Communication

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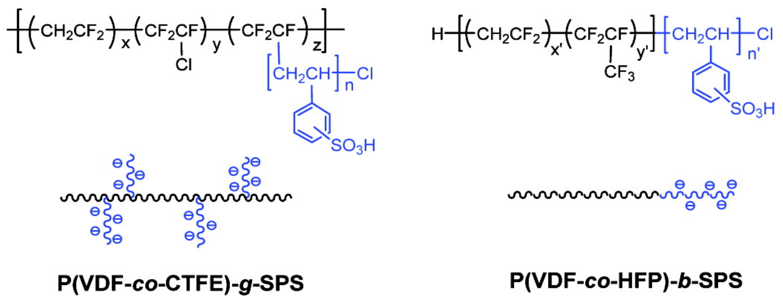

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Considerations of Macromolecular Structure in the Design of Proton Conducting Polymer Membranes: Graft versus Diblock Polyelectrolytes

Emily M. W. Tsang,[†] Zhaobin Zhang,[†] Zhiqing Shi,[‡] Tatyana Soboleva,[†] and Steven Holdcroft*[,†,‡]

Department of Chemistry, Simon Fraser University, Burnaby, BC V5A 1S6, Canada, and Institute of Fuel Cell Innovation, National Research Council Canada, 3250 East Mall, Vancouver, BC V6T 1W5, Canada

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This Communication addresses issues surrounding the design of ionic polymers for solid polymer electrolytes and more specifically, proton conducting polymers for fuel cells. Despite intensive research effort in the search for cheaper, higher performing, and more versatile proton conducting polymer membranes,[1] the role of polymer architecture on the morphology of the membrane and on properties such as proton conductivity, proton mobility, and water content are still poorly understood. Questions concerning the preference of diblock, multiblock, graft, or random ionic copolymers for proton conducting media are relatively unexplored.[2] In this context, model polymer systems, in which the large number of compositional variations is kept to a minimum, are useful for gaining insights into aspects of membrane design and preferred structures. Here, we describe the synthesis and characterization of graft and diblock ionic copolymers containing both fluorous and sulfonated polystyrene segments (Figure 1). The two series are designed to possess similar composition but considerably different architecture, the nature of which will be shown to significantly affect the morphology of the membranes and, in turn, their respective properties.

Graft copolymers of partially sulfonated poly([vinylidene difluoride-*co*-chlorotrifluoroethylene]-*g*-styrene [P(VDF-*co*-CTFE)-*g*-SPS][3] were prepared via graft-atom transfer radical polymerization (g-ATRP) of styrene onto a P(VDF-*co*-CTFE) macroinitiator synthesized with controlled Cl content, followed by postsulfonation (see Supporting Information for experimental details). The fluorous backbone possessed a $M_{n\,GPC}$ of 312 000 g/mol. The combined molecular weight of all styrene segments was estimated to be 136 000 g/mol.

The synthesis of proton-conducting diblock copolymers of partially sulfonated poly([vinylidene difluoride-*co*-hexafluoropropylene]-*b*-styrene) [P(VDF-*co*-HFP)-*b*-SPS] involved the ATRP of styrene onto a CCl_3-terminated fluorous macroinitiator followed by postsulfonation.[4] The $M_{n\,GPC}$ of the fluorous and the styrene segments were estimated to be 17900 g/mol and 8100 g/mol, respectively.

The graft and the diblock copolymers were synthesized so as to contain a similar ratio of fluorous to styrene components, and similar chemical compositions, but distinct macromolecular structures: P(VDF-*co*-CTFE)-*g*-SPS consisted of a hydrophobic fluorous backbone with ionic sulfonated styrenic side chains, P(VDF-*co*-HFP)-*b*-SPS possessed a hydrophobic fluorous segment linearly connected to an ionic sulfonated styrenic segment. Both copolymers were sulfonated to different degrees to provide two series of copolymers, which were cast into membranes possessing varying ion exchange capacity (IEC). Membranes were converted to their protonic form, and their IECs, water contents, molar ratios of water to sulfonic acid groups (λ), and analytical [H^+] were measured (see Supporting Information).

