalyzed oxidative coupling reaction. These DPh-PPO oligomers with controlled chain length were readily obtained, since 2,6-diphenylphenol is comparatively much less reactive than 2,6-dimethylphenol.^[14] The experimental Y values (graft chain repeat units) of oligomers were determined as approximately 6.2, 8.5 and 12.3 from the ^1H NMR spectra, which are similar to the values determined from GPC results (Table S1). The DPh-PPO-OH oligomers were converted to reactive fluorine-terminated oligomers (DPh-PPO-F) by end-capping with hexafluorobenzene (HFB) (Scheme S1), which was confirmed by the ^1H NMR and GPC results (Table S1).

The comb copolymers **3**(Xx - Yy) were synthesized in quantitative yield from PAES- x -OH (X) and DPh-PPO-F(Y) oligomers by a nucleophilic aromatic substitution reaction. Postsulfonation with chlorosulfonic acid yielded the sulfonated comb copolymers **4**(Xx - Yy) having the target structure without detectable chain degradation or crosslinking, which was confirmed by the viscosity measurements. ^1H NMR analysis confirmed 100% sulfonation (sulfonation on every phenylene ring in the side chain of DPh-PPO) of **3** without any sulfonation of the hydrophobic polymer main chain. The ion-exchange capacities (IEC) of the **4** comb copolymers ranged from 0.92 to 1.72 meq g^{-1} . Details of the synthesis and polymer characterization are available in the Supporting Information.

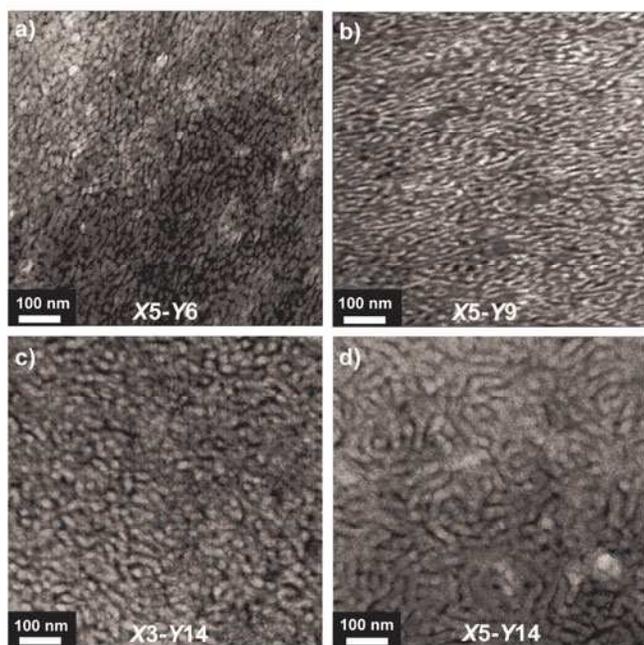


Figure 2. TEM phase images of comb copolymer membranes **4** with IEC in the range of 0.92 - 1.72 meq./g.

We hypothesized that the hydrophobic polymer main chain is immiscible with the highly sulfonated flexible grafting chain, thus driving **4** to self-assemble and form nanoscale domains that contain enhanced local concentrations of sulfonic acid, which facilitate proton transport. To test this hypothesis, the structures of these comb polymers were characterized using transmission electron microscopy (TEM). Figure 2 shows the TEM images of lead-stained comb copolymer membranes **4**; the dark areas correspond to the hydrophilic PPO graft chains. TEM images clearly show phase-separated wormlike domains. The distinct ionic domain connectivity with different sizes of ionic domains is dependent on the IEC value and graft length. In the case of **4**($X5$ - $Y6$) with an IEC value of 0.92 meq g^{-1} , a wormlike and interconnected hydrophilic network of small ionic clusters of 3-5 nm in size were observed (Figure 1a), similar to the archetypical Nafion[®], which has a 'cluster-network' morphology composed of ~5 to 10 nm ionic clusters interconnected by narrow ionic nanochannels.^[17] The interconnectivity of ionic clusters appeared to be more pronounced for higher IEC value **4**($X5$ - $Y14$, IEC=1.72 meq g^{-1}) membranes, which exhibited larger nanochannel size of ca. 15-20 nm (Figure 1 c, d). Of considerable significance, there is little evidence for dead end channels or larger spheroidal clusters as seen in previously reported ionomers.^[12d] This unique morphology was expected to provide a nanochannel pathway for efficient proton-transport.

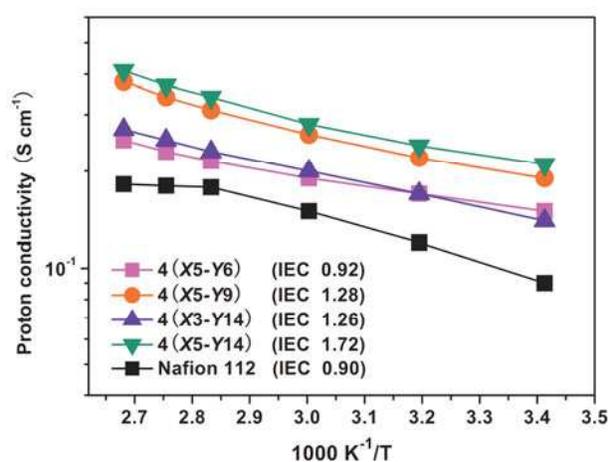


Figure 3. Temperature dependence of proton conductivity (measured in water) Arrhenius plot for the comb copolymer membranes and Nafion 112.

