Chem. Mater. **2007,** *19,* 5937–5945

Synthesis and Characterization of Self-Assembled Sulfonated Poly(styrene-*b*-vinylidene fluoride-*b*-styrene) Triblock Copolymers for Proton Conductive Membranes

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Received June 18, 2007. Revised Manuscript Received August 28, 2007

The synthesis of novel ionic triblock copolymers, sulfonated poly(styrene-*b*-vinylidene fluoride-*b*-styrene), with varied degrees of sulfonation is described. The synthetic strategy involves a new approach to a chain-end-functionalized fluoropolymer as a macroinitiator followed by atom transfer polymerization of styrene and sulfonation. Characterization of the polymers has been extensively carried out by ^{1}H and ^{19}F nuclear magnetic resonance and Fourier-transform infrared spectroscopy, differential scanning calorimetry, and thermogravimetry analysis. Tapping mode atomic force microscopy and transmission electron microscopy were applied to image the microphase separation and ionic aggregates. The dependence of ion-exchange capacity, water uptake, and proton conductivity on the degree of sulfonation has been studied. It has been found that the conductivities of the block copolymers are considerably higher than the random copolymers of polystyrene and sulfonated polystyrene possessing similar ion-exchange capacities. The proton conductivity of the membranes has also been investigated at different temperature and humidity conditions.

Introduction

Recent renewed interest in alternative energy sources has prompted extensive theoretical, physical, and chemical studies of proton exchange membranes (PEMs), a key component in polymer electrolyte membrane fuel cells (PEMFCs).[1–5] PEMFCs offer a highly efficient and environmentally benign alternative to current power sources for portable, stationary, and automotive applications.[6] The protons released during the oxidation of hydrogen or methanol are transported across the membrane to derive electricity directly from chemical energy. Generally, PEMs are ion containing polymers bearing pendent cation-exchange sites such as sulfonic acids.[1,2] Among various requirements for PEMs, the most essential property is proton conductivity. Although a systematic relationship between polymer structure and proton conductivity has yet to be revealed, polymer morphology appears to play a dominant role in proton conduction.[7–10] The perfluorosulfonated polymers represented by Nafion are the currently preferred electrolyte materials for PEMFCs.[11] While a real morphological model for Nafion remains elusive, it is currently believed that aggregations of hydrophilic pendent SO_3^- groups form isolated ionic clusters in the hydrophobic perfluorinated polymer matrix.[12] At a low hydrate state, a random distribution of spherical ionic clusters gives rise to poor proton conduction. When hydrated, the clusters of sulfonated groups are expanded, leading to an interconnected network of ionic channels that account for efficient ionic transport. Enhanced proton conductivity has also been observed in the Nafion films that are stretched to induce an oriented morphology consisting of elongated ionic domains.[13]

More recently, the block copolymers containing sulfonated or ionic segments, i.e., block copolymer ionomers, are being developed as a new form of PEMs. These include sulfonated hydrocarbon block copolymers such as poly(styrene-*b*-[ethylene-*co*-butylene]-*b*-styrene) (S-SEBS),[14–17] poly(styrene-*b*-ethylene-*alt*-propylene) (S-SEP),[18] poly(styrene-*b*-isobutylene-*b*-styrene) (S-SIBS),[19–22] and polystyrene-*b*-poly-

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10.1021/cm071626s CCC: $37.00

(arylene ether sulfone)-*b*-polystyrene (PS-*b*-PAES-*b*-PS)[23] and fluorocarbon block copolymers such as sulfonated polysulfone-*b*-poly(vinylidene fluoride) (PSF-*b*-PVDF)[24] and sulfonated poly([vinylidene fluoride-*co*-hexafluoropropylene]-*b*-styrene) [P(VDF-*co*-HFP)-*b*-SPS].[25,26] Self-organization of block copolymers offers the opportunity for precise control of film morphology via manipulating chemical compositions and relative volumes of the constituent blocks.[27] The block copolymer ionomers with tunable ionic microdomains are thus of special interest as model systems for a comprehensive investigation of the correlation between polymer structure, membrane morphology, and proton conductivity. A clear understanding of fundamental structure–property relationships is crucial for development of new high-performance PEMs. Additionally, it is envisaged that conductivity could be enhanced if protons are transferred in the continuous ionic channels yielded from phase separation of block copolymers. Indeed, superior proton conductivities have been observed in PSF-*b*-PVDF and P(VDF-*co*-HFP)-*b*-SPS compared to those in the corresponding homopolymers and random copolymers.[24,25] More interestingly, the membranes based on the fluorocarbon block copolymers exhibit much higher proton conductivities than their hydrocarbon counterparts.[25] This is presumably due to a high dissimilarity of the fluorinated and hydrocarbon segments in the block copolymers, which promotes the formation of more favorable morphologies for proton transport.[28]

It is important, therefore, to investigate a variety of fluorocarbon block copolymers for complete elucidation of intrinsic differences between fluorinated and hydrocarbon polymers in membrane microstructure and their impacts on proton transport and water diffusion. Unfortunately, ion-containing fluorocarbon block copolymers available for PEM study are very limited because of great difficulties in their preparation. Fluorinated alkenes cannot be readily polymerized via living anionic/cationic polymerization[29] or controlled radical polymerization,[30] the methods commonly adopted in the preparation of hydrocarbon block copolymers. The synthesis of fluorinated block copolymers generally proceeds through telomerization, which involves a chain transfer mechanism to prepare a fluorinated segment possessing functional groups at one or both chain ends.[31] The resulting chain-end-functionalized fluoropolymer is subsequently condensed with dissimilar polymers with complementary reactive terminal groups or used as a macroinitiator for polymerization of hydrocarbon monomers to form multiblock copolymers. However, molecular weights of the fluorinated segments yielded from the telomerization approach are less than 3000 g/mol in most cases,[32] which are usually too low for block copolymers to preserve the unique characteristics of fluoropolymers and to self-assemble into a variety of microstructures.

