Materials Science

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

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Efficient and selective transport of protons is critical both in biological systems 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 proton-exchange membrane (PEM) is one limitation to the achievement of affordable fuel-cell (FC) technology.[2] Arylene-based PEMs are attracting much attention as alternatives to established perfluorinated polymer membranes, such as Nafion, because they have advantages in terms of cost, monomer safety, and structural diversity.[3] A critical requirement for FC use in the automotive industry is that PEMs should be able to maintain sufficiently high proton conductivity with decreasing relative humidity.[3a] In a reduced-humidity environment, PEM dehydration typically occurs, and leads to a collapse of the physical architecture, thus resulting in a significant loss of conductivity.[4] As a consequence, the performance of current PEMFCs is critically dependent on the operating humidity of the membranes.[5]

The key to proton transport in PEMs is believed to be nanochannels that contain sulfonic acid groups, through which "hydrated" protons can pass efficiently.[6] Several approaches to form PEM nanochannels have been examined to improve proton conductivity values under reduced humidity and elevated temperature, such as changes in the acidity[7] and the position of sulfonic acid groups,[8] and the control of membrane morphologies by block copolymer architectures,[9] but these approaches had only limited success.[10] A remaining challenge in the materials science of membranes lies in the molecular design of proton-conducting channels with optimized properties similar to those of the well-known perfluorinated polymer electrolytes. Our research group and others have demonstrated that use of graft or comb-shaped copolymer architectures result in valuable conductivity and morphological properties for PEMs,[11] but fuel-cell performance declined rapidly when these polymers were used because of the chemical instability of the aliphatic sites of the polystyrene graft chain.[12] Herein, we report a novel class of fully aromatic comb-shaped polymers with highly sulfonated graft chains that can self-assemble into nanoscale organized structures, display high proton conductivity over a wide range of humidity, and have improved stability (Figure 1).

The synthesis of the fully aromatic comb-shaped copolymers used in this study involves the combination of an OH-functionalized polymer main chain with the monofunctional terminus of an aromatic oligomer. Functional polymers **2** (PAES-*x*-OH; PAES = poly(arylene ether sulfone) Scheme S1 in the Supporting Information) were readily obtained and contained different amounts (*x*) of OH groups (X),[11d] as confirmed by ^{1}H NMR spectroscopy (Figure S1). To avoid the instability of aliphatic graft chains, fully aromatic graft poly(phenylene oxide) (PPO) oligomers were incorporated into the molecular design. PPO derivatives are unique among aromatic polymers as they have single phenoxide-terminated chain ends and higher stability than aliphatic systems.[13]

In the present work, poly(2,6-diphenyl phenylene oxide) (DPh-PPO) oligomers with M_n values in the range 1750–3500 g mol^{-1}, depending on the reaction temperature, were synthesized by a 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 (of graft chain repeat units, Y) of the

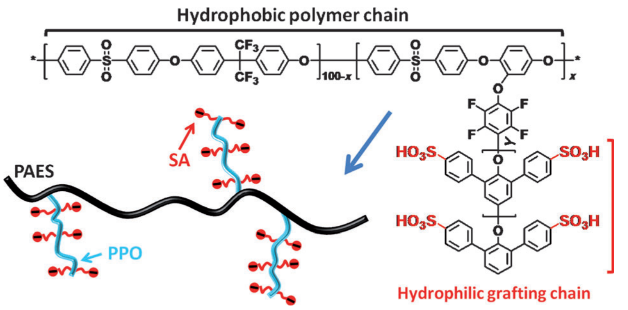

Figure 1. Structure and simplified illustration of fully aromatic comb-shaped copolymers **4**. SA = sulfonic acid.

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oligomers were determined from ^{1}H NMR spectra as approximately 6.2, 8.5, and 12.3 (Figure S2), 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 S2), which was confirmed by the ^{1}H NMR and GPC results (Table S1).