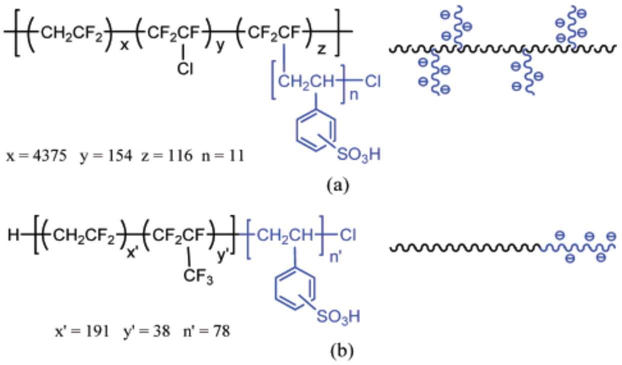

Figure 1. Chemical structures of (a) P(VDF-*co*-CTFE)-*g*-SPS graft and (b) P(VDF-*co*-HFP)-*b*-SPS diblock copolymers.

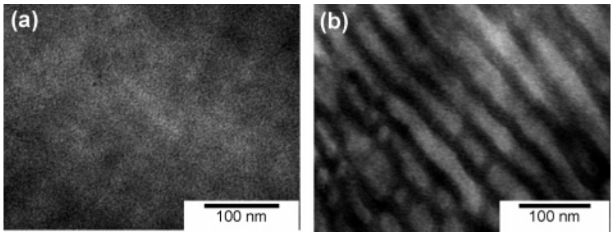

Figure 2. TEM micrographs of (a) P(VDF-*co*-CTFE)-*g*-SPS (IEC = 1.95 mmol/g) and (b) P(VDF-*co*-HFP)-*b*-SPS (IEC = 0.72 mmol/g) membranes. Note: dark areas, ionic domains; bright areas, fluorous domains.

TEM analyses were performed on ~100 nm-thick cross-sectional slices of dry graft and diblock membranes. TEM micrographs reveal that the morphologies of the graft membranes are characterized by an interconnected network of small ionic clusters of 2−3 nm in size (Figure 2a), similar to the archetypical proton conducting membrane, Nafion, in which a "cluster-network" composed of ~5 to 10 nm ionic clusters interconnected by narrow ionic channels.[5] In stark contrast, the diblock membranes possess well-segregated morphologies of ionic-rich, lamellar (or perforated lamellar) structures. These interconnected ionic channels are ~8 to 15 nm in width with a fluorous interdomain spacing of 20−40 nm (Figure 2b).

The water contents (λ) of the membranes are plotted against IEC (Figure 3a). Diblock membranes exhibit a much more substantial increase in water content with increasing IEC. Diblock membranes possessing IEC > 1.31 mmol/g (not shown) swell excessively in water, are gelatinous, and exhibit poor mechanical properties. This is a consequence of the lamellar-like nature of the membrane, and the inability of the fluorous matrix to prevent excessive expansion in the direction perpendicular to the lamellae.[6] In contrast, the graft membranes uptake significantly less water for similar IECs, and their λ remains moderately low even for IECs as high as 2.22 mmol/g. The small ionic cluster morphology is believed to be responsible

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[†] Simon Fraser University.
[‡] National Research Council Canada.