In this work, we report the synthesis of new triblock copolymers, sulfonated polystyrene-*b*-poly(vinylidene fluoride)-*b*-polystyrene (S-PS-*b*-PVDF-*b*-PS), containing a fluorinated block and sulfonic ionic segments, via a tandem method. The incorporated fluorocarbon block is prepared via a general and facile approach based on functionalized benzoyl peroxides (BPO).[33] This approach permits the preparation of chain-end-functionalized fluorinated polymers with molecular weights significantly higher than the previous examples, which not only warrants occurrence of phase separation in the films but also ensures desirable mechanical properties. The influence of polymer structures on membrane morphology, water uptake, and proton conductivity is examined.

Experimental Section

Materials. Unless otherwise noted, all solvents and reagents were purchased from Aldrich and used as received. All manipulations of gas-condense transfer were carried out with rigorous exclusion of oxygen and moisture on a dual-manifold Schlenk line with 10^{-6} Torr high vacuum. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen. Vinylidene fluoride was purchased from SynQuest Laboratory Inc. and purified by the freeze–thaw process prior to use. Styrene was passed through a column of neutral alumina to remove inhibitor before use. Nafion 117 films were pretreated with 3 vol % H_2O_2 aqueous solution for 1 h, rinsed in boiling deionized water repeatedly, boiled in 5 wt % HNO_3 aqueous solution at 90 °C for 30 min, rinsed again with water three times, and stored in deionized water.

Synthesis of 4-Chloromethyl Benzoyl Peroxide (2). To a stirred solution of 4-chloromethyl benzoic acid (**1**) (4.0 g, 23.5 mmol) in anhydrous dichloromethane (20 mL) was added oxalyl chloride (3.2 g, 25 mmol) and a few drops of DMF at 0 °C. After 2 h, the solvent was removed under vacuum, and the solid was dissolved in Et_2O/hexane (40 mL, 1:1). The resulting solution was added during a period of 30 min to a 20 mL rapidly stirred aqueous solution of Li_2O_2 (1.38 g, 30 mmol) at 0 °C. After 2 h, the reaction mixture was diluted by addition of chloroform (100 mL) and washed with water (30 mL). The organic phase was separated, and the aqueous phase was extracted with chloroform (2 × 20 mL). The combined organic phases were dried over $MgSO_4$. Removal of solvent yielded a white solid (1.8 g, 45%). ^{1}H NMR ($CDCl_3$, ppm): δ 8.10 (d, 2H, ArH), 7.55 (d, 2H, ArH), 4.66 (s, 2H).

Synthesis of Chain-End-Functionalized PVDF (3). A stainless steel vessel equipped with a magnetic stir bar was charged with 170 mg (0.5 mmol) of 4-chloromethyl benzoyl peroxide (**2**) and 30 mL of acetonitrile. Vinylidene fluoride (25 mL, 0.26 mol) was transferred and condensed through a dual-manifold Schlenk line. The reactor was immersed in oil bath at 90 °C. After 6 h, the reactor was cooled down, the residual gases were discharged, and the solution was collected.

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The polymer was precipitated by addition of methanol and dried in vacuum at 60 °C to yield 3.4 g of white solid. ^{1}H MMR (d_6-DMSO, ppm): δ 8.04 (d, ArH), 7.66 (d, ArH), 4.85 (s, $-\mathrm{CH_2Cl}$), 4.68 (m, $-\mathrm{COOCH_2CF_2}-$), 2.9 ($-\mathrm{CF_2C}H_2-\mathrm{CF_2CH_2}-$, head-to-tail structure), 2.3 ($-\mathrm{CF_2C}H_2-\mathrm{CH_2CF_2}-$, tail-to-tail structure). ^{19}F NMR (d_6-DMSO, ppm): δ −92.6 ($-\mathrm{CH_2CF_2}-\mathrm{CH_2C}F_2-\mathrm{CH_2CF_2}-$), −95.2 ($-\mathrm{CH_2CF_2}-\mathrm{CF_2CH_2}-\mathrm{CH_2C}F_2-\mathrm{CH_2CF_2}-$), −114.3 ($-\mathrm{CH_2CF_2}-\mathrm{CH_2C}F_2-\mathrm{CF_2CH_2}-$), −116.1 ($-\mathrm{CH_2CF_2}-\mathrm{C}F_2\mathrm{CH_2}-\mathrm{CH_2CF_2}-$). $M_{\mathrm{n(NMR)}} = 56\,600$ g/mol.

