Synthesis and Proton Conductivity of Partially Sulfonated Poly([vinylidene difluoride-*co*-hexafluoropropylene]-*b*-styrene) Block Copolymers

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ABSTRACT: A series of novel, amphiphilic block copolymers comprising of sulfonated poly([vinylidene difluoride-*co*-hexafluoropropylene]-*b*-styrene) [P(VDF-*co*-HFP)-*b*-SPS] were synthesized. The number-average molecular weights of the fluorous and polystyrene segments were 17 900 and 8100 g/mol, respectively. Sulfonation of the polystyrene segment to different extents provided a series of polymers which were cast into films to yield proton exchange membranes with varying ion exchange capacity (IEC). Proton conductivity of the membranes increased significantly when the IEC was increased from 0.5 to 1.2 mmol/g. For 0.9−1.2 mmol/g IEC membranes, the conductivity was similar to Nafion 117, significantly higher than random copolymers of polystyrene and sulfonated polystyrene, and twice that of nonfluorous block copolymer membranes based on sulfonated poly(styrene-*b*-[ethylene-*co*-butylene]-*b*-styrene) (S-SEBS) and sulfonated hydrogenated poly(butadiene-*b*-styrene) (S-HPBS) copolymers. TEM revealed a disruption in ordered morphology with increasing degree of sulfonation. Morphological structures of membranes having 0.6−1.2 mmol/g IEC comprised of interconnected networks of ion channels, each of 8−15 nm width.

Introduction

Proton exchange membranes (PEMs) play a central role in proton exchange membrane fuel cells (PEMFCs), serving as both electrolyte and separator. An ideal membrane should possess chemical and electrochemical stability, mechanical strength and integrity, and high proton conductivity.[1−3] In the past decade, many polymers have been designed and studied in an effort to address the poor high-temperature proton conductivity, high methanol permeability, and high cost of perfluorosulfonic acid (PFSA) membranes.[4,5] Despite numerous efforts, alternate materials still fail to meet the stringent requirements for high volume commercial markets. It is argued that a greater understanding of fundamental structure−property relationships of PEMs is required in order to make significant technological breakthroughs.[1,6]

A rudimentary requirement for PEMs is adequate proton conductivity. Conductivity is affected by the polymer's chemical structure (i.e., its composition and nature), ion exchange capacity (IEC), water content, and morphology. PEMs generally consist of ion-containing polymers that possess a hydrophobic polymer backbone and pendent proton exchange sites. In a solid-state matrix of hydrophobic polymer, ionic groups aggregate.[7] However, it is not fully understood how these interactions are influenced by the polymer architecture and how aggregation affects the membrane's morphology and conductivity. The search, design, and synthesis of model polymers that phase separate into proton conducting and hydrophobic domains is an important area of research both for obtaining insights into proton transport and for the design and implementation of next generation membranes.

Block copolymer ionomers are a potentially useful family of materials for studying structure−property relationships in PEMs since they can be prepared with well-defined structures that confer uniquely ordered morphologies in the solid state. Several reports on the morphology and physical properties of proton conducting membranes based on the polystyrene-containing block copolymers have been published. These include partially sulfonated poly(styrene-*b*-[ethylene-*co*-butylene]-*b*-styrene) (S-SEBS),[8−16] sulfonated poly(styrene-*b*-isobutylene-*b*-styrene) (S-SIBS),[17−21] sulfonated hydrogenated poly(butadiene-*b*-styrene) (S-HPBS),[22,23] sulfonated poly(styrene-*b*-ethylene-*alt*-propylene) (S-SEP),[24,25] and poly(styrene-*b*-ethylene/propylene-*b*-styrene) (S-SEPS) copolymer.[24] In related block copolymer studies, graft copolymers of PS-*g*-*mac*PSSA show enhanced conductivity compared to that of random copolymers of styrene and styrenesulfonic acid (PS-*r*-PSSA).[26−29] More recently, block copolymers based on sulfonated bisphenol A polysulfone and poly(vinylidene difluoride) (PSF-*b*-PVDF) were observed to exhibit enhanced proton conductivity compared to that of homopolymers of sulfonated bisphenol A polysulfone.[30]

In this work, proton-conducting diblock copolymers, sulfonated poly([vinylidene difluoride-*co*-hexafluoropropylene]-*b*-styrene) [P(VDF-*co*-HFP)-*b*-SPS], incorporating a nonionic fluorous block and a sulfonated ionic block are synthesized according to Scheme 1. There are several motivations to investigate these particular fluoropolymers. First, the two segments of block polymer are incompatible which ensures self-assembly and ionic aggregation. Second, since controlled radical polymerization is employed to grow the polystyrene segment, the length and/or ionicity of the hydrophilic block, and thus IEC, can be controlled by adjusting either the length of the sulfonated polystyrene chains or the degree of sulfonation. This paper describes the synthesis of a series of sulfonated fluorous block copolymer mem-

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Scheme 1. Synthetic Scheme for P(VDF-*co*-HFP)-*b*-SPS
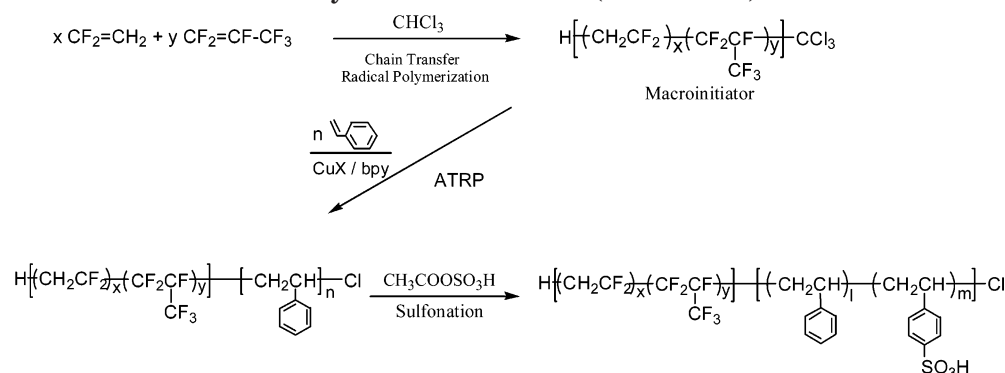
branes possessing different degrees of sulfonation. The correlation between composition, structure, and proton conductivity is reported.