The comb-shaped copolymers **3**(X*x*-Y*y*) were synthesized in quantitative yield from PAES-*x*-OH and DPh-PPO-F(*y*) oligomers by a nucleophilic aromatic substitution reaction (Scheme S3). Postsulfonation with chlorosulfonic acid resulted in the sulfonated comb-shaped copolymers **4**(X*x*-Y*y*) that have the target structure. No chain degradation or cross-linking was detected, as confirmed by viscosity measurements (Table S2). ^{1}H NMR analysis (Figures S3 and S4) 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 comb-shaped copolymers **4** ranged from 0.92 to 1.72 meq g^{-1}. Thermogravimetric analysis (TGA, Figure S5) indicated that the onset weight loss temperature of **4** membranes was approximately 300 °C, which was higher than those of comb-shaped copolymers based on aliphatic graft chains (about 200 °C).[11c] Furthermore, the **4** membranes showed better oxidative stability with lower decreases in weight and inherent viscosity (Table S3). Compared with previously reported multiblock copolymers,[9a] these compounds were also more stable to oxidation. The comb-shaped copolymers showed negligible degradation by accelerated hydrolytic stability testing. Details of the synthesis and polymer characterization are given in the Supporting Information.

The nanoscale morphologies of the comb-shaped copolymers were characterized by using transmission electron microscopy (TEM). Figure 2 shows the TEM images of lead-stained comb-shaped 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 of the copolymers. In the case of **4**(X5-Y6), which has an IEC value of 0.92 meq g^{-1}, a wormlike interconnected hydrophilic network of small ionic clusters 3–5 nm in size were observed (Figure 2 a); this structure is similar to that of Nafion, which has a 'cluster-network' morphology composed of 5–10 nm ionic clusters interconnected by narrow ionic nanochannels.[15] The magnification of images shows apparently well-connected hydrophilic nanochannels, with little evidence for the dead-end channels or larger spheroidal clusters seen in previously reported ionomers.[11d] The interconnectivity of ionic clusters appears to be more pronounced for **4**(X5-Y14) membranes (IEC = 1.72 meq g^{-1}), which had a larger nanochannel size of 15–20 nm (Figure 2 c, d). The results of small-angle X-ray scattering (SAXS) of **4** membranes are in agreement with the TEM results. The distance *d* between hydrophilic or hydrophobic domains was in the range 30–45 nm (Figure S6), which is much higher than that of previously reported multiblock copolymers and Nafion.[9a,11c] This large *d* value probably originates from the unique comb-shaped copolymer morphology, which can facilitate phase separation between hydrophilic and hydrophobic aggregates to form nanochannels.

Mesoscale simulation (Figure S7 and details in the Supporting Information) was also employed to investigate the phase morphology of **4** membranes. As shown by the periodic 3D images (Figure 3), all the **4** membranes display well-connected hydrophilic nanochannels (blue areas), which become thicker and more interconnected as the graft chain length increases. This unique morphology is consistent with

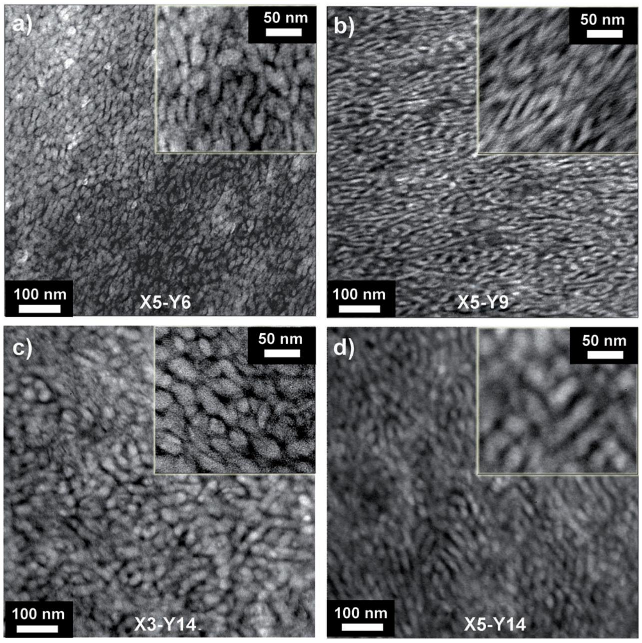

Figure 2. TEM phase images of comb-shaped copolymer membranes **4** with IEC values in the range 0.92–1.72 meq g^{-1}.