Preparation of PS-*b*-PVDF–PS. Phenylmethyl chloride-terminated PVDF (**3**) (1.8 g, $M_{\mathrm{n(NMR)}} = 56\,600$ g/mol), styrene (7.5 mL), pentamethyldiethylenetriamine (PMDETA, 100 mg, 0.6 mmol), and CuCl (75 mg, 0.75 mmol) were dissolved in anhydrous DMF (15 mL). The reaction mixture was degassed by argon with three freeze–pump–thaw cycles. The mixture was subsequently heated at 110 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into methanol/water (30 mL, 1:1) to precipitate the resulting triblock copolymer. The copolymer was collected by filtration, washed by cyclohexane (2 × 10 mL), and dried under vacuum at 60 °C. ^{1}H NMR (d_7-DMF, ppm): δ 7.32 (br s, ArH), 6.80 (br s, ArH), 2.9 ($-\mathrm{CF_2C}H_2-\mathrm{CF_2CH_2}-$, head-to-tail structure), 2.3 ($-\mathrm{CF_2C}H_2-\mathrm{CH_2CF_2}-$, tail-to-tail structure), 1.96 (br s), 1.60 (br s). ^{19}F NMR (d_6-DMSO, ppm): δ −92.2 ($-\mathrm{CH_2CF_2}-\mathrm{CH_2C}F_2-\mathrm{CH_2CF_2}-$), −95.0 ($-\mathrm{CH_2CF_2}-\mathrm{CF_2CH_2}-\mathrm{CH_2C}F_2-\mathrm{CH_2CF_2}-$), −114.2 ($-\mathrm{CH_2CF_2}-\mathrm{CH_2C}F_2-\mathrm{CF_2CH_2}-$), −116.0 ($-\mathrm{CH_2CF_2}-\mathrm{C}F_2\mathrm{CH_2}-\mathrm{CH_2CF_2}-$). $M_{\mathrm{n(NMR)}} = 95\,000$ g/mol.

Sulfonation of PS-*b*-PVDF-*b*-PS. To a 50 mL flask equipped with a dropping funnel, 20 mL of 1,2-dichloroethane and 0.5 g of the triblock copolymer PS-*b*-PVDF-*b*-PS were added. The mixture was cooled to 0 °C using an ice bath and stirred for 0.5 h. Then a 1,2-dichloroethane solution (5 mL) of chlorosulfuric acid with a calculated amount, for example, 0.4 mmol of chlorosulfuric acid (47 mg) which is 20 mol % of the total molar amount of polystyrene repeating units, was added dropwise via an additional funnel and stirred for 2 h. The sulfonated polymer was precipitated in hexane, washed with methanol several times, and dried under vacuum at 60 °C. The degree of sulfonation (DS) of the resulting copolymer was confirmed by ^{1}H NMR, 23% in this case, indicating that the DS could be controlled by the feed ratio of chlorosulfuric acid to PS-*b*-PVDF-*b*-PS copolymer. ^{1}H NMR (d_7-DMF, ppm): δ 7.78 (br s, ArH), δ 7.31 (br s, ArH), 6.83 (br s, ArH), 2.9 ($-\mathrm{CF_2C}H_2-\mathrm{CF_2CH_2}-$, head-to-tail structure), 2.3 ($-\mathrm{CF_2C}H_2-\mathrm{CH_2CF_2}-$, tail-to-tail structure), 1.96 (br s), 1.60 (br s).

Membrane Preparation. 0.5 g of the sulfonated copolymer was dissolved in DMF (5 mL) and stirred overnight. The solution was cast on a Teflon sheet. Drying the solution at 65 °C under atmospheric pressure for 4 h and then under vacuum for 4 h gave a slight yellow and transparent membrane. The resulting membranes were treated with 2 M HCl for 6 h, washed several times with deionized water, and then stored in deionized water. The average thickness of the membranes ranged between 60 and 85 μm.

Structural Characterization. ^{1}H and ^{19}F NMR spectra were recorded on a Bruker AM-300 spectrometer instrument. Gel permeation chromatography (GPC) was performed in a THF mobile phase with a Waters 1515 isocratic HPLC pump. The thermal transition data were obtained by a TA Instruments Q100 differential scanning calorimeter (DSC) at a heating rate of 10 °C/min. The thermogravimetric analysis (TGA) measurement was performed on a TA Instruments model 2950 at a heating rate of 20 °C/min under N_2 from room temperature up to a maximum of 680 °C. FTIR spectra were recorded on a Varian Digilab FTS-800 spectrometer. Tapping mode atomic force microscopy (AFM) was performed with a Veeco Digital Instruments CP II using microfabricated cantilevers with a force constant of ~30 N/m. The ratio of amplitudes used in feedback control was adjusted to 0.3 of the free air amplitude for the reported phase images. Transmission scanning microscopy (TEM) experiments were performed using JEOL JEM-1200 EX II TEM equipment. For TEM measurement, the membranes cast from DMF solution of the sulfonated copolymers were stained by a saturated lead acetate solution, washed with water, and dried under vacuum. The stained membranes were embedded in epoxy resin, cut into ultrathin sections with a microtome, and then put on copper grids.

Ion-Exchange Capacity (IEC). The IEC of the sulfonated copolymers was determined by titration of the sulfonic acid groups. Membranes were equilibrated in a large excess of 2 M NaCl solution for at least 4 h at room temperature prior to titration. The protons released into solution were titrated with 0.0226 M NaOH aqueous solution using phenolphthalein as an indicator. The theoretical IEC values were calculated on the basis of the DS and the number of repeat units of polystyrene blocks according to the literature method.[25]

Water Uptake and Water Sorption. Membrane was dried under vacuum for 12 h at 70 °C and cooled to room temperature in a desiccator before measuring the weight in "dry" state, W_{d}. The membrane was equilibrated in water overnight at room temperature. After removal of the surface water, the weight in "wet" state, W_{w}, was measured. The water uptake and water sorption of the membrane were calculated as the percentage increase from the "dry" to "wet" weight related to W_{d} and W_{w}, respectively.