As shown in Table 1, comb copolymers **4** showed higher water uptake than that of the Nafion 112 membranes, while exhibiting strongly anisotropic dimensional swelling behavior, with larger dimensional change in the through-plane (thickness) direction, but exceptionally low dimensional swelling in the in-plane direction (Figure S5). Impedance spectroscopy (100% relative humidity and room temperature) revealed that the comb copolymer **4** membranes had excellent proton conductivities, which were much higher than those observed for Nafion (ca. $>10^{-1}$ S cm^{-1}) (Table 1). The high connectivity nanochannels could be the principal reason for the attainment of high conductivities, which were comparable to Nafion, at similar IEC values. The **4**($X5$ - $Y6$, IEC=0.92 meq g^{-1}) having shorter graft chains had similar proton conductivity to that of **4**($X3$ - $Y15$, IEC=1.26 meq g^{-1}), in spite of the lower IEC and water uptake (WU) of **4**($X5$ - $Y6$). Unlike previously reported multiblock copolymers, in which the longer block length induced higher proton conductivity,^[9] the shorter graft chain of copolymers **4** tended to

result in higher proton conductivity. A possible explanation for this behaviour is that shorter graft chains are distributed more homogeneously than their longer graft counterparts, though a more complete study of different graft lengths would be needed to explain this phenomenon. The proton conductivities over the 20-100 °C range at 100 % RH are shown in Figure 3. The copolymer **4** membranes exhibit qualitative increases in conductivity with temperature as shown in the Arrhenius plot. Higher temperatures increase the conductivity due to the enhanced charge transport. The proton conductivity displays a remarkably stable behaviour, with values above $2 \times 10^{-1} \text{ S cm}^{-1}$ even at 100 °C - the temperature at which water evaporation dramatically affects the hydration of Nafion and typical hydrocarbon-based PEMs.^[11a,b]

Table 1. Properties of comb copolymer membranes **4**.

samples	IEC _w ^a	IEC _v	DS (%)	WU (wt %) ^b	σ (S cm ⁻¹) ^b
4(X5-Y6)	0.92	1.24	100	28.2	0.15
4(X5-Y9)	1.28	1.77	100	52.3	0.19
4(X3-Y14)	1.26	1.74	100	60.5	0.14
4(X5-Y14)	1.72	2.46	100	75.6	0.21
Nafion	0.90	1.78	--	19.2	0.09

[a] measured by titration; [b] measured in water at room temperature.

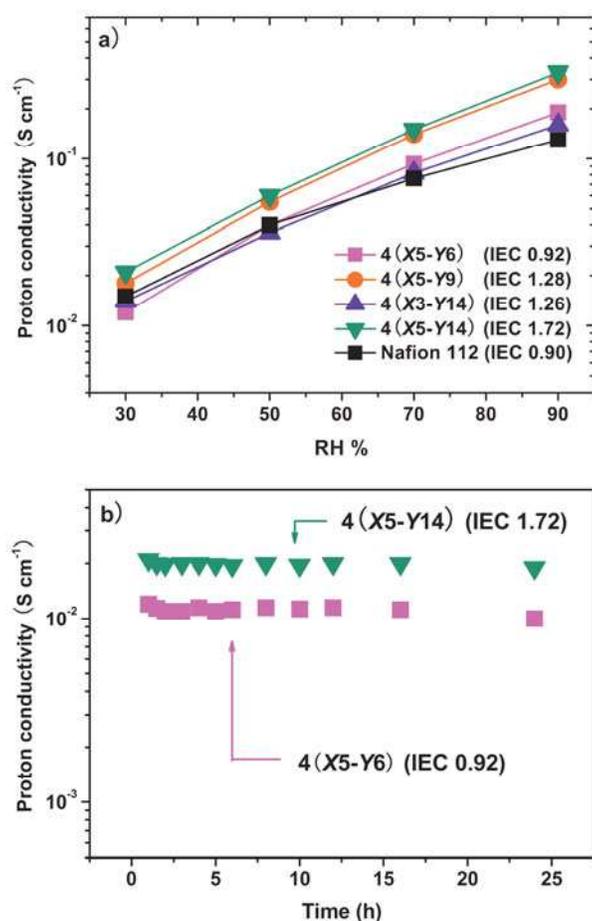


Figure 4. a) Water uptake and proton conductivity of comb copolymer **4** membranes at 90 °C as a function of relative humidity, b) conductivity as a function of test time at 30 % RH and 90 °C.

A main goal of this study was to determine the effect of relative humidity on proton conductivity. Surprisingly, we observed high conductivity values ($\sim 10^{-2}$ to $>10^{-1} \text{ S cm}^{-1}$) for comb copolymer **4** membranes over a large range of 30-90 % relative humidity (Figure 4a); values were higher or similar in comparison to that of Nafion, even at the lowest IEC values. **4**(X5-Y6) with the IEC value of only 0.92 meq. g⁻¹ displayed a proton-conductivity value of $1 \times 10^{-2} \text{ S cm}^{-1}$ at 30 % relative humidity. This represents an unprecedented result in the molecular design of new proton-conducting platforms with optimized properties. To the best of our knowledge, the proton conductivity is the highest reported for an arylene-based PEMs with an IEC value <1.0 meq./g. If the density of **4**(X5-Y6) (1.36 g/cm^3) and Nafion (1.98 g/cm^3) are taken into account, the volumetric IEC value of 1.24 meq./cm^3 for **4**(X5-Y6) is much lower than that of Nafion (1.78 meq./cm^3). Thus, proton conducting nanochannel morphology in the comb copolymers contribute strongly to the high proton conductivity. As demonstrated by McGrath and co-workers, the continuity of nanoscale domains is critical to efficient proton transport in sulfonated polymers.^[18] For these comb copolymers, the well-defined and connected nanochannels clearly enhances proton conductivity under partial hydration conditions by almost ten times compared with that of the multiblock copolymers with highly sulfonated blocks.^[9d] To further explore the reliability of the comb copolymers, we monitored the proton-conductivity values at 90 % relative humidity over a period of 24 hours. Figure 4b clearly shows that the proton conductivity is nearly constant (with values of about $10^{-2} \text{ S cm}^{-1}$) over the monitoring period. These results corroborate the robustness and reliability of fully aromatic comb copolymers with highly sulfonated graft blocks.

In summary, comb copolymers with fully aromatic structure and highly sulfonated graft chains are reported for the first time. The novel comb copolymers exhibit organized phase-separated morphology with well-connected nanochannels, resulting in a dramatic enhancement in proton conductivity under partially hydrated conditions relative to other hydrocarbon-based PEMs. We consider that this comb copolymer approach could lead to new PEM materials that meet the demanding requirements for automotive fuel cells. The PPO graft platform is versatile because it can be prepared to contain either methyl or aryl groups,^[19] which may be further modified for various applications. For example, PPO methyl groups can be modified by bromination, followed by quaternary ammonium^[13b,20] or ATRP^[21] for water treatment applications or anion exchange membranes. Thus, fully aromatic comb copolymer architecture based on PPO oligomers, prepared by viable synthetic pathways of nucleophilic aromatic substitution or other strategies such as 'click chemistry', provide new and more stable structures with interesting properties that have the potential to address various industrial and energy applications. Further investigations on this class of comb copolymers are ongoing in our laboratory.