Experimental Section

1. Materials. Sulfuric acid (Anachemia, 95−98%, ACS reagent), acetic anhydride (Caledon, reagent grade), and 1,2-dichloroethane (Caledon, reagent grade) were used as-received. Nafion 117 (Aldrich) films were pretreated with 3 vol % H_2O_2 and 5 wt % HNO_3 aqueous solution at 90 °C for 30 min, respectively, rinsed with Millipore water three times, and stored in water. Poly([vinylidene difluoride-*co*-hexafluoropropylene]-*b*-polystyrene was synthesized by atom transfer radical polymerization (ATRP) of styrene initiated by a trichloromethyl-terminated fluorous macroinitiator. The macroinitiator was prepared by emulsion polymerization in the presence of chloroform, which served as a chain transfer agent. A detailed procedure of this synthesis is reported elsewhere.[31] The following conditions for ATRP were used: (1) the concentrations of fluoropolymer macroinitiator [P(VDF-*co*-HFP), $M_{n,GPC} = 17\,900$ g/mol, $M_w/M_n = 1.48$], dipyridyl (bpy), copper-(I) chloride (CuCl), and styrene were 0.012, 0.34, 0.17, and 2.8 M, respectively; (2) the reaction was run for 24 h at 110 °C; (3) the conversion of styrene was terminated at 36.2% in order to limit the length of the polystyrene block. Based on the conversion of styrene, the estimated M_n of the polystyrene segment was 8700 g/mol, and the estimated M_n of the block copolymer was 26 600 g/mol.

Acid-bearing polymers were prepared by sulfonation of the polystyrene segment. Sulfonation was carried out in 1,2-dichloroethane using the procedure described in ref 11, except a reaction temperature of 40 °C was used. A typical sulfonation reaction is as follows: to a 50 mL three-neck flask equipped with a dropping funnel and condenser, 15 mL of 1,2-dichloroethane and 0.6 g of P(VDF-*co*-HFP)-*b*-PS were added, and the mixture was heated to 50 °C under N_2 and stirred until the copolymer completely dissolved. Acetyl sulfate was prepared by injecting 1 mL of acetic anhydride and 3 mL of dichloroethane into a nitrogen-purged vial. The solution was cooled to ~0 °C in a 10% $CaCl_2$ ice bath, and 0.3 mL of 95−97% sulfuric acid was injected. The resultant acetyl sulfate was immediately transferred to the polymer solution at 40 °C using a dropping funnel. Samples with different degrees of sulfonation were periodically extracted and precipitated in 50/50 ethanol/hexanes. The precipitate was washed with water until the residual water was pH 7. Sulfonated polymers were dried under vacuum at 60 °C overnight. Highly sulfonated polymer was dissolved in water, and the solution was purified by dialysis using a cellulose dialysis tube (Fisherbrand, Standard Grade, nominal MWCO 12 000−14 000) for 3 days. The polymer solution was evaporated, and the polymer was dried at 60 °C for 2 days under vacuum.

2. Membrane Preparation, IEC, and Water Sorption. Membranes were prepared by dissolving the sulfonated block copolymers in THF and casting on a Telfon sheet. Films were dried at room temperature and 60 °C for 2 h in vacuo. The sulfonated membranes were treated with 2 M HCl overnight.

Membranes were washed several times with Millipore deionized water for 30 min periods.

Membranes were equilibrated in 2 M NaCl solution for at least 4 h at room temperature prior to titration. The protons released into solution were titrated with 0.025 M NaOH. Following titration, membranes were placed in 2 M HCl for a minimum of 4 h in order to reprotonate the membranes, dried under vacuum for 2 h at 70 °C, and placed in a desiccator to cool before determining the membrane's "dry" weight. The IEC of the membrane (mmol/g) was calculated according to eq 1

$$\text{IEC} = \frac{V_{NaOH}M_{NaOH}}{W_{dry}} \tag{1}$$

where V_{NaOH} and M_{NaOH} are the volume (mL) and molar concentration of NaOH solution used in titration, respectively. W_{dry} is the dry weight of the sample.

The membranes were equilibrated in Millipore water overnight at room temperature and blotted with a Kimwipe to remove surface water, and the "wet" weight (W_{wet}) was measured. The water uptake of the membranes was calculated as the percentage increase over the "dry" weight according to eq 2. In contrast, the water content of the membranes was calculated as the percentage of water in the "wet" membrane according to eq 3. IEC, water uptake, and water content values were taken as the average of three samples.

$$\text{water uptake} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \tag{2}$$

$$\text{water content} = \frac{W_{wet} - W_{dry}}{W_{wet}} \times 100\% \tag{3}$$

$[H_2O]/[SO_3^-]$, the number of water molecules per ion exchange site, was calculated using eq 4.

$$[H_2O]/[SO_3^-] = \frac{\text{water uptake (\%)} \times 10}{18 \times \text{IEC (mmol/g)}} \tag{4}$$

The proton concentration in wet membranes was calculated using eq 5.

$$[H^+] = \frac{W_{dry}\,(g)}{vol_{wet}\,(cm^3)} \times \text{IEC (mmol/g)} \tag{5}$$

3. Techniques. The molecular weight of the block copolymer was determined by gel permeation chromatography (GPC) using three µ-Styragel columns, a Waters 510 HPLC, polystyrene standards, THF eluant, and a Waters 410 differential refractometer. The degree of sulfonation of the membranes was estimated by ^{1}H NMR (in d_6-acetone) using a 400 MHz Bruker AMX400 spectrometer. FTIR spectra were recorded on spin-cast thin films on a sodium chloride disk using a Bomem 155 FT-IR spectrometer. Differential scanning calorimetry (DSC) was performed on a TA Instruments Q10 differential scanning

calorimeter using a heating rate of 10 °C/min under N₂. Data were collected from −100 to 200 °C. T_g values were determined from the second thermal cycle. Thermal gravimetric analysis (TGA) of the membranes prepared with various degrees of sulfonation was performed using a TA Instruments model 2950 at a heating rate of 20 °C/min under N₂. Prior to DSC and TGA measurements, all samples were dried under vacuum at 80 °C overnight.

In-plane proton conductivity was measured by ac impedance spectroscopy with a HP 8753 network analyzer using a frequency range of 300 kHz to 1 GHz. A gold-plated coaxial probe was used as previously described.[27,32] The accuracy of the measurements was verified by the reported values of Nafion 117 (0.07−0.08 S/cm). An ESPEC SH-240 temperature/humidity chamber and a conductivity cell similar to that described in ref 33 were used for the measurement of membrane conductivity under conditions of variable temperature and humidity.

Samples for transmission electron microscopy (TEM) were prepared using the following steps: (1) Membranes (∼0.1 mm thick) were cast from THF solutions and stained by placing them overnight in a saturated lead acetate solution. (2) Films were rinsed with water and dried under vacuum at room temperature for a minimum of 4 h. (3) Membranes were embedded in Spurr's epoxy resin. (4) The blocks were sectioned to yield slices 60−100 nm thick, using a Reichert OM3 microtome, and picked up on copper grids. Images were taken on a Zeiss 10C transmission electron microscope using an accelerating voltage of 80 kV.