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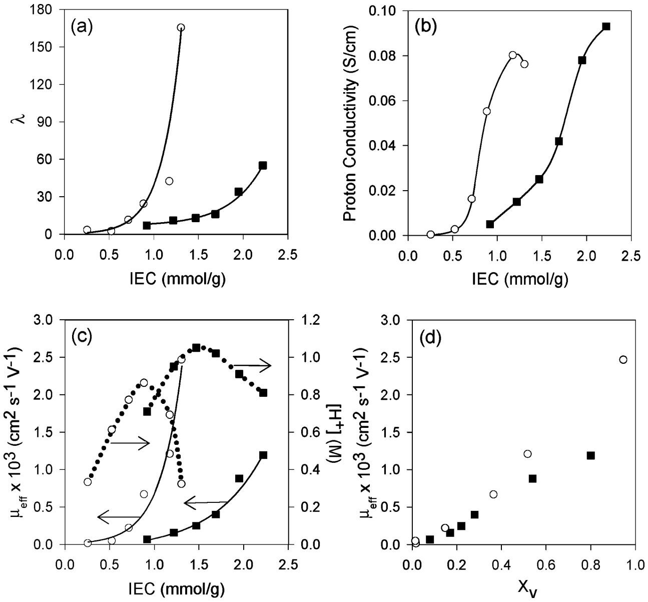

Figure 3. Plots of (a) water content (λ) vs IEC, (b) *in-plane* proton conductivity vs IEC, (c) effective proton mobility (μ_{eff}) (solid line) and analytical [H^+] (dotted line) vs IEC, (d) μ_{eff} vs volume fraction of water (X_v) of P(VDF-*co*-CTFE)-*g*-SPS (■) and P(VDF-*co*-HFP)-*b*-SPS (○) membranes.

for the lower water sorption: the formation of small ionic clusters allows for a more continuous and cohesive hydrophobic matrix that opposes the increasing osmotic pressure induced by increasing ionicity. Consequently, graft copolymers possessing very high ion contents remain insoluble in water. WAXS analysis revealed that the fluorous domains in both the graft and the diblock membranes were amorphous, indicating that differences in water sorption are not a result of differences in crystallinity.

Figure 3b compares the *in-plane* proton conductivity of the graft and the diblock membranes as a function of IEC. The graft membranes possess a significantly higher percolation threshold than the diblock membranes, ~1.0 to 1.2 mmol/g for grafts and ~0.6 mmol/g for diblocks, which correlates with water uptake.

The *effective* proton mobility (μ_{eff}) through the membranes was estimated from the measured proton conductivity and the measured analytical [H^+] in hydrated membranes.[7] Estimates of μ_{eff} prove useful for gaining insights into the extent of proton "pinning" caused by their association with polymer-bound anions and the tortuosity of the interconnected ion networks.[7] The μ_{eff} and analytical [H^+] for the hydrated membranes are plotted as a function of IEC in Figure 3c. The μ_{eff} is much lower for the graft membranes, but their analytical [H^+] is much higher, a consequence of their low water sorption. The μ_{eff} is generally much higher for the diblock membranes and increases at a much lower IEC threshold, with the commensurate increase in water uptake. However, as a result of the excessive water sorption and relatively lower IEC, [H^+] is relatively low and in fact decreases for membranes possessing IEC > ~1 mmol/g to the extent that [H^+] for diblock membranes possessing IECs of 0.26 and 1.31 mmol/g are similar.

Under the assumption that protons travel through the aqueous domains of the membrane, a plot of μ_{eff} versus water volume fraction (X_v) (Figure 3d) reveals that, for a given water volume, the diblock membranes do indeed provide a less encumbered pathway, from which it can be inferred that the ionic domains are well-interconnected. This highly interconnected nature of the ionic channels is also supported by the TEM images shown previously (Figure 2a).

Inducing ionic groups in a morphologically organized manner has anisotropic implications. To examine the anisotropic nature of proton conductivity, *through-plane* conductivity values were measured for the graft and the diblock membranes possessing similar water volume fractions, that is, IECs of 1.95 and 0.89 mmol/g, respectively (see Supporting Information). The *in-plane* proton conductivity of the diblock membranes is found to be ~2.4 times greater than *through-plane* conductivity indicating a mild degree of anisotropy. In contrast, the graft membranes were found to possess very similar in-plane and through-plane proton conductivity (anisotropy = 0.95). As a point of reference, the conductivity anisotropy of Nafion-112 membranes is found to be ~1.4, which is in close agreement to previous reports.[8]