Experimental Section

Typical synthesis of a poly(2,6-phenyl-1,4-phenylene oxide) (DPh-PPO) oligomer: To a 250 mL wide-mouthed Erlenmeyer flask equipped with a magnetic stirrer and oxygen inlet was added 100 mL of toluene. Oxygen was bubbled through the vigorously stirred toluene (500 mL/min), to which was added dropwise over a 1 h period a solution consisting of 10 g (40 mmol) of 2,6-diphenylphenol, 0.28 g (2 mmol) of copper (I) bromide and 0.23 g (2 mmol) of TMEDA dissolved in 50 mL of toluene (under N₂). After stirring for a further 3 h at 25 °C, the product was isolated by adding the reaction mixture dropwise to 0.5 L of methanol, to which was added 5 mL of concentrated hydrochloric acid, and the resulting product was removed by filtration. The precipitate was redissolved in 50 mL of chloroform, filtered

through Celite, and reprecipitated by the dropwise addition of 0.5 L of methanol. The resulting red precipitate was recovered by filtration and washed with methanol and water, and then dried in vacuo at 80 °C overnight. There was obtained 8.6 g (87% yield) of DPh-PPO-OH(14) oligomer.

Typical end-capping of poly(2,6-phenyl-1,4-phenylene oxide) oligomer with HFB (DPh-PPO-F(14)): 7.2 g (2 mmol) of DPh-PPO-OH(3) oligomer, 0.5528 g (4.0 mmol) of potassium carbonate and 2.2 g (12 mmol) of HFB were charged into a 100 mL flask equipped with a magnetic stirrer. Anhydrous DMF (50 mL) and toluene (10 mL) were added to the flask. The reaction temperature was set to 80 °C, and allowed to proceed for 36 h. The resulting green colored solution was then cooled to room temperature and precipitated in methanol. The oligomer was filtered and washed several times with methanol and water. The DPh-PPO-F(14) oligomer was dried at 80 °C in vacuo for 24 h.

Comb copolymers synthesis: $3(Xx-Yy)$, where x refers to the Me-HQ monomer molar content, and y refers to the number of phenylene oxide repeat units of the DPh-PPO oligomer. PAES-5-OH (1.1 g, 0.1 mmol of OH group), DPh-PPO-F(14) (0.41 g, 0.12 mmol), K_2CO_3 (0.02 g, 0.14 mmol), 10 mL of NMP, and 2 mL of toluene were added into an argon flushed reactor equipped with a Dean-Stark trap. The reaction mixture was heated to 105 °C for 12 h and then the reaction temperature was gradually increased over a period of 6 h to ~160 °C, then maintained at this temperature for an additional 20 h. The mixture was coagulated into a large excess of dilute HCl (5 wt %) with vigorous stirring and the polymer washed with water. The resulting comb copolymers $3(X5-Y14)$ were dried under vacuum at 100 °C for 24 h.

Sulfonation of the comb copolymer and membrane preparation: To a round-bottomed flask containing 1 g of $3(X3-Y14)$ was added dry dichloromethane (40 mL) from a dropping funnel. To the mixture was added dropwise a solution of chlorosulfonic acid (0.6 mL, 3 mmol) in dry dichloromethane (20 mL) at room temperature, and the mixture was stirred vigorously at this temperature for 30 min until a brown product precipitated out of the solution. The precipitate was filtered, and washed with water several times and dried overnight under vacuum at 80 °C for 10 h to give sulfonated comb-shaped copolymer $4(X3-Y14)$.

A solution of the obtained copolymer (1 g) in DMSO (10 mL) was filtered (10 μ m filter) and then cast onto a flat glass plate with a doctor blade. The cast solution was dried at 80 °C overnight to give a transparent, tough film. The film was dried further in a vacuum oven at 100 °C for 20 h. The resulting film was treated with 2 M H_2SO_4 for 24 h, washed with water several times, and dried at room temperature.

Received: ((will be filled in by the editorial staff))

Published online on ((will be filled in by the editorial staff))

Keywords: Comb copolymers · proton transport · nanochannels · proton conductive membranes · fuel cells

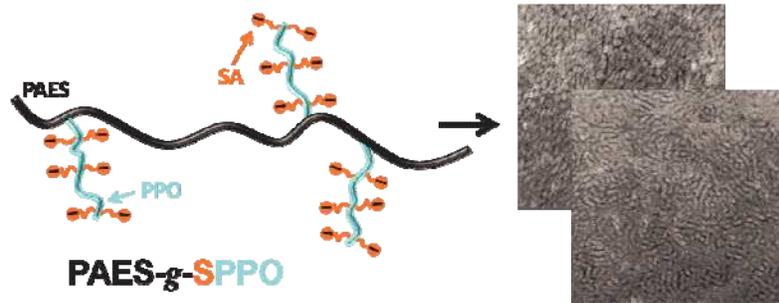
[1] a) R. J. P. Williams, *Annu. Rev. Biophys. Biophys. Chem.* **1988**, *17*, 71–97; b) K. D. Kreuer, *Chem. Mater.* **1996**, *8*, 610–641.
[2] a) M. Z. Jacobson, W.G. Colella, D. M. Golden, *Science* **2005**, *308*, 1902–1905; b) B.C.H. Steele, A. Heinzl, *Nature* **2001**, *414*, 345–352
[3] a) M. A. Hickner, H.Ghassemi, Y. S. Kim, B. R.Einsla, J. E. McGrath, *Chem. Rev.* **2004**, *104*, 4587–4612; b) M. Rikukawa, K. Sanui, *Prog. Polym. Sci.* **2000**, *25*, 1463–1502.