Results and Discussion

Degree of Sulfonation and IEC. The composition of the poly(VDF-*co*-HFP) macroinitiator was determined by ¹⁹F NMR spectroscopy, as previously described,[31] and found to comprise of 16.7 mol % of HFP and 83.3 mol % of VDF. It possessed a number-average molecular weight of 17 900 g/mol and polydispersity index of 1.48, as determined by GPC analysis calibrated with polystyrene standards. The number of VDF and HFP repeating units was calculated to be 191 and 38, respectively. The number-average molecular weight of poly(VDF-*co*-HFP)-*b*-PS block copolymer was 26 000 g/mol and possessed a polydispersity index of 1.35. The molecular weight of the polystyrene segments is estimated to be 8100 g/mol, and thus the number of styryl repeat units is 78. The ratio of fluoropolymer to polystyrene segments is 2.2:1 based on the respective molecular weights and 2.9:1 based on the number of repeat units. The polystyrene units in the block copolymer represent 31 wt %.

FTIR spectroscopy was used to confirm sulfonation of the block copolymer and to estimate the ion exchange capacity.[28] FTIR spectra of the block copolymer before and after sulfonation are shown in Figure 1. The strong absorbance at 1129 cm⁻¹ is due to C−F stretching. The two peaks situated at 699 and 757 cm⁻¹ are assigned to the C−H bond of unsubstituted phenyl rings, while the two peaks at 1453 and 1493 cm⁻¹ are assigned to stretching vibrations of unsubstituted phenyl rings. These four characteristic peaks for unsubstituted phenyl rings in polystyrene segments disappear following sulfonation. The appearance of characteristic peaks due to symmetric stretching of SO₃⁻ at 1035 cm⁻¹ and in-plane bending of para-substituted phenyl ring at 1008 cm⁻¹ confirm introduction of sulfonic groups.

NMR spectroscopy was used to quantify sulfonation. ¹H NMR spectra of both partially sulfonated and fully sulfonated block copolymers are shown in Figure 2. The pristine polymers exhibit peaks at 6.4−6.8 ppm (protons "a") and 6.9−7.3 ppm (protons "b") due to *ortho* and *meta/para* protons on the phenyl ring, respectively.
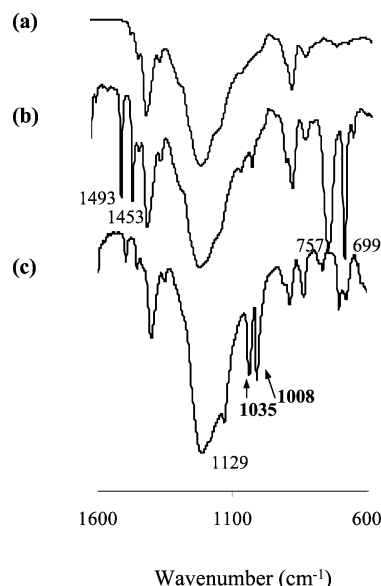
Figure 1. FTIR spectra of (a) P(VDF-*co*-HFP), (b) P(VDF-*co*-HFP)-*b*-PS, and (c) sulfonated block copolymer P(VDF-*co*-HFP)-*b*-SPS.
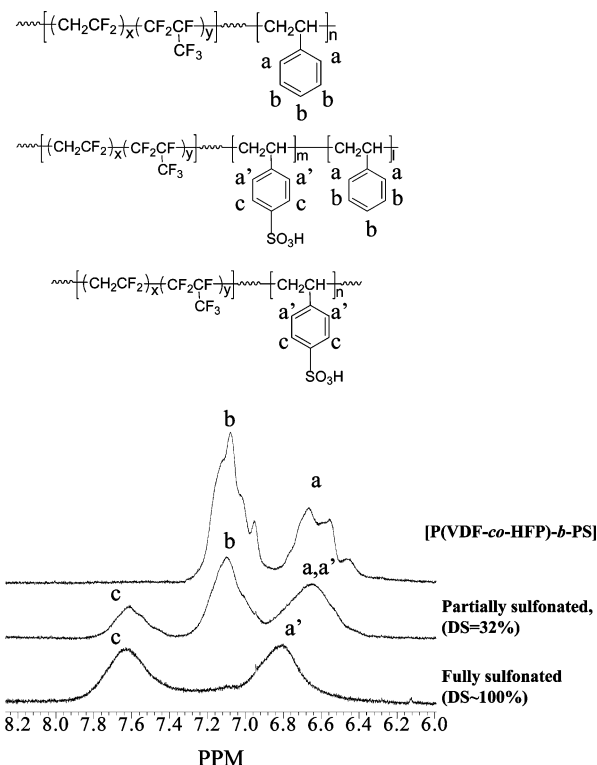
Figure 2. ¹H NMR spectra of [P(VDF-*co*-HFP)-*b*-PS], partially sulfonated (DS = 32%), and fully sulfonated (DS = 100%).

Upon full sulfonation, a broad peak is observed at 7.62 ppm due to protons adjacent to the sulfonate group (protons "c") and peaks due to protons "b" disappear. A broad peak is also observed at 6.82 ppm and is assigned to aromatic protons adjacent to the main chain on sulfonated phenyls (protons "a'''"). The partially sulfonated polymers exhibit all the above peaks and the ratio of integrals was used to quantify the degree of sulfonation, represented as DS (%), according to eq 6

$$\mathrm{DS}\ (\%) = \frac{m}{m+l} \times 100\% = \frac{C/2}{C/2 + B/3} \times 100\% \quad (6)$$

where m and l are the number of repeat units of

Table 1. Properties of [P(VDF-*co*-HFP)-*b*-SPS] Block Copolymer Membranes as a Function of Sulfonation Reaction Time of the Base Polymer

reaction time (min)	5	10	15	30	45	70	1200
degree of sulfonation (%)	12	17	22	32	40	49	∼100
calculated IEC[a] (mmol/g)	0.35	0.49	0.62	0.89	1.08	1.31	2.40
measured IEC[b] (mmol/g)	0.26 ±0.01	0.53 ±0.02	0.72 ±0.08	0.89 ±0.03	1.18 ±0.09	1.31	
conductivity[c] (S/cm)	$(1.6 \pm 0.9) \times 10^{-4}$	$(2.5 \pm 0.2) \times 10^{-3}$	0.016 ± 0.002	0.055 ± 0.001	0.080 ± 0.002	0.076	
water conent[d] (wt %)	<1.5	<1.5	12 ± 2	28 ± 3	47 ± 2	80	
water uptake[d] (wt %)	<1.5	<1.5	14 ± 3	38 ± 3	89 ± 7	388	
$[H_2O]/[SO_3^-]$	<3	<2	11 ± 1	24 ± 2	42 ± 6	165	
$[H^+]$ (M)	0.33 ± 0.03	0.61 ± 0.02	0.77 ± 0.03	0.86 ± 0.10	0.69 ± 0.04	0.32	

