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A Self-organized Network of Nanochannels Enhances Ion Conductivity through Polymer Films

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The proton-exchange membrane (PEM) is an integral component of solid polymer electrolyte fuel cells. The membrane acts as a separator to prevent mixing of reactant gases and as an electrolyte for transporting protons from anode to cathode.[1] High proton conductivity, mechanical strength, and chemical stability of the membrane are factors that affect fuel cell performance.[2,3]

Many PEM materials, including the widely studied Nafion series of membranes, are ionomers that consist of a hydrophobic backbone possessing pendant cation exchange sites such as SO_3^-. According to the Eisenberg−Hird−Moore (EHM) model,[4,5] the ionic sites aggregate to form multiplets. To explain conductivity through Nafion, Gierke proposed a “cluster-network” model in which clusters of ions, separated by a polymer backbone matrix, are connected via short, narrow channels (~1 nm in diameter).[6,7] However, it has yet to be proven that the formation of cluster networks is necessary to achieve high conductivity in PEMs. That is, for a given ion content, is proton conductivity served better by having the ions form a cluster network rather than having them dispersed homogeneously throughout the membrane?

To examine the relationship between structure, morphology, and conductivity, we report the synthesis, film formation, and properties of a novel class of well-defined graft polymers comprising styrene and sodium styrene sulfonate (PS-*g*-PSSNa). This system was chosen because it enabled control of both the copolymer’s ion content and morphology. PS-*g*-PSSNa was prepared via the stable free radical polymerization of sodium styrene sulfonate (SSNa),[8−10] and the “living” terminus of PSSNa reacted with divinylbenzene (DVB) to yield PSSNa possessing a terminal vinyl group (PSSNa−DVB). The degree of polymerization, molecular weight, and polydispersity of PSSNa were 32, 6.5×10^3, and 1.25, respectively. The resultant macromonomer was emulsion-copolymerized with styrene as illustrated in Scheme 1. PSSNa−DVB inserts into the propagating polystyryl chains (PS), as graft chains, because the DVB terminus is located in the core of the polymerizing micellar particles. By adjusting the feed ratio of PSSNa−DVB to styrene, a series of copolymers with uniform graft chain length and controlled graft density was

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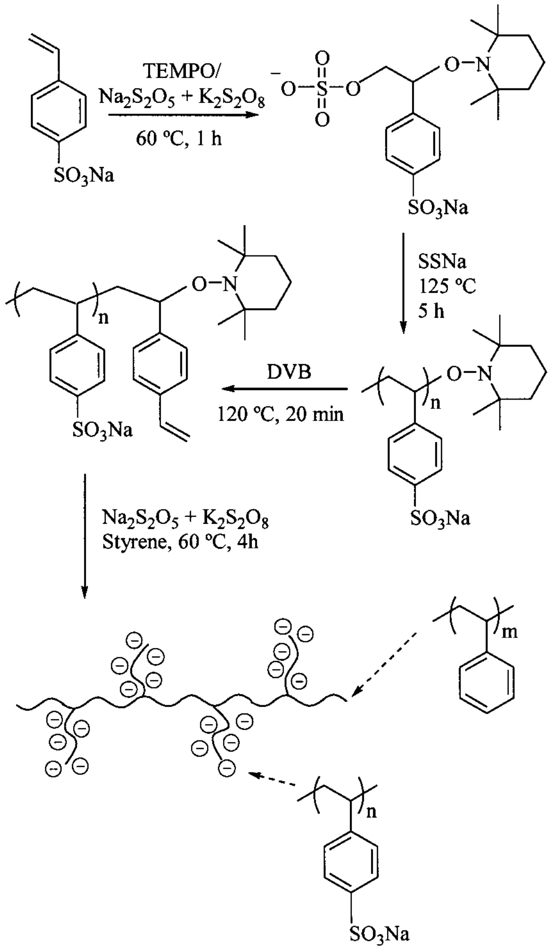
Scheme 1. Synthesis of PS-*g*-PSSNa Graft Copolymers



obtained. For comparative purposes, random copolymers of styrene and sodium styrene sulfonate (PS-*r*-SSNa) were prepared using a conventional emulsion copolymerization as described by Weiss and Turner.[11,12]

Infrared spectra of the graft copolymers exhibited peaks at 1010 cm^{-1}, assigned to in-plane bending of the para-substituted benzene ring,[13,14] and 1453 cm^{-1} attributed to stretching vibrations of the unsubstituted phenyl ring. These peaks were used to determine compositions of copolymers, that is, mol % SSNa, through calibration with values of sulfur content obtained by elemental analysis. Polymer compositions are listed in Table 1.