[4] V. Anantaraman, C. L. Gardner, *J. Electroanal. Chem.* **1996**, *414*, 115 – 120.
[5] N. L. Garland, J. P. Kopasz, *J. Power Sources* **2007**, *172*, 94 – 99.
[6] a) O. Diat, G. Gebel, *Nature Mater.* **2008**, *7*, 13–14; b) K. Schmidt-Rohr, Q. Chen, *Nature Mater.* **2008**, *7*, 75–83; c) J. A. Elliott, S. Hanna, A. M. S. Elliott, G. E. Cooley, *Macromolecules* **2000**, *33*, 8708–8713.
[7] a) K. Yoshimura, A. Yashiro, M. Nodono, **2003**, US 2003/0180596A1; b) H. Ghassemi, J. E. McGrath, T. A. Zawodzinski, *Polymer* **2006**, *47*, 4132 – 4139; c) T. J. Peckham, S. Holdcroft, *Adv. Mater.* **2010**, *22*, 4667–4690.
[8] a) S. Matsumura, A. R. Hlil, C. Lepiller, J. Gaudet, D. Guay, Z. Shi, S. Holdcroft, A. S. Hay, *Macromolecules* **2008**, *41*, 281 – 284; b) S. Tian, Y. Meng, A. S. Hay, *Macromolecules* **2009**, *42*, 1153 – 1160; c) K. Matsumoto, T. Higashihara, M. Ueda, *Macromolecules* **2009**, *42*, 1161–1166; d) C. C. de Araujo, K. D. Kreuer, M. Schuster, G. Portale, H. Mendil-Jakani, G. Gebel, J. Maier, *Phys. Chem. Chem. Phys.* **2009**, *11*, 3305 – 3312.
[9] a) B. Bae, T. Yoda, K. Miyatake, H. Uchida, M. Watanabe, *Angew. Chem., Int. Ed.* **2010**, *49*, 317–320; b) A. S. Badami, A. Roy, H.-S. Lee, Y. Li, J. E. McGrath, *J. Membr. Sci.* **2009**, *328*, 156 – 164; c) H. S. Lee, A. Roy, O. Lane, S. Dunn, J. E. McGrath, *Polymer* **2008**, *49*, 715 – 723; d) K. Nakabayashi, T. Higashihara, M. Ueda, *J. Polym. Sci.: Part A: Polym. Chem.* **2010**, *48*, 2757–2764.
[10] Y. Yang, S. Holdcroft, *Fuel Cells* **2005**, *5*, 171–186.
[11] a) J. F. Ding, C. Chuy, S. Holdcroft, *Adv. Funct. Mater.* **2002**, *12*, 389–392; b) E. M.W. Tsang, Z. Zhang, Z. Shi, T. Soboleva, S. Holdcroft, *J. Am. Chem. Soc.* **2007**, *129*, 15106 – 15107; c) T. B. Norsten, M. D. Guiver, J. Murphy, T. Astill, T. Navessin, S. Holdcroft, B. L. Frankamp, V. M. Rotello, J. Ding, *Adv. Funct. Mater.* **2006**, *16*, 1814–1822; d) D. S. Kim, G. P. Robertson, M. D. Guiver, *Macromolecules* **2008**, *41*, 2126 –2134; e) Y. Chen, M. Thorn, S. Christensen, C. Versek, A. Poe, R. C. Hayward, M. T. Tuominen, S. Thayumanavan, *Nat. Chem.* **2010**, *2*, 503–508.
[12] D. S. Kim, Y. S. Kim, M. D. Guiver, J. Ding, B. S. Pivovar, *J. Power Sources*, **2008**, *182*, 100–105.
[13] a) A. S. Hay, *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 505–517; b) T. Xu, D. Wu, L. Wu, *Prog. Polym. Sci.* **2008**, *33*, 894–915; c) K. P. Chan, D. S. Argyropoulos, D. M. White, G. W. Yeagers, A. S. Hay, *Macromolecules* **1994**, *27*, 6371–6375.
[14] S. Hay, *Macromolecules* **1969**, *2*, 107–108.
[15] K. Mühlbach, V. Percec, *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 2605–2627.
[16] K. Saito, T. Tago, T. Masuyama, H. Nishide, *Angew. Chem. Int. Ed.* **2004**, *43*, 730 –733.
[17] a) W. Y. Hsu, T. D. Gierke, *Macromolecules* **1982**, *15*, 101–105; b) L. Rubatat, A. L. Rollet, G. Gebel, O. Diat, *Macromolecules* **2002**, *35*, 4050–4055.
[18] Roy, M. A. Hickner, X. Yu, Y. Li, T. E. Glass, J. E. McGrath, *J. Polym. Sci. Part B: Polym. Phys.* **2006**, *44*, 2226–2239.
[19] a) H. Yang, A. S. Hay, *J. Polym. Sci. Part A: Polym. Chem.* **1993**, *31*, 1261–1273; b) A. S. Hay, *Prog. Polym. Sci.* **1999**, *24*, 45–80.
[20] a) T. W. Xu, W. H. Yang, *J. Membr. Sci.* **2001**, *190*, 159–166; b) S. L. Zhang, T. W. Xu, C. M. Wu, *J. Membr. Sci.* **2006**, *269*, 142–151.
[21] a) M. Liang, Y. J. Jhuang, C. F. Zhang, W. J. Tsai, H. C. Feng, *Eur. Polym. J.* **2009**, *45*, 2348–2357; b) C. G. Cho, H. Y. Jang, Y. G. You, G. H. Li, S. G. An, *High Perform. Polym.* **2006**, *18*, 579–591.

Materials Science

Nanwen Li, Chenyi Wang, So Young Lee, Young Moo Lee*, Michael D. Guiver * _____ Page – Page

Enhancement of Proton transport by Nanochannels in Comb Copoly(arylene ether sulfone)s



Nanochannels in comb copolymers: Fully aromatic comb copolymers with highly sulfonated PPO graft chains have been synthesized and organize to provide nanochannel morphology (see picture) for efficient proton transport. These comb molecular structures show a dramatic enhancement in proton conductivity under partially hydrated conditions compared with typical hydrocarbon polymer electrolytes.

Supporting Information

Enhancement of Proton Transport by Nanochannels in Comb Copoly(arylene ether sulfone)s

Nanwen Li, Chenyi Wang, So Young Lee, Young Moo Lee*, Michael D. Guiver*

WCU Department of Energy Engineering, College of Engineering, Hanyang University, Seoul 133-791, Republic of Korea

School of Chemical Engineering, College of Engineering, Hanyang University, Seoul 133-791, Republic of Korea

Institute for Chemical Process and Environmental Technology, National Research Council, Ottawa, Ont. K1A 0R6, Canada

E-mail: michael.guiver@nrc-cnrc.gc.ca, ymlee@hanyang.ac.kr

1. Experimental section

Materials. Bis(4-fluorophenyl) sulfone (DFDPS) was obtained from Sigma-Aldrich and dried under vacuum at room temperature overnight. 4,4'-(Hexafluoroisopropylidene)diphenol (6F-BPA) and 2-methoxyhydroquinone (MeHQ) were purchased from Sigma-Aldrich and recrystallized twice from toluene. 2,6-diphenylphenol, copper(I) bromide, and N,N,N',N'-tetramethylethylenediamine (TMEDA) were dried in vacuum at room temperature overnight before use. Toluene was purchased from Sigma-Aldrich and distilled from calcium hydride before use. Hexafluorobenzene (HFB) and all other solvents and reagents were reagent grade obtained from Sigma-Aldrich and were used as received.