[a] From NMR and GPC data. [b] By titration. [c] Room temperature and 100% RH. [d] Room temperature.
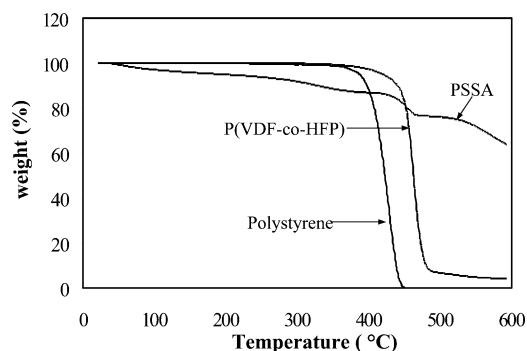
Figure 3. TGA curves of polystyrene, sulfonated polystyrene (acid form), and P(VDF-*co*-HFP) copolymer.

Figure 4. TGA curves of P(VDF-*co*-HFP)-*b*-SPS block copolymer membranes possessing different degrees of sulfonation.

sulfonated styrene and unsulfonated styrene; *C* and *B* represent the integrals of "c" and "b" peaks, respectively. These data are listed in Table 1. The degree of sulfonation is observed to increase with reaction time, and the polystyrene segments are fully sulfonated after 20 h.

With knowledge of DS and the number of repeat units in the polystyrene segment, the IEC of the membranes was calculated. Table 1 lists these values in addition to IECs determined by titration. There is agreement between the theoretical and measured IECs and a few inconsistencies which are most likely due to the inaccuracy of the GPC and inaccuracies in integrating NMR peaks for low degrees of sulfonation. The observation that experimental and theoretical IECs are similar, even for membranes with very low IECs, suggests that all sulfonic acid sites are accessible to aqueous solution and that the hydrophilic domains are interconnected.

Thermal Gravimetric Analysis (TGA). The thermal stability of the membranes was investigated by TGA. To aid discussion, TGA of related polymers P(VDF-*co*-HFP), PS, and PSSA under nitrogen was performed, and the data are presented in Figure 3. The temperature of degradation, expressed as the onset temperature at which significant mass loss occurs, is 393 and 449 °C for PS and P(VDF-*co*-HFP), respectively. For PSSA, loss of residual water occurs between 50 and 200 °C, and sulfonic acid groups are eliminated at ∼300 °C.
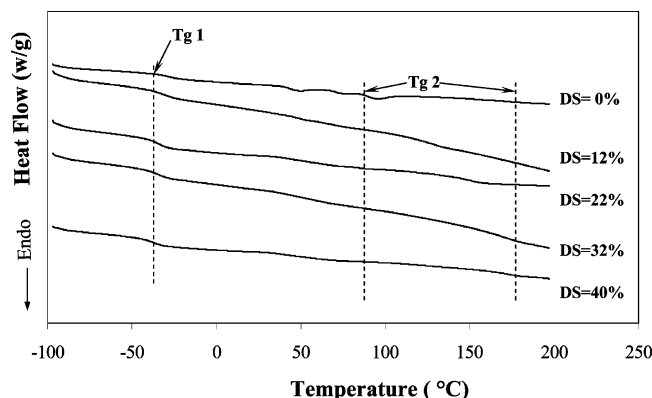
TGA curves for the [P(VDF-*co*-HFP)-*b*-SPS] block copolymers prepared in this work are shown in Figure 4 for four different degrees of sulfonation. Loss of residual water begins at 50 °C and continues up to ∼200 °C because of strong interactions with the sulfonic acid groups.[34,35] The percentage decrease in mass due to water loss (up to 200 °C) increases with the degree of sulfonation: the loss of water accounts for 8% of the membrane having a DS of 49% compared to ∼3% for the membrane having a DS of 40%. This larger water
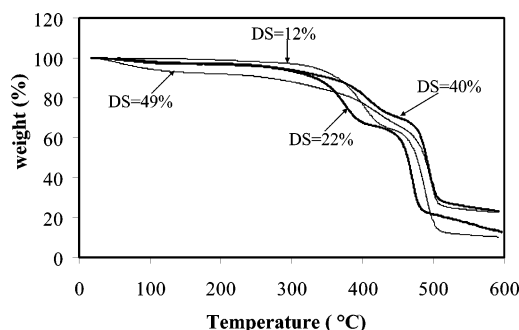
uptake of the more highly sulfonated membranes was verified by DSC analysis (not shown).

In addition to water loss, TGA curves of the P(VDF-*co*-HFP)-*b*-SPS block copolymer membranes (Figure 4) exhibit three other regions of mass loss: elimination of sulfonic acid groups commencing at ∼300 °C; decomposition of the polystyrene block between 350 and 390 °C, where the onset temperature increases from 352 to 390 °C as the DS increases from 12% to 49%; and decomposition of the fluoropolymer segment between 430 and 490 °C, where the onset temperature increases from 457 to 482 °C with increasing DS of the polymer. It is noted that degradation of this segment occurs at a higher temperature than P(VDF-*co*-HFP) copolymer (449 °C), which is consistent with a previous report indicating that the stability of sulfonated SEBS block copolymers is higher than its base polymer (SEBS) and that the onset temperature for degradation increases with degree of sulfonation.[11]

Differential Scanning Calorimetry (DSC). The first DSC scan (between −100 and 200 °C) of P(VDF-*co*-HFP)-*b*-SPS membranes gives rise to a broad endothermic peak between 80 and 200 °C due to loss of water absorbed from the atmosphere. T_g's were readily determined from the second thermal cycle except for the membrane possessing a DS of 49%, which exhibits a persistent endothermic peak after three scans due to the presence of residual water. DSC curves of P(VDF-*co*-HFP)-*b*-SPS possessing different degrees of sulfonation are shown in Figure 5. Two T_g's are observed: one due to the fluoropolymer segment (T_g1), which occurrs at ∼ −35 °C, and the other due to partially sulfonated polystyrene (T_g2), which varies in temperature between 120 and 166 °C. The unsulfonated block copolymer (DS = 0%) exhibits T_g's of −34 and 86 °C for the fluoropolymer and PS, respectively. It also exhibits additional thermal transitions between 40 and 80 °C due to the fluoropolymer segment.[36] Since partial sulfonation of the polystyrene segment in the block copolymer is statistically random, this segment is es-

Figure 5. DSC curves of P(VDF-*co*-HFP)-*b*-SPS block copolymer membranes possessing different degrees of sulfonation.