Ionomer membranes were prepared by compression molding at 230 °C. Sodium ions were exchanged for protons by soaking the membranes in 0.5 M H_2SO_4 for 2 days, followed by rinsing and immersion in deionized water. Protonic forms of the graft and random copolymer membranes are named PS-*g*-PSSA and PS-*r*-SSA, respectively. Equivalent weights of the protonated membranes (i.e., gram of polymer/SO_3^- equiv) were also determined by titration. EW values are in excellent agreement (±2%) with those determined by IR analysis, indicating that all ions in the membrane are accessible to aqueous solution. Water contents and molar ratios of water to sulfonic acid groups ($[H_2O]/[SO_3^-]$) are listed in Table 1. For PS-*g*-PSSA copolymers, the $[H_2O]/[SO_3^-]$ ratio increases from ~11 to 17 as a function of increasing ion content (~10−19 mol %). The $[H_2O]/[SO_3^-]$ ratio increases more dramatically, from 10 to 27, in the random copolymers membranes over a narrower range of ion content (~10−17 mol %).

Table 1. Composition and Properties of PS-*g*-PSSA and PS-*r*-SSA Copolymer Membranes

polymer	SS%[a,b]	EW (IR)[c] (g/mol)	H_2O%[d] (vol %)	$[H_2O]/[SO_3^-]$[d]	σ[d] ($S\ cm^{-1}$)
		PS-*g*-PSSA			
1	10.1	1127	9.9	11.4	0.0069
2	11.9	979	12.8	11.6	0.013
3	16.1	748	21.0	13.3	0.054
4	19.1	648	37.3	17.1	0.24
		PS-*r*-SSA			
1	9.6	1291	12.3	10.1	0.00058
2	12.0	970	24.2	17.2	0.0023
3	16.8	721	40.5	27.2	0.0041

[a] mol % styrene sulfonate determined by FTIR. [b] Na^+ form. [c] Equivalent weight (g/mol), IR method. [d] H^+ form.

TEM analysis was performed on 40-nm-thick slices of ultramicrotomed Pb^{2+}-stained PS-*g*-PSSNa and PS-*r*-SSNa membranes. While it is recognized that micrographs are of "dry" membranes and that there may be dimensional changes upon their hydration, they are believed to provide a representative picture of structural morphology. Typical micrographs illustrating the difference in morphologies of PS-*g*-PSSNa and PS-*r*-SSNa films containing similar ion content are shown in Figure 1. Dark regions represent the localization of ionic domains; lighter regions represent hydrophobic PS domains. In the graft copolymer membranes, ionic channels 5−10-nm wide are visibly connected to yield a continuous ionic network. The ionic network is developed to a greater extent and a lesser extent, respectively, for PS-*g*-PSSNa membranes possessing higher and lower ion contents (not shown). In contrast, micrographs of the random copolymer membranes show little evidence of microphase separation. This is explained on the basis that styrene and sulfonated styrene moieties are intimately connected through the polymer backbone in the random fashion. The lack of phase separation and, by inference, weaker hydrophobic interactions in the random copolymers also explains why they take up more water than the graft copolymer for a given ion concentration.

Proton conductivities (Table 1) were measured by impedance spectroscopy in the frequency range of 100 Hz to 40 MHz as described by Gardner and Anantaraman.[15,16] A Hewlett-Packard 4194-A Impedance Analyzer equipped with a 16047 Test Fixture was used in conjunction with a gold-plated coaxial probe. The accuracy of the measurements was verified by obtaining