In conclusion, we demonstrate that the nanoarchitectured morphology plays an essential role in determining the properties of proton conducting membranes. In the model fluorous-ionic systems studied herein, the graft copolymers yield membranes which tolerate much higher ionic contents without excessive swelling and dissolution, and which leads to membranes that possess highly concentrated, isotropically connected ionic domains. In contrast, the diblock copolymers provide a higher degree of long-range, ionic order. Ironically, this can lead to membranes that swell excessively at low IEC, thereby diluting the proton concentration, and limiting the IEC attainable. Furthermore, proton conductivity in the diblock membranes is lower in the through-plane direction; it is through-plane that is relevant to proton conduction in fuel cells. Such factors must be considered in the design of novel membranes based on block architectures.

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Supporting Information Available: Experimental preparation of the graft copolymers, membrane preparation and properties, GPC traces, ^1H NMR and ^{19}F NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Rikukawa, M.; Sanui, K. *Prog. Polym. Sci.* **2000**, *25*, 1463−1502. (b) Jannasch, P. *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 96−102. (c) Li, Q.; He, R.; Jensen, J. O.; Bjerrum, N. J. *Chem. Mater.* **2003**, *15*, 4896−4915. (d) Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem. Rev.* **2004**, *104*, 4587−4612. (e) Smitha, B.; Sridhar, S.; Khan, A. A. *J. Membr. Sci.* **2005**, *259*, 10−26. (f) Miyatake, K.; Watanabe, M. *Electrochem. (Japan)* **2005**, *73*, 12−19. (g) Hamrock, S. J.; Yandrasits, M. A. *Polym. Rev.* **2006**, *46*, 219−244. (h) Saarinen, V.; Kreuer, K. D.; Schuster, M.; Merkle, R.; Maier, J. *Solid State Ionics* **2007**, *178*, 533−537.

(2) (a) Cornet, N.; Diat, D.; Gebel, G.; Jousse, F.; Marsacq, D.; Mercier, R.; Pineri, M. *J. New. Mater. Electrochem. Syst.* **2000**, *3*, 33−42. (b) Kreuer, K. D. *J. Membr. Sci.* **2001**, *185*, 29−39. (c) Elabd, Y. A.; Napadensky, E.; Sloan, J. M.; Crawford, D. M.; Walker, C. M. *J. Membr. Sci.* **2003**, *217*, 227−242. (d) Yang, Y.; Holdcroft, S. *Fuel Cells* **2005**, *5*, 171−186.

(3) The grafting of styrene from commercially available P(VDF-*co*-CTFE) has been recently reported [Zhang, M.; Russell, T. P. *Macromolecules* **2006**, *39*, 3531−3539].

(4) (a) Shi, Z.; Holdcroft, S. *Macromolecules* **2004**, *37*, 2084−2089. (b) Shi, Z.; Holdcroft, S. *Macromolecules* **2005**, *38*, 4193−4201.

(5) (a) Hsu, W. Y.; Gierke, T. D. *Macromolecules* **1982**, *15*, 101−105. (b) Rubatat, L.; Rollet, A. L.; Gebel, G.; Diat, O. *Macromolecules* **2002**, *35*, 4050−4055.

(6) (a) Folkes, M. J.; Keller, A. J. *Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 833−846. (b) Albalak, R. J.; Capel, M. S.; Thomas, E. L. *Polymer* **1998**, *38*, 1647−1656.

(7) (a) Kreuer, K. D.; Paddison, S. J.; Spohr, E.; Schuster, M. *Chem. Rev.* **2004**, *104*, 4637−4678. (b) Peckham, T. J.; Schmeisser, J.; Rodgers, M.; Holdcroft, S. *J. Mater. Chem.* **2007**, *17*, 3255−3268.

(8) Ma, S.; Siroma, Z.; Tanaka, H. *J. Electrochem. Soc.* **2006**, *153*, 2274−2281.

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