Table 2. T_g's of P(VDF-*co*-HFP)-*b*-SPS Possessing Different Degrees of Sulfonation

deg of sulfonation (mol %)	0	12	22	32	40
T_g1 (°C)	−34	−36	−39	−40	−43
T_g2 (°C)	86	120	145	164	166

sentially a random copolymer of sulfonated polystyrene and polystyrene, and hence only one T_g is observed. Sulfonation of this segment causes the T_g to increase due to the bulkiness of the sulfonate group and due to the ionomeric effect.[23] T_g of H-SPS, for example, is reported to increase from 107 to 158 °C when the DS of sulfonated polystyrene (H-SPS) increases from 3.4% to 20.1%,[37] and Mauritz et al.[16] report that the T_g of S-SEBS is raised from 114 to 166 °C when DS increases from 2.8 to 14.3%.

Table 2 lists the T_g of the fluoropolymer and sulfonated polystyrene segments as a function of DS. The T_g of the unsulfonated polystyrene segment in the block copolymer is 86 °C, which is lower than polystyrene homopolymer (T_g = 100 °C), due to the influence of the low-T_g P(VDF-*co*-HFP) copolymer matrix. This is consistent with other reports of styrenic block copolymers: a lower T_g (82 °C[16] and 90 °C[23]) is reported for polystyrene when coupled to poly(ethylene-*co*-butylene) and polybutadiene, respectively. As the degree of sulfonation increases, the T_g of the sulfonated polystyrene segment increases from 120 °C (DS = 12%) to 166 °C (DS = 40%). T_g of P(VDF-*co*-HFP) segments varies little (±9 °C) compared to those changes observed in the sulfonated polystyrene segments. Again, this is consistent with other block copolymer studies: the T_g of the EB block varies only ±3 °C in the S-SEBS block copolymer series.[16]

Water Sorption. Water uptake by the membranes in their protonic form was measured, and their water contents were calculated. These are listed in Table 1. As expected, the amount of water absorbed by the membrane increases with increasing sulfonation. The membranes are flexible and pliable and can be easily handled when hydrated. However, membranes comprising of polymers having a DS of 49%, or greater, take up a very large amount of water (>388% water uptake), are fragile, and exhibit poor mechanical properties. The fully sulfonated polymer completely dissolves in water, and thus only FTIR and NMR data are available. The water content and water uptake of Nafion 117 were measured to be 23% and 29%, respectively. The P(VDF-*co*-HFP)-*b*-SPS block copolymer membrane possessing a similar IEC (0.89 mmol/g, DS = 32%) to Nafion 117
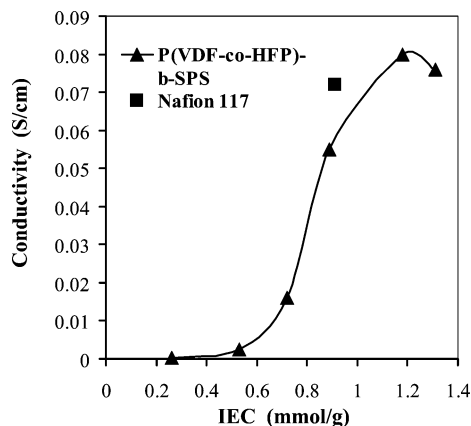

Figure 6. Proton conductivity vs IEC for P(VDF-*co*-HFP)-*b*-SPS block copolymer membranes.

(IEC = 0.91 mmol/g) absorbs a slightly higher amount of water than Nafion—its water content and uptake being 28% and 38%, respectively.

The water content and water uptake values provide insight into the continuity of the hydrophobic regions and the ability of the fluoropolymer matrix to oppose osmotic pressure forces—the latter tend to favor high values of lambda (λ = [H_2O]/[SO_3^-]). If the osmotic pressure exceeds the elastic forces of the matrix, dissolution will occur. It is useful therefore to compare water sorption properties of other block copolymers with those of the present system. Relevant data are reported in Table 1. Water absorption values of partially sulfonated poly(styrene-*b*-[ethylene-*co*-butylene]-*b*-styrene) (S-SEBS) block copolymer membranes, for a similar range of IEC[38] and/or degree of sulfonation, have been reported.[13] Values for water uptake of ~15%, ~40%, and ~70% were reported by Kim et al. for S-SEBS block copolymers (28% polystyrene) having degrees of sulfonation of 22%, 34%, and 42%, respectively.[13] They also report that S-SEBS membranes possessing a high degree of sulfonation (>47%) absorbed large amounts of water (>100 wt % uptake), and as a result their mechanical strength is poor.

It is found that when IEC is <0.5 mmol/g and the degree of sulfonation is <17%, for P(VDF-*co*-HFP)-*b*-SPS the difference in mass between wet and dry membrane weights cannot be accurately measured. Very low values of water uptake were also observed for the S-SEBS block copolymer membranes with low sulfonation degree. Weiss et al.[11] report 0.40% and 2.35% water uptake at room temperature for SEBS block copolymers (29.8 wt % polystyrene) sulfonated to 5.2 and 11.9 mol %.

Proton Conductivity. Proton conductivities of copolymer membranes possessing different degrees of sulfonation were measured by ac impedance spectroscopy. Conductivity data are listed in Table 1 and plotted in Figure 6 as a function of IEC and in Figure 7 as a function of λ. The conductivity of Nafion 117 is included for comparison. Generally, proton conductivity increases with increasing IEC because conductivity depends on the ion content of the membrane. As shown in Figure 6, the incremental increase in conductivity with IEC is initially small but increases significantly between 0.5 and 0.8 mmol/g. Conductivity levels off at 1.2 mmol/g and decreases slightly with a further increase in IEC. These observations are correlated to the water content of the membranes. Membranes with low IEC absorb
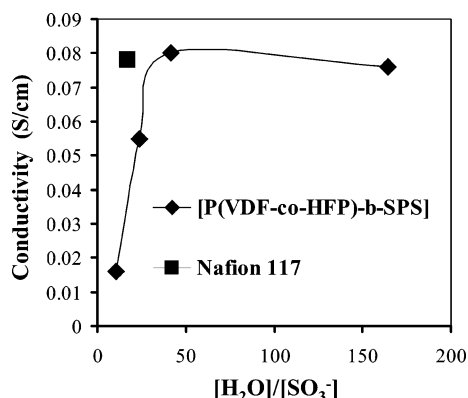
Figure 7. Plot of conductivity vs λ for P(VDF-*co*-HFP)-*b*-SPS block copolymer membranes.