Proton Conductivity Measurement. In-plane proton conductivity (σ) of the membranes was measured by a four-probe ac impedance method.[34] Impedance data were acquired using an Agilent multifrequency LCR meter (E4980) over the frequency range from 20 Hz–2 MHz. Conductivity measurements under fully hydrated conditions at room temperature were performed after the samples were equilibrated in water for at least 24 h and immediately following the removal of water. An ESPEC SH-241 temperature/humidity chamber was used to control the conductivity measurement conditions. Proton conductivity of the membranes under variable temperature (30–90 °C) and humidity (45–95%) were obtained.[35]

Results and Discussion

Synthesis and Structural Characterization. From our previous studies, the functionalized BPOs were found to be effective initiators for the preparation of the fluorinated polymers containing well-defined functional end groups in free radical polymerization.[33] The absence of disproportionation in termination of perfluoroalkyl radical chains leads to high fidelity of incorporation of the functional groups from the initiators into polymer chain ends.[36] As outlined in Scheme 1, 4,4′-chloromethyl benzoyl peroxide was prepared via acylation of $\mathrm{Li_2O_2}$ with 4-chloromethylbenzoyl chloride and used as an initiator in the polymerization of vinylidene fluoride. The presence of phenylmethyl chloride groups at the poly(vinylidene fluoride) (PVDF) chain ends was confirmed by the ^{1}H NMR spectrum (Figure 1a). End-group analysis[37] by integration the terminal aromatic and methylene protons against the hydrogens in PVDF revealed a number-average molecular weight (M_{n}) of 56 600 g/mol, which is about 20-fold higher than the chain-end-functionalized fluo-

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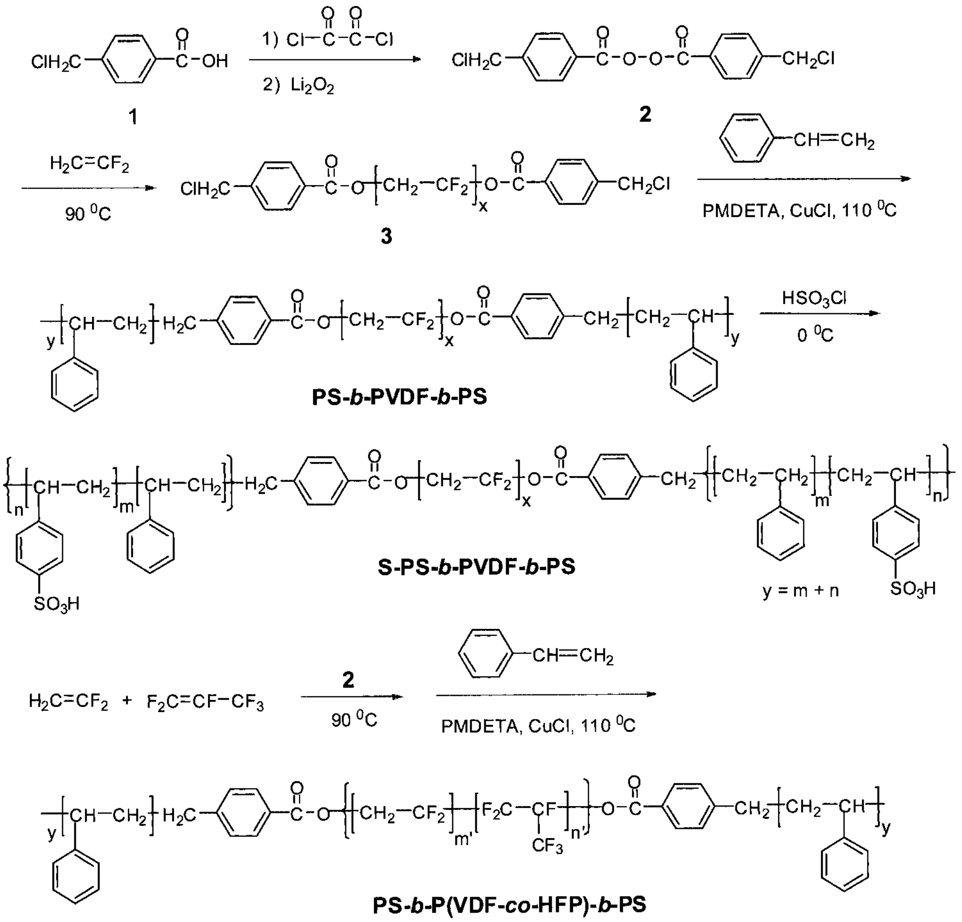
Scheme 1. Synthesis of 4-Chloromethyl Benzoyl Peroxide and the Triblock Copolymers