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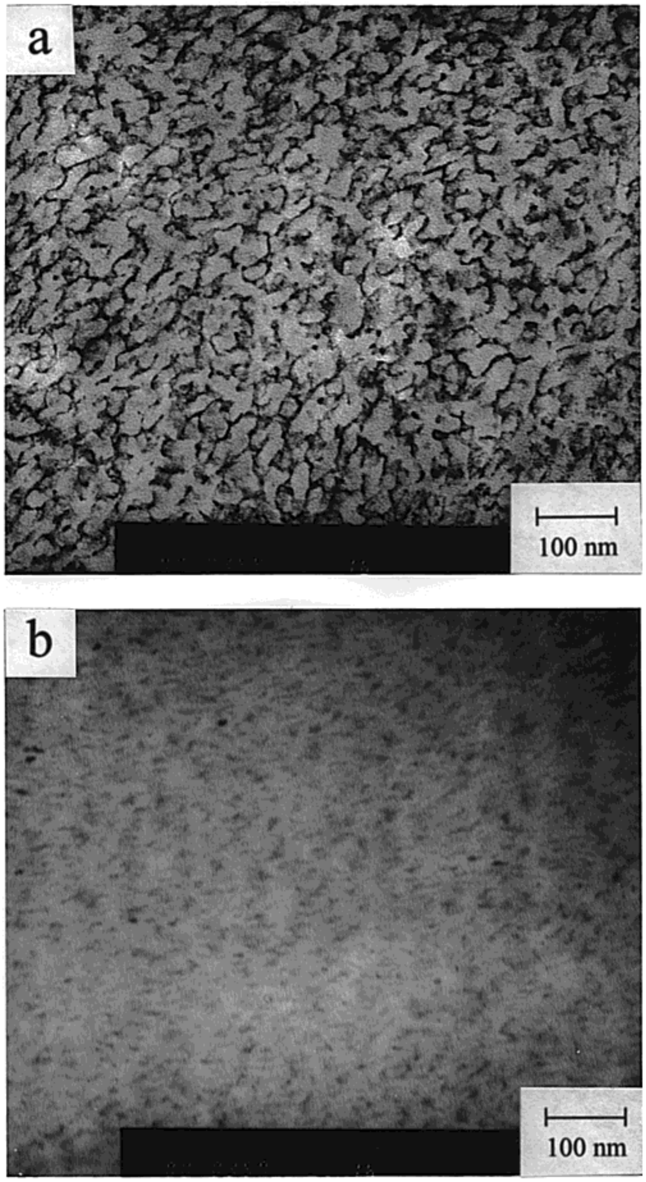

Figure 1. TEM micrographs of copolymer membranes: (a) PS-*g*-PSSA (11.9% SSA); (b) PS-*r*-SSA (12.0% SSA).

conductivity values for Nafion117 (0.07–0.08 S/cm), which are consistent with published results.[16–18]

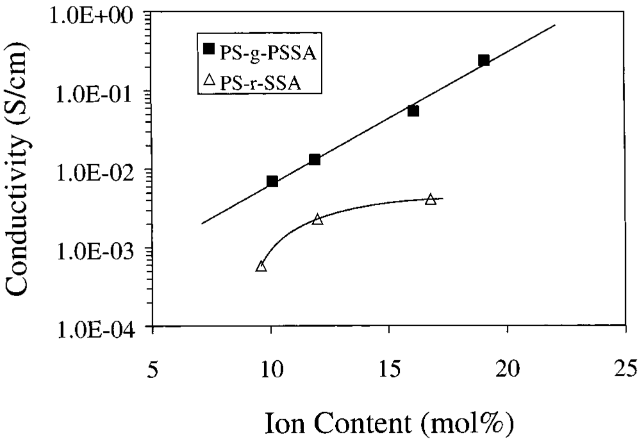

Figure 2. Proton conductivity of PS-*g*-PSSA (square) and PS-*r*-SSA (triangle) copolymer membranes as a function of ion content (mol % styrene sulfonate).

Figure 2 compares the proton conductivity of PS-*g*-PSSA membranes to that of PS-*r*-SSA membranes as a function of ion content. The graft copolymer membranes exhibit a significantly higher conductivity. In comparing graft and random copolymer membranes with ~16.1 and 16.8 mol % of sulfonic acid, respectively, the conductivity of the graft copolymer is an order of magnitude higher, even though its water content is 60% lower. That is, PS-*g*-PSSA membranes use their associated water more effectively in the transport of protons. This is a significant result because conductivity is usually promoted by increasing the water content of membranes. The PS-*g*-PSSA membrane with 19.1 mol % SSA possesses a conductivity of 0.24 S/cm yet contains only 37 vol % water. This conductivity is 3–5 times larger than that of Nafion 117 for a similar water content (Nafion 117 contains 34 vol % H_2O).[3]

While it should be recognized that hydrocarbon-based proton-exchange membranes, such as those described here, are unsuitable for high power density fuel cells because of their poor chemical stability, this work demonstrates unambiguously that polymer morphology can play a strong role in determining ionic conductivity. Specifically, compelling evidence is presented indicating that ion conductivity is enhanced by the formation of nanochannels of polyelectrolyte. These channels result from phase separation that is facilitated by the design of graft polymers. These concepts should be valuable not only in the design of PEMs for fuel cell applications but also in the design of ion-conducting membranes for battery applications, electrosynthesis, and water purification.

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Supporting Information Available: Experimental data on the synthesis of PS-*g*-PSSNa and on the water content of the membranes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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