Table 3. Proton Conductivity of Sulfonated Polystyrene Membranes

polymers	DS (%)	IEC (mmol/g)	conductivity (S/cm)	ref
P(VDF-*co*-HFP)-*b*-SPS[a]	32	0.89	0.055	this work
(31 wt % PS)	40	1.08	0.080	this work
SPS (random)[b]	15	1.24	0.0015	39
	12	0.93	0.0023	28
S-SEBS triblock[c]		0.94	0.03	38
		1.12	0.05	
S-SEBS triblock[c]	34	(0.92)[g]	0.032	13
(28 wt % PS)	42	(1.13)[g]	0.037	
S-SIBS triblock[d]		0.97	0.025	17
(31 wt % PS)				
S-HPBS diblock[c]	40	(1.15)[g]	0.015	23
(30 wt % PS)				
SPS (graft)[f]	12	1.02	0.012	28

[a] Sulfonated poly([vinylidene difluoride-*co*-hexafluoropropylene]-*b*-styrene) block copolymers. [b] Sulfonated polystyrene. [c] Sulfonated poly(styrene-*b*-[ethylene-*co*-butylene]-*b*-styrene) copolymers (S-SEBS). [d] Sulfonated poly(styrene-*b*-isobutylene-*b*-styrene) block copolymers (S-SIBS). [e] Sulfonated hydrogenated poly(butadiene-*b*-styrene) diblock copolymers (S-HPBS). [f] PS-*g*-macPSSA graft copolymers. [g] Calculated from weight percentage of polystyrene and degree of sulfonation.

very little water, and the volume of the hydrophilic regions is not sufficient to form a percolated network of ions. Between 0.5 and 0.6 mmol/g (DS 17 and 22%) a percolation threshold is achieved. Sulfonated poly-(styrene-*b*-[ethylene-*co*-butylene]-*b*-styrene) (S-SEBS) block copolymer membranes exhibit a similar percolation threshold in the same region of IEC—it was found by Kim et al.[13] that proton conductivity of S-SEBS increased sharply when DS of the PS blocks exceeds 15 mol % ($\sim$0.4 mmol/g IEC). For graft copolymers of styrene and sodium styrenesulfonate, Ding et al.[28] found that the conductivity increased significantly when the ion content (equivalent to degree of sulfonation) is >13%. A similar percolation threshold is observed by Carretta et al. for a DS of $\sim$15 mol % for partially sulfonated polystyrene membranes.[39] However, it should be noted that for sulfonation of PS homopolymers a DS of $\sim$15 mol % gives rise to a much higher IEC (1.24 mmol/g IEC) than the block copolymers because of the absence of a nonstyrenic phase, and thus care should be taken in comparing polymers based solely on DS.

Because of a significant increase in water uptake and a resulting drop in proton concentration, the proton conductivity does not increase upon increasing the IEC of the membranes from 1.18 (0.08 S/cm) to 1.31 mmol/g (0.076 S/cm). Proton concentrations of the P(VDF-*co*-HFP)-*b*-SPS membranes were calculated using eq 5 and are listed in Table 1. [H$^+$] for the 1.31 mmol/g IEC membrane is 0.32 M, which is half that of the 1.18 mmol/g membrane (0.69 M). Similar effects of increasing water content and decreasing proton concentration on proton conductivity have been observed in other polymer systems. The conductivity of sulfonated trifluorostyrene copolymers dropped significantly above 1.96 mmol/g IEC due to a substantial decrease in proton concentration.[38] For block copolymers, conductivity of S-SIBS membranes leveled off at 0.94 mmol/g IEC,[17] and for S-SEBS the conductivity did not increase between 1.12 and 1.71 mmol/g IEC.[38] In contrast, the conductivity of ETFE-*g*-PSSA radiation graft membranes is reported to continuously increase with IEC in the range of 2.45–3.27 mmol/g,[38] but this is due to the rigid nature of the base polymer membrane which prevents the membrane from swelling excessively.

λ indicates the average number of water molecules associated with each sulfonic acid site. It is reported that the proton conductivity of perfluorosulfonic acid membranes increases significantly when λ values are >6.[40] Figure 7 plots the relationship between conductivity and

λ for partially sulfonated P(VDF-*co*-HFP)-*b*-SPS membranes. For membranes possessing IEC < 0.5, mmol/g λ is 2–3, indicating an extremely "water-poor" environment, in the context of aiding proton conductivity, and consequently, proton conductivities are low (10^{-4}–10^{-3} S/cm). When the IEC of the membranes is such that the λ values increase from 11 to 42, the proton conductivity sharply increases. Note that proton concentrations for each membrane are similar, indicating that the increase in conductivitiy is largely due to increased mobility of the protons. In a similar range of λ, conductivity increases for sulfonated trifluorostyrene (λ, 10–33) and S-SEBS block copolymers (λ, 24–46).[38] A similar observation is observed for P(VDF-*co*-HFP)-*b*-SPS membranes: when λ is > $\sim$40, conductivity no longer increases with λ, and as λ is increased from 42 to 165, the conductivity decreases from 0.08 to 0.076 S/cm. Similarly, no increase in conductivity was observed for S-SEBS block membranes when λ increased from 46 to 147.[38] It is concluded that for sulfonated block copolymer membranes increasing λ values (when λ is <40–50) increases proton conductivity by enhancing proton mobility, but above this value, increasing λ simply serves to dilute the proton concentration and this effect outweighs any further increase in proton mobility.

When the IEC of the P(VDF-*co*-HFP)-*b*-SPS membranes lies between 0.9 and 1.1 mmol/g, the conductivity is 0.06–0.08 S/cm, which is comparable to that of Nafion 117. Table 3 lists conductivity values of several other sulfonated block, graft, and randomly sulfonated polystyrene membranes possessing degrees of sulfonation between 32 and 40 mol % or IECs between 0.9 and 1.1 mmol/g. For S-SEBS triblock and S-SPBS diblock membranes, IEC values are calculated according to the weight percentage of polystyrene and the degree of sulfonation reported. Partially sulfonated polystyrenes can be considered to be random copolymers of polystyrene and sulfonated polystyrene. The conductivity of random copolymer membranes is reported to be in the range 0.0015–0.0023 S/cm for IECs of 0.93–1.24 mmol/g. The proton conductivities of all the block or graft copolymer membranes listed in Table 3 lie between 0.012 and 0.080 S/cm and possess IECs between 0.89 and 1.15 mmol/g. It can be concluded from

Table 3 that the conductivities of the P(VDF-*co*-HFP)-*b*-SPS block copolymer membranes are at least an order of magnitude higher than those of the randomly structured sulfonated polystyrene membranes.[28,39] Second, comparing fluorous block copolymer membranes with nonfluorous (block and graft), it can be observed that the conductivity of P(VDF-*co*-HFP)-*b*-SPS membranes is higher. For example, the conductivity of P(VDF-*co*-HFP)-*b*-SPS membranes having 0.89 mmol/g IEC is 0.055 S/cm, while that for S-SEBS block membranes is reported to be 0.03 S/cm for 0.92−0.94 mmol/g IEC, and the conductivity of S-SIBS block membranes is 0.025 S/cm at 0.97 mmol/g IEC. The conductivity of P(VDF-*co*-HFP)-*b*-SPS block membrane with 1.08 mmol/g IEC is 0.080 S/cm, while the conductivity of S-SEBS block membranes is reported to be 0.037−0.05 S/cm for 1.12−1.13 mmol/g IEC; the conductivity of S-HPBS block membrane is only 0.015 S/cm at 1.15 mmol/g IEC.