ropolymers prepared via telomerization. The ^{19}F NMR spectrum exhibits a characteristic signal at −93.0 and −95.2 ppm corresponding to the head-to-tail (H–T) VDF units in the polymer chain and multiplets at −114.3 and −116.1 ppm attributed to the difluoromethylene groups from head-to-head (H–H) sequences of VDF. The mole fraction of H–T sequence assessed from the integrals of the characteristic peaks is around 95%.[33] The phenylmethyl chloride-terminated PVDF was then employed as a macroinitiator in atom transfer radical polymerization (ATRP) of styrene in the presence of CuCl as catalyst, *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine as ligand, and DMF as solvent at 110 °C.[30] Figure 1b shows a ^{1}H NMR spectrum of the resulting PS-*b*-PVDF-*b*-PS triblock copolymer. Additional peaks assigned to polystyrene (PS) segments at 7.4–6.4 ppm (aryl, 5H), 1.3–1.7 ppm (methylene, 2H), and 1.8–2.0 ppm (benzylic, 1H) were observed. The molecular weight of PS in the triblock copolymer was calculated by comparing the integration of the ^{1}H NMR resonances assigned to the methylene protons in PS to those of methylene protons in PVDF (2.9 and 2.3 ppm corresponding to the methylene protons of H–T and T–T sequences of VDF, respectively), which correlates well with the predicted molecular weight ($M_{\mathrm{n,PS}}$ = 38 400 g/mol). Attempts of characterization of chain-end-functionalized PVDF and PS-*b*-PVDF-*b*-PS using GPC were not successful due to their limited solubility in THF, eluent of our GPC system. To further verify the formation of the block copolymer, THF-soluble poly(vinylidene fluoride-*co*-hexafluoropropene) (P(VDF-*co*-HFP)) with phenylmethyl chloride end groups and triblock copolymer, polystyrene-*b*-poly(vinylidene fluoride-*co*-hexafluoropropene)-*b*-polystyrene (PS-*b*-P(VDF-*co*-HFP)-*b*-PS), were prepared using the same approach as depicted in Scheme 1. As revealed in Figure 2, the resulting triblock copolymer shows an increase in molecular weight from the original chain-end-functionalized P(VDF-*co*-HFP) and a monomodal GPC trace with a polydispersity of 1.35. The change of GPC chromatograms from a negative signal characteristic of the fluorinated backbones to a positive peak also clearly demonstrates the incorporation of PS into the copolymers, which is in accordance with the previous studies.[38,39]

By controlling the feed ratio of chlorosulfuric acid to PS-*b*-PVDF-*b*-PS, a series of sulfonated triblock copolymers, S-PS-*b*-PVDF-*b*-PS, with different degrees of sulfonation (DS) were obtained. Figure 1c shows a ^{1}H NMR spectrum of a fully sulfonated S-PS-*b*-PVDF-*b*-PS, in which the peaks at 7.2–7.5 ppm corresponding to meta/para protons on the phenyl ring in PS-*b*-PVDF-*b*-PS downfield-shift to 7.6–7.9 ppm due to protons adjacent to the sulfonate group. The calculated DS based on integral

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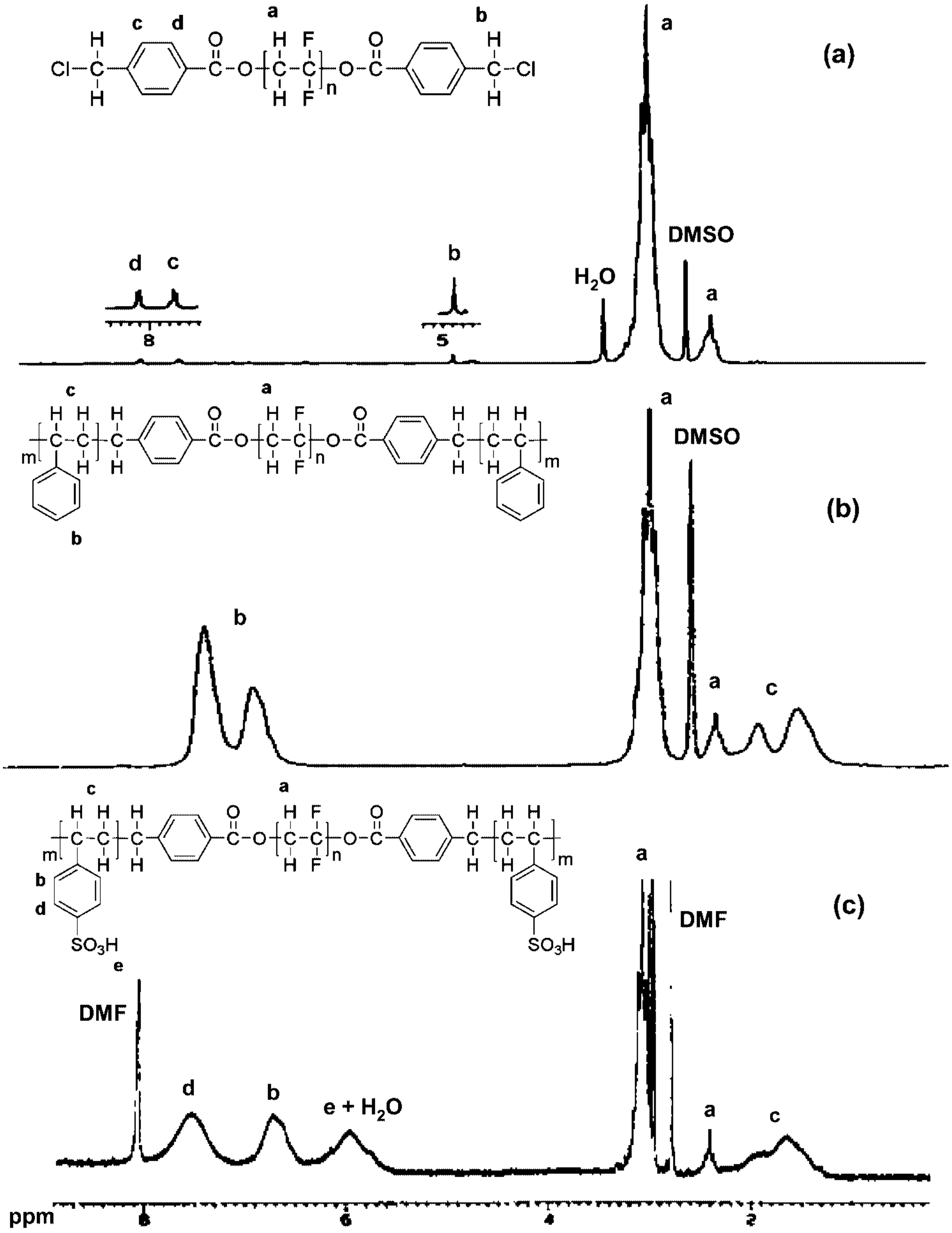