Synthesis of copoly(arylene ether sulfone) containing –OCH₃ groups (PAES-*x*-Me). A typical synthetic procedure for methylether-substituted polymer, illustrated by the preparation of PAES-5-Me copolymers (Me-HQ/6F-BPA = 5/95), is described

as follows. Into a three-neck flask equipped with a mechanical stirrer, Dean-Stark trap, and an argon gas inlet were added 20 mmol of DFDPS, 1 mmol of Me-HQ, 19 mmol of 6F-BPA, and 24 mmol of K_2CO_3 . Then, 30 mL of NMP and 15 mL of toluene were charged into the reaction flask under an argon atmosphere and the reaction mixture was heated to 145 °C. After dehydration and removal of toluene for several hours, the reaction temperature was increased to about 170 °C. When the increase of the solution viscosity became obvious, the mixture was cooled to room temperature and coagulated into a large excess of deionized water with vigorous stirring. The resulting fibrous copolymer was washed thoroughly with water or ethanol several times and dried under vacuum at 100 °C for 24 h. The copolymer was denoted PAES-5-Me, where x (5) refers to the Me-HQ molar content. Yield: 97%.

Synthesis of copoly(arylene ether sulfone) containing –OH groups (PAES- x -OH) by demethylation. PAES-5-Me (10 g) was dissolved into 200 mL of chloroform in a 500 mL, three-neck flask equipped with a mechanical stirrer and an argon gas inlet. BBr_3 (1 mL) was mixed with chloroform (10 mL) and the resulting solution was added dropwise to the PAES-5-Me solution at room temperature. After 8 h, the copolymer was filtered and washed with methanol and deionized water. The resulting copolymer **2** (PAES-5-OH) was dried under vacuum at 100 °C for 24 h. Yield: 98%.

Measurements. 1H NMR spectra were measured at 300 MHz on an AV 300 spectrometer using $DMSO-d_6$ or $CDCl_3$ as solvent. Ion exchange capacities (IEC) of the membranes were determined by back-titration and 1H NMR spectroscopy.

Sulfonated membrane was equilibrated in a large excess of 0.5 M NaCl aqueous solution for 3 days. The protons released (HCl) by the ion exchange were titrated with standard 0.01 M NaOH solution to determine IEC. The reduced viscosities were determined for 0.5 g dL⁻¹ concentrations of polymer in NMP or DMSO with an Ubbelohde capillary viscometer at 30 ± 0.1 °C. The molecular weights of polymers were determined by gel permeation chromatography (GPC) using a Waters 515 HPLC pump, coupled with a Waters 410 differential refractometer detector and a Waters 996 photodiode array detector. THF was used as the eluant and the μ -Styragel columns were calibrated by polystyrene standards.

Water uptake and proton conductivity were measured with a solid electrolyte analyzer system equipped with a temperature and humidity controllable chamber. Vacuum drying for 10 h at 100 °C gave the weight of dry membranes and exposure to a given humidity for at least 6 h gave the weight of hydrated membranes. Weight of the membranes was measured by magnetic suspension balance at given humidity and then, water uptake was calculated as follows.

$$\text{Water uptake (\%)} = [(W_w - W_d)/W_d] \times 100 \% \quad (1)$$

where W_w and W_d are the weight of dry and corresponding water-swollen membranes, respectively.

Dimensional swelling of the membranes in water was investigated by immersing samples into water at room temperature for a given time, the changes of in-plane and thickness direction were calculated from:

$$\Delta t = (T - T_s) / T_s$$

$$\Delta l = (L - L_s) / L_s \quad (2)$$

where T_s and L_s are the thickness and diameter of the membrane at dry state, respectively; T and L refer to those of the membrane immersed in liquid water for 5 h.

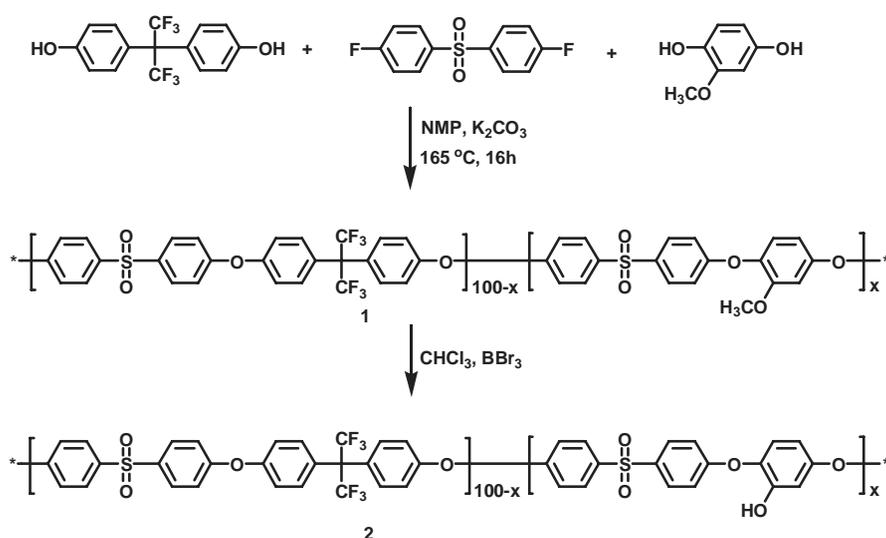
The density of membrane was measured from a known membrane dimension and weight after drying at 100 °C for 24 h. From this, the volume-based water uptake (WU) was obtained. A volume-based IEC (IEC_v) was obtained by multiplying the membrane density by the IEC_w values which were estimated from the copolymer structure. This calculation resulted in IEC_v (dry) based on the dry membrane density. An IEC_v (wet) was then calculated based on membrane water uptake.