The fluorous-containing block copolymer membranes exhibit almost twice the proton conductivity of non-fluorinated block and graft copolymer membranes. It is known that fluoropolymers possess much lower surface tension than other polymer structures. It can be concluded that the dissimilarity of the two segments improves phase separation and enhances the proton conductivity. Nevertheless, poly(vinylidene difluoride) is only a partially fluorinated polymer, and its surface tension (33.2 dyn/cm at 20 °C) is higher than perfluoropolymers such as PTFE (23.9 dyn/cm at 20 °C).[41] Accordingly, we predict that the proton conductivity of similar block copolymer membranes prepared with perfluoropolymer segments would be even higher.

TEM Morphology. Information on membrane morphology can be acquired from TEM images. To investigate phase separation and ionic aggregation, membranes were stained with lead acetate. In the TEM images, therefore, the dark areas represent regions of high ionicity and the brighter areas, hydrophobic regions. Morphologies of dry proton conducting membranes reported in the literature are spherical, lamella, or wormlike. For example, Nafion membranes exhibit 2−10 nm nearly spherical ion clusters,[42–45] whereas wormlike ionic domains are observed for graft ionomers.[26–29] For S-SEBS block copolymer ionomers a three-phase microstructure consisting of 3−4 nm ionic domains in 20−30 nm polystyrene block domains was suggested on the basis of SAXS and TEM analysis. The TEM image of 27% sulfonation of S-SEBS block copolymer, cast from the THF solution and stained with RuO₄, exhibited a well-ordered lamellar morphology.[14]

TEM images for the P(VDF-*co*-HFP)-*b*-SPS membranes possessing different degrees of sulfonation are shown in Figure 8. No distinct ion phase separation morphology is observed for the membrane possessing the lowest DS (12 mol %, IEC = 0.26 mmol/g). No clear phase separation is observed for the 17% DS membrane (not shown). Both these membranes exhibit poor proton conductivity (10^{-4}−10^{-3} S/cm). With increasing DS (20−40 mol %), a distinct morphology develops as observed in Figure 8B−D. Ordered ionic channels are clearly connected and form an ionic channel network possessing 20−40 nm interdomain spacings. The width of the channels is estimated to be in the range 8−15 nm. The TEMs indicate the network is 3-dimensional.

Upon traversing the series of membranes with increasing DS, a disruption in ordered morphology is observed (see Figure 8E,F). Although soluble in water,
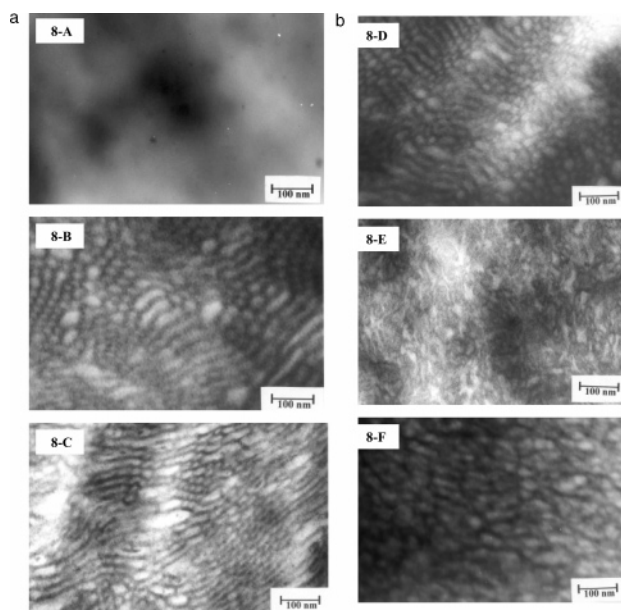

Figure 8. TEM images of P(VDF-*co*-HFP)-*b*-SPS block copolymer membranes: (A) DS, 12%; IEC, 0.23 mmol/g; σ, 1.6 × 10^{-4} S/cm; (B) DS, 22%; IEC, 0.62 mmol/g; σ, 1.6 × 10^{-2} S/cm; (C) DS, 32%; IEC, 0.89 mmol/g; σ, 5.5 × 10^{-2} S/cm; (D) DS, 40%; IEC, 1.08 mmol/g; σ, 8.0 × 10^{-2} S/cm; (E) DS, 49%; IEC, 1.31 mmol/g; σ, 7.6 × 10^{-2} S/cm; (F) DS, 100%.

the membrane with 100% degree of sulfonation did not dissolve in lead acetate solution, and hence a TEM image could be obtained, which is shown in Figure 8F. It is observed that at this high ion content the interface between ion channels and the hydrophobic matrix is less sharp and the ionic domains aggregate, tending toward disordered structures.

Conductivity as a Function of Temperature and Humidity. Proton conductivity of polymer membranes is known to be a function of both temperature and water content,[2,46] and it is therefore pertinent to determine the influence of external conditions on conductivity so that limitations of operation can be identified. Generally, for a given humidity, conductivity increases with temperature until dehydration becomes a predominant factor, whereas at constant temperature conductivity decreases as humidity decreased. As examples, the conductivity of Nafion 117 under 100% RH increases from 0.1 to 0.2 S/cm when the temperature is raised from 30 to 85 °C,[47] and at 30 °C the conductivity of Nafion 117 decreases from 0.066 to 0.000 14 S/cm as RH decreases from 100% to 34%.[48] At 100% RH, the proton conductivity of sulfonated poly(styrene-*b*-isobutylene-*b*-styrene) block copolymer membrane (S-SIBS, 0.96 mmol/g IEC) is 0.025 S/cm at 21/22 °C and increases to 0.083 S/cm at 80 °C.[17]