Figure 1. ^{1}H NMR spectra of (a) phenylmethyl chloride-terminated PVDF, (b) PS-*b*-PVDF-*b*-PS, and (c) S-PS-*b*-PVDF-*b*-PS.

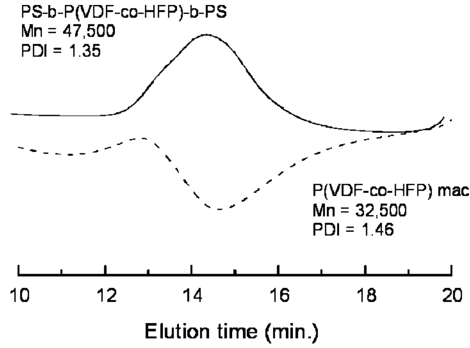

Figure 2. GPC traces of the phenylmethyl chloride-terminated P(VDF-*co*-HFP) and PS-*b*-P(VDF-*co*-HFP)-*b*-PS.

Table 1. Characteristics of the S-PS-*b*-PVDF-*b*-PS Membranes

membrane	degree of sulfonation (mol %)	IEC (mmol/g) IEC[a]	IEC[b]	water uptake (wt %)	water content (wt %)	λ	T_g (°C)
I	13	0.49	0.51	3.4	3.3	3.7	92
II	23	0.87	0.87	8.1	7.5	5.1	108
III	31	1.17	1.10	29	22	14.6	114
IV	42	1.59	1.49	41	29	15.3	118
V	49	1.90	1.85	225	70	67.6	127

[a] Calculated based on the NMR data. [b] Determined by titration.

ratios of the NMR resonances are listed in Table 1. The introduction of sulfonic groups into the polymers was further confirmed by FTIR spectroscopy (Figure 3). The characteristic peaks at 1033 and 1006 cm^{-1} assigned to symmetric stretching of SO_3^- and in-plane bending of para-substituted phenyl ring, respectively, were observed for the sulfonated copolymers, and the intensities of these two peaks increase with the DS. The absorption bands of unsubstituted phenyl ring at 699 and 759 cm^{-1} (C–H bond) and 1493 and 1453 cm^{-1} (stretching vibrations) disappear following sulfonation. The resulting sulfonated copolymers are readily soluble in polar organic solvents

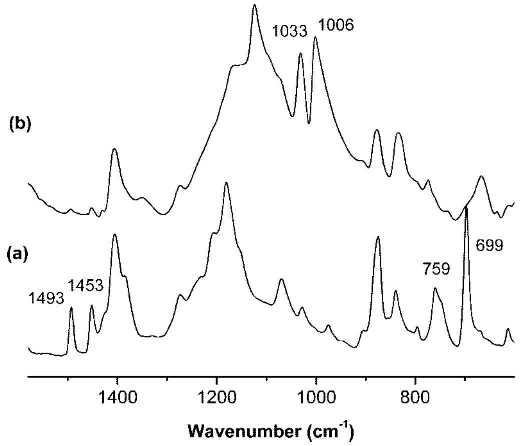

Figure 3. FTIR spectra of (a) PS-*b*-PVDF-*b*-PS and (b) fully sulfonated S-PS-*b*-PVDF-*b*-PS.

such as DMF, NMP, and DMSO. As listed in Table 1, the ion-exchange capacities (IEC) determined by titration are in the range 0.51–1.85 mequiv/g, which are in good agreement with the theoretical values calculated from the structure and composition of the block copolymers.

Thermal Analysis. Only one glass transition temperature (T_g) corresponding to partially sulfonated PS segments was observed in DSC studies, while T_g of PVDF block was not clearly discernible. As summarized in Table 1, the T_g increases progressively from 92 °C for PS-*b*-PVDF-*b*-PS to 134 °C for fully sulfonated S-PS-*b*-PVDF-*b*-PS as the DS increases. This increase is consistent with previous reports, which is attributed to the bulkiness of the sulfonate group and the ionomer effect.[40] A bimodal endothermic peak around 160 °C due to the melting of PVDF segments was detected in the thermograms. These double endotherms are caused by a temperature-dependent bimodal distribution of lamellar thickness, in which the lower melting peak is related to melting of crystals originally present and the higher melting peak is attributed to melting of crystals reorganized upon heat treatment.[41]