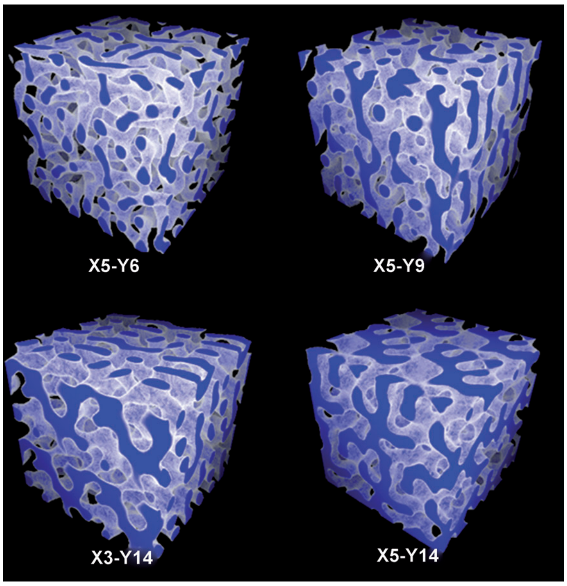

Figure 3. Phase diagram of **4** membranes (hydrophilic side chain (blue) surrounded by an isodensity surface (white), 64 nm × 64 nm × 64 nm).

Table 1: Properties of comb-shaped copolymer membranes **4**.

Samples	IEC[a]	IEC$_v$	DS [%][b]	WU [wt%][c]	σ [S cm^{-1}][c]
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 112	0.90	1.78	–	19.2	0.09

[a] Measured by acid–base titration. [b] DS = degree of sulfonation. [c] Measured in water at room temperature.

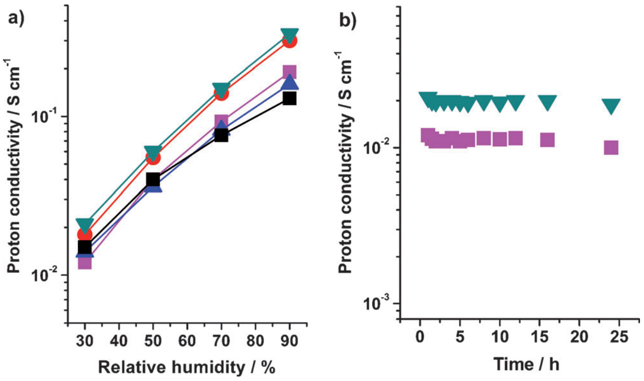

Figure 4. a) Proton conductivity of **4**(X5-Y6) (■), **4**(X5-Y9) (●), **4**(X3-Y14) (▲), **4**(X5-Y14) (▼) and Nafion 112 (■) membranes at 90 °C as a function of relative humidity; b) proton conductivity of **4**(X5-Y6) (■) and **4**(X5-Y14) (▼) membranes as a function of test time at 30% RH and 90 °C.

the TEM and SAXS results, thus suggesting nanochannel pathways for efficient proton transport.

As shown in Table 1, comb-shaped copolymers **4** showed higher water uptake (WU) than that of the Nafion 112 membrane, while exhibiting strongly anisotropic dimensional swelling behavior, with a larger dimensional change in the through-plane direction, but exceptionally low dimensional swelling in the in-plane direction (Figure S8). Impedance spectroscopy (in water and at room temperature) revealed that the comb-shaped copolymer **4** membranes had excellent proton conductivities (σ), which were much higher than those observed for Nafion 112 (> 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 112, at similar IEC values. Membrane**4**(X5-Y6) (IEC = 0.92 meq g^{-1}), which has shorter graft chains, had a similar proton conductivity to that of **4**(X3-Y14) (IEC = 1.26 meq g^{-1}), despite the lower IEC and water uptake 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 behavior 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% relative humidity (RH) are shown in the Arrhenius plot in Figure S9. Membranes of copolymer **4** exhibit qualitative increases in conductivity with temperature. The proton conductivity displays remarkably stable behavior, with values above 2×10^{-1} S cm^{-1}, even at 100 °C, which is the temperature at which water evaporation dramatically affects the hydration of Nafion and typical hydrocarbon-based PEMs.[11a,b]