As shown in Figure 9, the conductivity of partially sulfonated P(VDF-*co*-HFP)-*b*-SPS copolymer membranes increases with increasing RH at 30 °C. Comparing the 0.89 mmol/g IEC membranes with Nafion 117, it is found that P(VDF-*co*-HFP)-*b*-SPS block membrane possesses a similar trend. Since water absorption is directly related to the ambient RH, these data reflect the change in conductivity with water content. Because of dehydration of the membranes at low RH (<65%), the conductivity of the membranes is less than 0.01 S/cm. With increasing RH the conductivity of these membranes increases exponentially. Similar observations are reported for Nafion 117[48,49] and S-PEEK.[2]
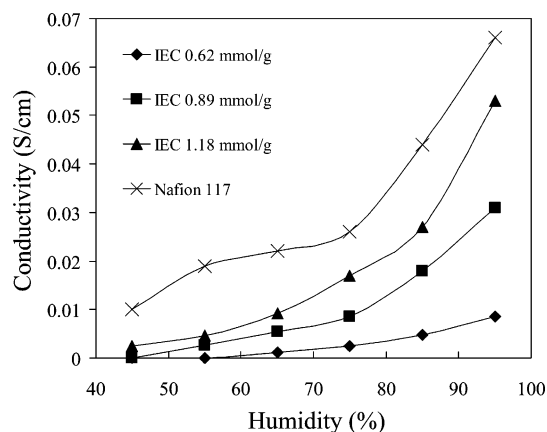
Figure 9. Proton conductivity vs relative humidity for P(VDF-*co*-HFP)-*b*-SPS membranes possessing different IEC, and Nafion 117, at 30 °C.
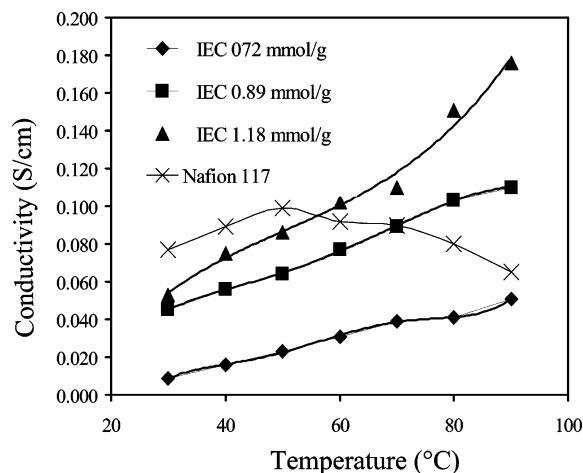
Figure 10. Proton conductivity vs temperature for P(VDF-*co*-HFP)-*b*-SPS membranes possessing different IEC, and Nafion 117, under constant humidity (95% RH).

The relationship between conductivity and temperature for membranes with different IEC in a 95% relative humidity environment is shown in Figure 10. The conductivity of three different IEC membranes increases with temperature from 30 to 90 °C. Although further work is required to determine whether this trend extends to higher temperatures, this is an interesting observation since not all PEMs continue to increase in conductivity up to 90 °C. The conductivity of Nafion 117 under the same conditions increases between 30 and 50 °C but decreases above 50 °C. A similar observation is reported for Nafion (EW = 1100 g/mol) at 100% RH, with the maximum conductivity occurring at 60 °C.[50] Proton conductivity of S-PEEK membranes at 100% RH is also reported to decrease above 70 °C.[2]

From the slopes of natural logarithmic plots of conductivity vs $1000/T$ (not shown), the activation energy for proton transport was found to be 25.7, 13.9, and 17.1 kJ/mol for P(VDF-*co*-HFP)-*b*-SPS membranes with IEC of 0.72, 0.89, and 1.18 mmol/g, respectively. Compared with reported values of Nafion 117 membranes (7.8,[51] 9.6,[47] and 13.5[52] kJ/mol) and Nafion 112 (18.3 kJ/mol),[53] the activation energies of P(VDF-*co*-HFP)-*b*-SPS membranes are on average much higher than Nafion 117. The activation energies for proton conduction of S-SIBS block copolymer membranes are reported to be much higher still: 18.1 kJ/mol for a 0.96 mmol/g IEC membrane, 25.0 kJ/mol for

0.62 mmol/g IEC, and 41.2 kJ/mol for 0.45 mmol/g IEC membranes.[17] The activation energies for conductivity through P(VDF-*co*-HFP)-*b*-SPS membranes show a decreasing tendency from 25.7 to 17.1 kJ/mol as the IEC increase, which agrees with the experimental data for S-SIBS block copolymer membranes where the activation energy is reported to fall from 41.2 to 18.1 kJ/mol when the IEC increases from 0.45 to 0.96 mmol/g.[17] A similar trend was reported for S-PEEK membranes: the activation energy for a 39% DS membrane ($\sim$1.2 mmol/g IEC) is 41.0 kJ/mol and for a 47% DS S-PEEK ($\sim$1.35 mmol/g IEC), 33.5 kJ/mol. The lower IEC membranes possess lower ion content and form smaller, more isolated, ionic clusters; thus, proton conductivity is more restricted, and temperature plays a more dominant role.

Conclusion

Partially sulfonated poly([vinylidene difluoride-*co*-hexafluoropropylene]-*b*-styrene) copolymers were prepared for the purpose of investigating the role of chemical structure on PEM membrane properties. The thermal properties of the membranes, characterized by DSC, show two glass transitions for the two block segments; the T_g values of the sulfonated polystyrene segments increases with degree of sulfonation. Very low water contents are observed for membranes having a DS < 17%, whereas high λ values (165) are observed for the membranes sulfonated to >49 mol %. Proton conductivity is significantly larger when the IEC of the membranes is in the range 0.5−1.2 mmol/g; between 0.9 and 1.2 mmol/g, the conductivity is similar to that of Nafion 117. The conductivity of P(VDF-*co*-HFP)-*b*-SPS block copolymer membranes is shown to be higher than that of partially sulfonated nonfluorous block copolymer membranes. The microstructure of P(VDF-*co*-HFP)-*b*-SPS membranes shows a disruption in order with increasing degree of sulfonation. Connected networks of ion channels having 8−15 nm width are observed for dry P(VDF-*co*-HFP)-*b*-SPS membranes for polymers with 22−40 mol % sulfonation (0.6−1.2 mmol/g IEC). It may be concluded that fluoropolymer segments induce well connected channel networks which enhance proton transport. The conductivity of the membrane is strongly related to both chemical structure and morphology. It also suggests that block copolymers with perfluoropolymer segments would lead to even greater proton conductivity.

Research on the synthesis and characterization of fully sulfonated fluorous block copolymers with varied length of sulfonated polystyrene chains, and the relationship between proton conductivity and morphology, is underway and will be discussed in another paper. Although it is recognized that sulfonated polystyrene may not be sufficiently stable under fuel cell operating conditions, these results may be useful in the design of alternative PEM materials.

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