TGA was employed to examine the thermal stability of the block copolymers. As shown in Figure 4, for PS-*b*-PVDF-*b*-PS, the onset weight-loss temperatures are 390 and 460 °C for PS and PVDF blocks, respectively. TGA curves for S-PS-*b*-PVDF-*b*-PS are characterized by four distinct regions of mass loss: (i) loss of water that is bound to the sulfonic acid groups of the membranes at 50 to ~200 °C, (ii) elimination of sulfonic acids at 300 °C, (iii) degradation of PS block at 360 to 410 °C, and (iv) decomposition of PVDF segment at 460 to 510 °C. As the DS of the polymers increases from 13 to 42%, the percentage decrease in mass due to the loss of water increases gradually from 2 to 4%. Note that the thermal stability of PVDF and sulfonated PS blocks increase steadily with the increased DS, as observed in other ionic polymers.[15,25]

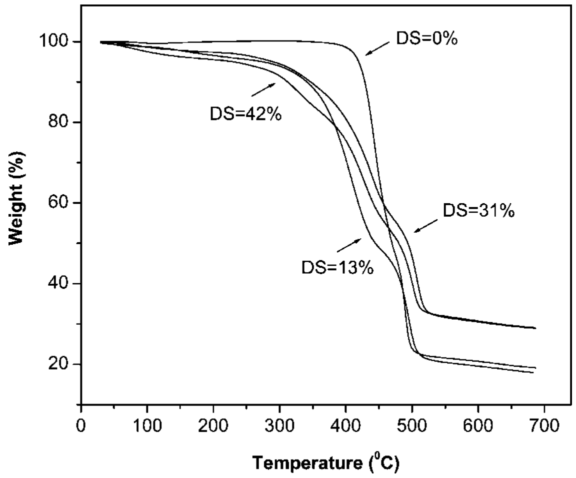

Figure 4. TGA curves of PS-*b*-PVDF-*b*-PS and S-PS-*b*-PVDF-*b*-PS.

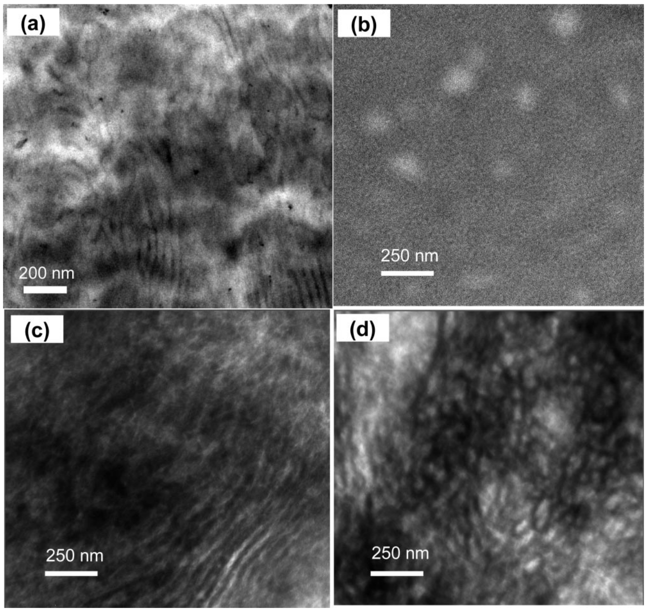

Figure 5. Transmission electron micrographs of (a) PS-*b*-PVDF-*b*-PS and S-PS-*b*-PVDF-*b*-PS with a DS of (b) 13%, (c) 23%, and (d) 31%.

Membrane Morphology. To investigate the morphology of the block copolymers, thin films of PS-*b*-PVDF-*b*-PS and S-PS-*b*-PVDF-*b*-PS were cast from DMF solution and stained with lead acetate. The films were then microtomed to yield slices with ~100 nm thickness for TEM analysis. The resulting micrograph of cross-sectional PS-*b*-PVDF-*b*-PS (Figure 5a) exhibits a lamellar morphology, as the dark and white areas correspond to PS and PVDF microdomains, respectively. It is interesting to note that such a microphase separation has not been observed in previous examples of fluorocarbon block copolymers,[25] owing to much lower molecular weights of the fluorinated blocks relative to the hydrocarbon segments. Featureless morphology was observed for the block copolymers containing a DS of 13% (Figure 5b). This is apparently due to the strong ionic interactions from sulfonic acid groups, which disrupt microphase separation of block copolymers and lead to a disordered morphology. As the DS increases, driven by electrostatic interactions among ion pairs, distinct large-scale phase separations develop in the thin films as illustrated in Figure 5c,d. The observed domain size and width of the channels from TEM micrograms are around 30 nm, which is larger than typical

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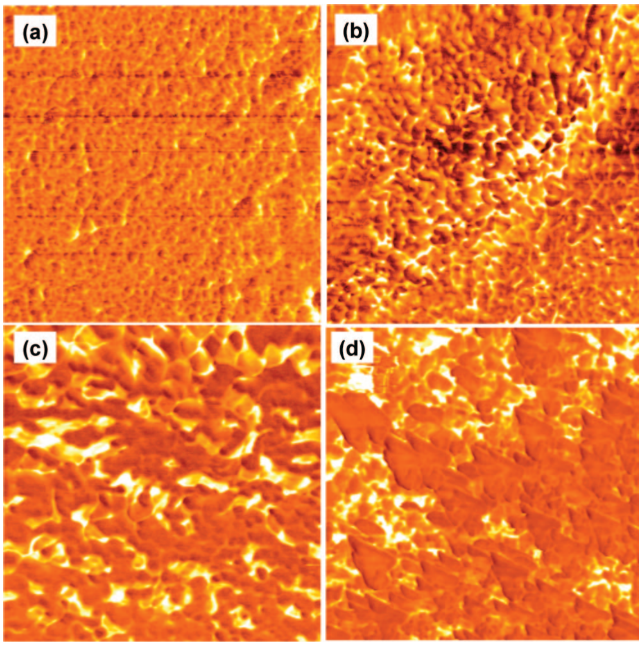