The proton conductivity (σ , $S\ cm^{-1}$) of each membrane sample (size: 1 cm \times 4 cm) was obtained using $\sigma = d / L_s W_s R$ (d is the distance between reference electrodes, and L_s and W_s are the thickness and width of the membrane, respectively). The resistance value (R) was measured over the frequency range from 100 Hz to 100 kHz by four-point probe alternating current (ac) impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzer (Solartron 1260) and an electrochemical interface (Solartron 1287, Farnborough Hampshire, ONR, UK). The

membranes were sandwiched between two pairs of gold-plate electrodes. The conductivity measurements under fully hydrated conditions in the longitudinal direction were carried out with the cell immersed in liquid water. Proton conductivity under partially hydrated conditions was performed at 90 °C. Membranes were equilibrated at different relative humidity for 2 h in a humidity-temperature oven before each measurement.

For transmission electron microscopy (TEM) observations, the membranes were stained with lead ions by ion exchange of the sulfonic acid groups in 0.5 M lead acetate aqueous solution, rinsed with deionized water, and dried in vacuum oven for 12 h. The stained membranes were embedded in epoxy resin, sectioned to 90 nm thickness with Leica microtome Ultracut UCT, and placed on copper grids. Electron micrographs were taken with a Hitachi H7600 transmission electron microscope using an accelerating voltage of 80 k.

2. Analyses of PAES-x-OH, PPO Oligomers and Comb Copolymers



Scheme S1. The synthesis of the polymers **2** (PAES-*x*-OH) with functional -OH groups.

Poly(arylene ether sulfone)s containing pendant methoxy groups (PAES-*x*-Me, where *x* is the mole ratio (%) of Me-HQ) were synthesized by polycondensation using various feed ratios of Me-HQ/6F-BP, so that polymers with different molar percentage of pendant group were obtained (Scheme 2). The conversion of the -OCH₃ groups to reactive -OH groups using BBr₃ was effectively conducted in chloroform, as reported previously,^[1,2] and confirmed by ¹H NMR, as shown in Figure S1. The -OCH₃ proton signals at 3.6 ppm disappeared, and -OH proton signals appeared at 10 ppm.

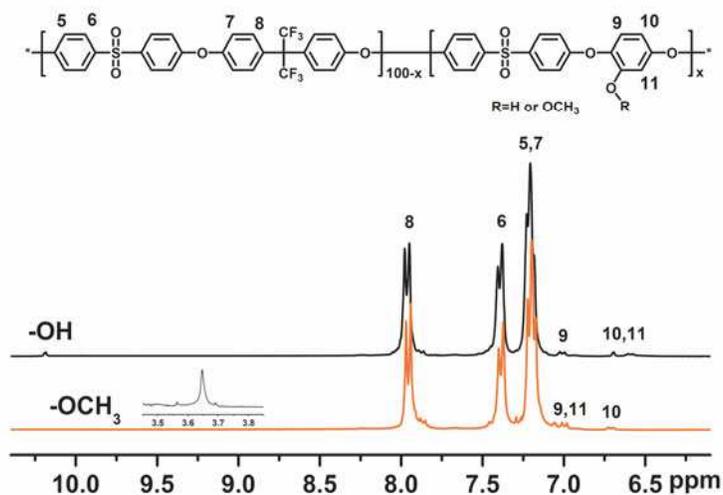
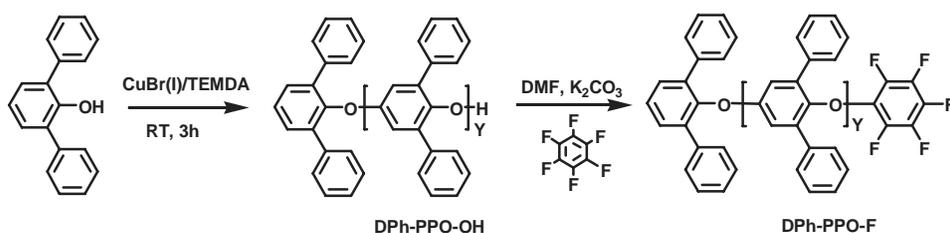


Figure S1. Comparative ¹H NMR spectra of PAES-5-CH₃ and PAES-5-OH in DMSO-*d*₆.



Scheme S2. The synthesis of the DPh-PPO-OH and DPh-PPO-F oligomers

Since both the PAES-OH and PPO oligomers have the same telechelic functionality (i.e., –OH end group), the oligomer chain ends were modified to enable a coupling reaction for producing comb-shaped copolymers.^[3] The PPO oligomer was end-capped with HFB to produce fluorine-terminated end group functionality (Scheme S2). The amount of the end-capping reagents used in the reaction was 400 % molar excess in order to avoid any inter-oligomer coupling, since HFB is multifunctional. Due to the poor solubility of PPO oligomer in polar organic solvent, the end-capping reactions took a long time to complete (about 36 h) when using mild temperature conditions (80 °C). In the ¹H NMR spectra of the end-capped oligomers, the disappearance of the –OH proton at 4.8 ppm confirmed the complete reaction with the end-capping reagent (Figure S2). While the absence of –OH signals are evidence of the end-capping reaction, there is still the possibility of inter-oligomer coupling through the multifunctional HFB. However, no increase in M_n of PPO oligomer after end-capping was observed by GPC, as shown in Table S1, indicating that this undesirable side reaction was avoided.

Table S1. Molecular Weight and Thermal Stability of the Oligomers PPO and FPPO.

Oligomers	M_n^a	Y^a	M_n^b	M_w^b	M_w/M_n^b	Y^b
DPh-PPO-OH(6)	1750	6.2	1800	2400	1.3	6.5
DPh-PPO-OH(9)	2300	8.5	2300	2800	1.2	9.2
DPh-PPO-OH(14)	3500	12.3	3800	4500	1.3	13.6
DPh-PPO- (6)	–	–	2000	2400	1.2	6.5
DPh-PPO- (9)	–	–	2500	2800	1.1	8.6
DPh-PPO- (14)	–	–	4100	4900	1.2	14.1

[a] determined by ^1H NMR, [b] determined by GPC.