A similar trend was observed at reduced RH values. The water uptake and proton conductivities of **4** membranes increase with increasing temperature up to temperatures as high as 90 °C at 50% RH (Figure S10). In contrast, water uptake and proton conductivity obtained from Nafion 112 decreases with increasing temperature when the 70 °C threshold is crossed. These results indicate that the water evaporation is suppressed at elevated temperatures in our membranes. This behavior is probably because of the capillary condensation of the nanochannels.[16]

Surprisingly, we observed high conductivity values ($\sigma \approx 10^{-2}$ to $> 10^{-1}$ S cm^{-1}) for **4** membranes over the 30–90% RH range (Figure 4a); values were higher than or similar to those of Nafion 112, even at the lowest IEC values. Membrane **4**(X5-Y6), which has an IEC value of only 0.92 meq g^{-1}, displayed a proton conductivity value of 1×10^{-2} S cm^{-1} at 30% RH. This value 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 less than 1.0 meq g^{-1}. If the density of **4**(X5-Y6) (1.36 g cm^{-3}) and Nafion 112 (1.98 g cm^{-3}) are taken into account, the volumetric IEC value (IEC$_v$) of 1.24 meq cm^{-3} for **4**(X5-Y6) is much lower than that of Nafion 112 (1.78 meq cm^{-3}). Thus, proton-conducting nanochannel morphologies in the comb-shaped copolymers contribute strongly to the high proton conductivity.[17] The proton conductivity at 90% RH over 24 h is nearly constant, with values of about 10^{-2} S cm^{-1} (Figure 4b). These results corroborate the robustness of fully aromatic comb-shaped copolymers with highly sulfonated graft blocks.

In summary, fully aromatic comb-shaped copolymers with highly sulfonated graft chains are reported. The novel comb-shaped copolymers exhibit organized phase-separated morphology with well-connected nanochannels, thus resulting in a dramatic enhancement in proton conductivity under partially hydrated conditions relative to other hydrocarbon-based PEMs. This comb-shaped 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,[13b,18] which may be further modified to address various industrial and energy applications. Further investigations on this class of comb-shaped copolymers are under way.

Experimental Section

Comb-shaped copolymers synthesis: **3**(X*x*-Y*y*), where *x* refers to the 2-methoxyhydroquinone (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 groups), DPh-PPO-F(14) (0.41 g, 0.12 mmol), K_2CO_3 (0.02 g, 0.14 mmol), *N*-methyl-2-pyrrolidinone (NMP; 10 mL), and toluene (2 mL) were added to 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 ca. 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-shaped copolymers **3**(X5-Y14) were dried under vacuum at 100 °C for 24 h.

Sulfonation of the comb-shaped copolymer and membrane preparation: Dry dichloromethane (40 mL) was added from a dropping funnel to a round-bottomed flask containing **3**(X3-Y14) (1 g). A solution of chlorosulfonic acid (0.6 mL, 3 mmol) in dry dichloromethane (20 mL) was subsequently added at room temperature, and the mixture was stirred vigorously at this temperature for 30 min until a brown product precipitated from 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).

Solutions of copolymers **4**(1 g) in DMSO (10 mL) were filtered (10 μm filter) and then cast onto glass plates with a doctor blade. Cast solutions were dried at 80 °C overnight to give transparent, tough films. The films were dried further in a vacuum oven at 100 °C for 20 h, and then treated with $2\,\mathrm{M}$ H_2SO_4 for 24 h, washed with water several times, and dried at room temperature.

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