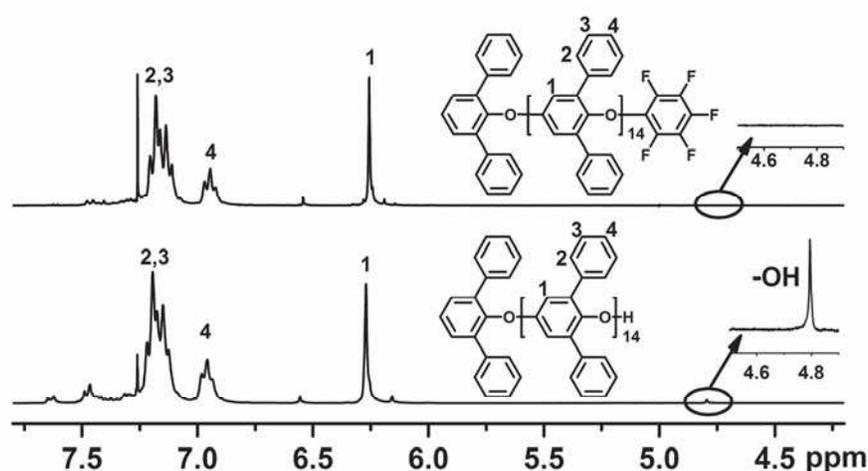


Figure S2. Comparative ^1H NMR spectra of DPh-PPO-OH(3) and DPh-PPO-F(3) in CDCl_3 .

To prepare the comb-shaped polymer **3**, PAES- x -OH was reacted with the activated fluorine atom of F-PPO by nucleophilic substitution, as shown in Scheme S3. The reactions proceeded smoothly, and no cross-linking was evident when the temperature and reaction time were well controlled by an oil bath. As shown in Figure S3, the polymer ^1H NMR spectrum showed the complete disappearance of the proton of the $-\text{OH}$ group at 10 ppm, and the PPO protons appeared at 6.28 and 7.01 ppm,

respectively. All of the non-sulfonated comb-shaped copolymers were readily soluble in NMP, CHCl₃ and CH₂Cl₂, but not in DMSO, DMF and DMAc.

The comb copolymers **3** were sulfonated with chlorosulfonic acid in dichloromethane solution. Based on the number of phenyl rings on the side chain obtained, a five molar excess of chlorosulfonic acid was applied for the sulfonation reaction of **3**. The reaction proceeded well at room temperature, and most of the sulfonated comb-shaped copolymers precipitated out of solution within 15 min. The reaction was continued for an additional 15 min to ensure completion of the sulfonation reaction. However, it was important to avoid extended sulfonation time (> 40 min), since insoluble gels resulted. In the present work, there was no evidence of chain degradation occurring under these conditions, as indicated by viscosity measurements (Table S2). The sulfonated products **4** were isolated as white powders, which were fully soluble only in DMSO. The sulfonated copolymers **4** showed partial solubility in common polar aprotic solvents (DMF, DMAc and NMP), resulting in opaque solutions. As shown in Figure S3, comparison of **4**(X5-Y14) with the parent copolymer **3**(X5-Y14) revealed that the signals assigned to the non-sulfonated pendent phenyl groups of PPO (H3, H4) disappeared, while the other aromatic protons (H5, H6, H7, H8) remained after the sulfonation reaction. A new signal assigned to the PPO sulfonated pendent phenyl groups appeared at 7.66 ppm. The absence of the H4 signal is indicative of complete sulfonation (100 % of degree of sulfonation - DS) on all the PPO pendent phenyl groups. The integration ratio of H1 to either H2 or H3 in PPO is close to 2:1, which suggests that substitution occurred only at the *para*

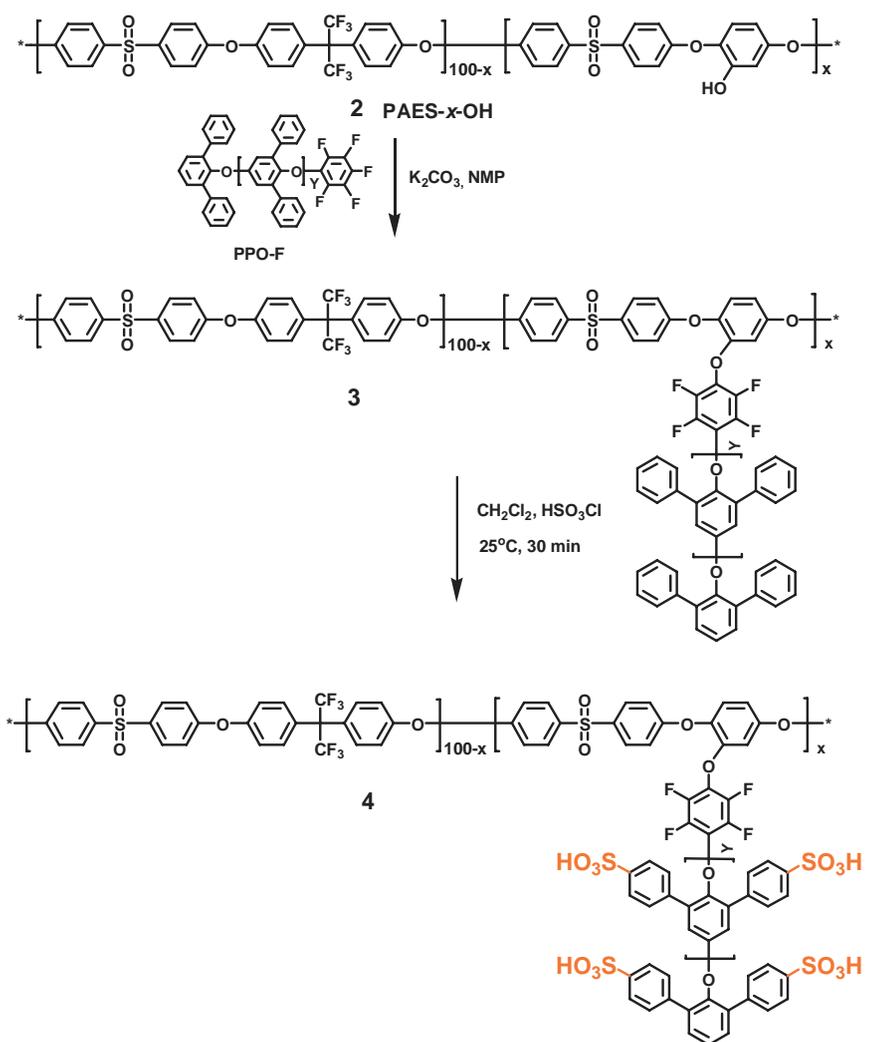
position of the pendent phenyl groups (Figure S4). The IEC of **4** was in the range of 1.33 to 2.44 meq./g according to the ^1H NMR results, which were consistent with the titration values (Table S2). Transparent and flexible **4** membranes were cast from DMSO solutions in the sulfonic acid form.

Table S2. IEC, Viscosity of the Comb-shaped Copolymers **4**.

samples	FPPO content [%]	η^a	η^b	IEC (^1H NMR)	IEC (titration)
4 (X5-Y6)	5 %	0.65	1.05	0.86	0.91
4 (X5-Y9)	5 %	0.56	1.10	1.32	1.28
4 (X3-Y14)	3%	0.57	0.96	1.33	1.26
4 (X5-Y14)	5 %	0.45	0.94	1.67	1.72

^a 0.5 g dL⁻¹ in NMP at 30 °C before sulfonation;

^b 0.5 g dL⁻¹ in DMSO at 30 °C after sulfonation.



Scheme S3. The synthesis of the sulfonated comb copolymers **4**.

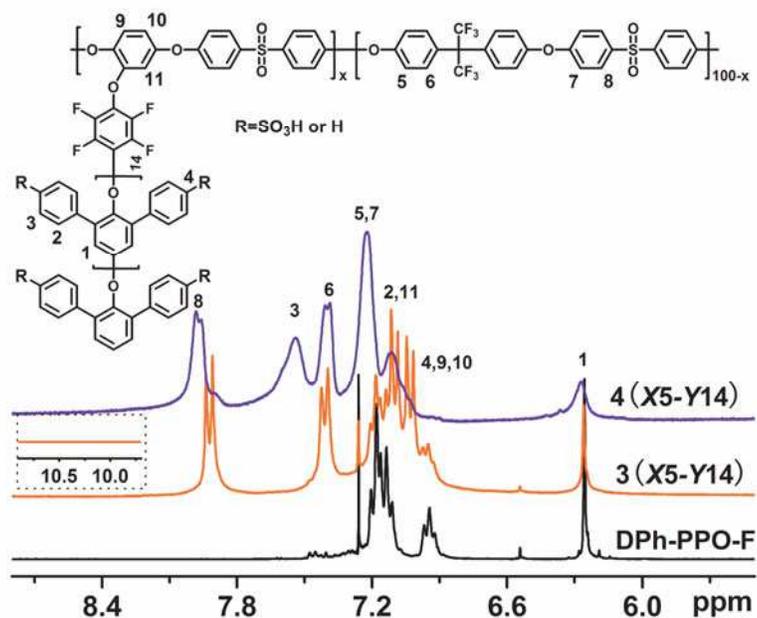


Figure S3. Comparative ^1H NMR spectra of DPh-PPO-F(3), 3(X5-Y14) (R = H) in CDCl_3 and 4(X5-Y14) (R = SO_3H) $\text{DMSO}-d_6$.

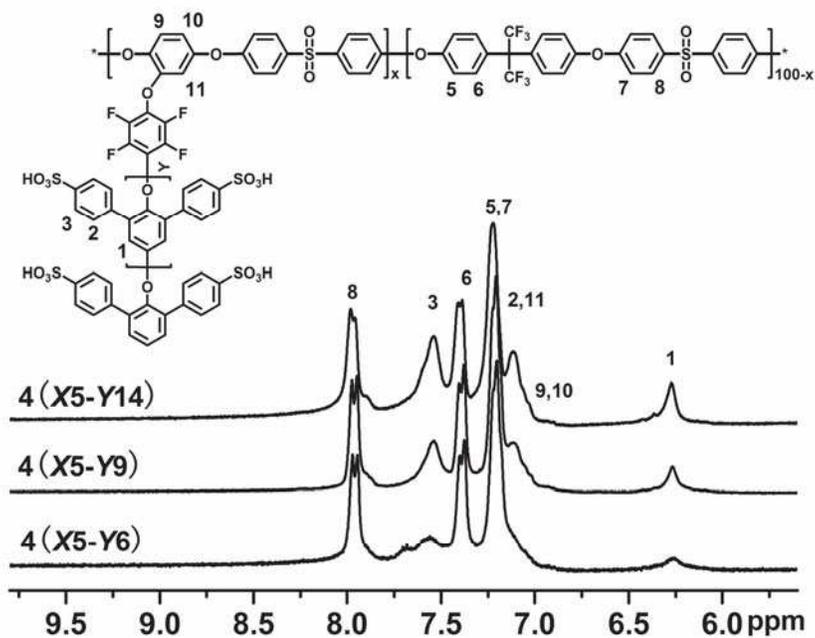


Figure S4. Comparative ^1H NMR spectra of 4(X5-Y6), 4(X5-Y9) and 4(X5-Y14) in $\text{DMSO}-d_6$.

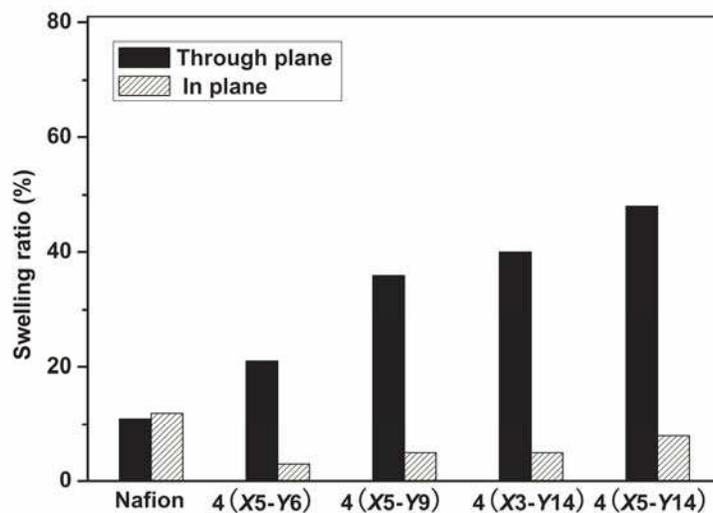


Figure S5. Comparison of dimensional swelling data for comb copolymers **4** and Nafion membranes in water at room temperature.

References:

- [1] B. R. Einsla, J. E. McGrath, *Am. Chem. Soc. Div. Fuel Chem.* **2004**, *49*, 616.
- [2] D. S. Kim, G. P. Robertson, M. D. Guiver, *Macromolecules*, **2008**, *41*, 2126–2134.
- [3] H. S. Lee, A. Roy, O. Lane, S. Dunn, J. E. McGrath, *Polymer* **2008**, *49*, 715-723