Figure 6. AFM tapping phase images for S-PS-*b*-PVDF-*b*-PS with a DS of (a) 13%, (b) 31%, (c) 49%, and (d) 100%. Scan boxes are 1 μm × 1 μm, and phase scales are 0–30°.

ionic aggregation in hydrocarbon polymers with similar ionic concentrations.[42–44] This larger aggregation is speculated in consequence of great phase separation in fluorocarbon block copolymers. Further studies on the membrane morphology by scattering and microscopy techniques and investigations on morphology transition as a result of interplay of association of ionic groups and thermodynamics-driven microphase separation are in progress.

Tapping mode AFM was used to differentiate between hydrophilic sulfonated ionic aggregates and hydrophobic polymer regions in the membranes. Figure 6 shows the tapping mode phase images of the sulfonated block copolymers recorded under ambient conditions, where the cluster-like dark structures correspond to softer regions and thus represent hydrophilic sulfonic acid groups. Distinct phase morphology was not observed for PS-*b*-PVDF-*b*-PS. On the other hand, both domain size of hydrophilic ionic regions and phase contrast between the hydrophobic and hydrophilic domains increase with increasing DS. For S-PS-*b*-PVDF-*b*-PS with a DS of 13% (Figure 6a), isolated ionic cluster region was formed with approximate diameters of 15–20 nm. As the DS increases, the phase images undergo significant changes, wherein the hydrophilic ionic domains are connected to form continuous ionic channel structures (Figure 6b–d). This result explains abrupt increases of proton conductivity and water absorption which are discussed in the subsequent sections.

Water Uptake and Proton Conductivity. Water uptake and water content of the membranes are reported in Table 1. As expected, the amount of water absorbed by the membranes increases exponentially with increasing sulfonation. The membrane made from the sulfonated copolymer containing a DS of 49% absorbs a very large amount of water (225 wt % water uptake) and displays poor mechanical properties. The fully sulfonated polymer is completely soluble in water. While the sulfonated copolymer with a DS of 31% has a very similar water uptake (29 wt %) and water content (22 wt %) as Nafion 117 (29 and 23 wt % for water uptake and water content, respectively), its IEC (1.10 mmol/g) is higher than that of Nafion (0.91 mmol/g). Water uptake for S-PS-*b*-PVDF-*b*-PS (8, 29, and 41 wt % for DS = 23, 31, and 42%, respectively) is generally lower than sulfonated hydrocarbon block copolymer S-SEBS having a similar DS value (15, 40, and 70 wt % for DS = 22, 34, and 42%, respectively),[16] indicating that the swelling behavior is related to both the concentration of sulfonic acid groups introduced into the polymers and the chemical structure of the polymer backbone.

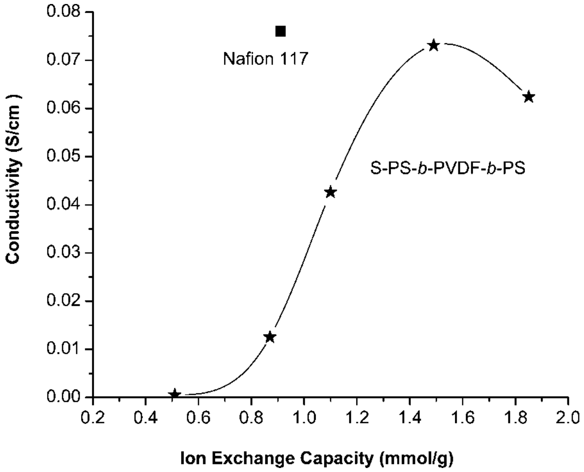

Figure 7. Conductivity of Nafion 117 and the block copolymer membranes as a function of ion-exchange capacity.

A strong dependence of proton conductivities of the membranes on IEC is described in Figure 7. The proton conductivity increases drastically with increasing IEC from 0.5 to 1.5 mmol/g because of improved ion contents of the membranes and thereafter levels off. A further increase in IEC leads to a decreased conductivity. This is attributed to reduced proton concentrations as a result of substantially increased water uptake from 41 wt % at 1.49 mmol/g IEC to 225 wt % at 1.85 mmol/g IEC, as similar phenomena have been observed in other ionic polymers.[25,45,46] Compared to Nafion, the conductivity of S-PS-*b*-PVDF-*b*-PS membrane with the same IEC is lower, which may relate to the lower pK_a of the sulfonic acid in Nafion. The conductivity of the copolymer membrane having an IEC of 1.49 mmol/g is 0.074 S/cm, comparable to that of Nafion 117. The conductivities of the membranes are in the range of 0.013– 0.043 S/cm for IECs of 0.87–1.10 mmol/g, which are considerably higher than the conductivities (0.0015–0.0023 S/cm) of the random copolymers of polystyrene and sulfonated polystyrene pos-

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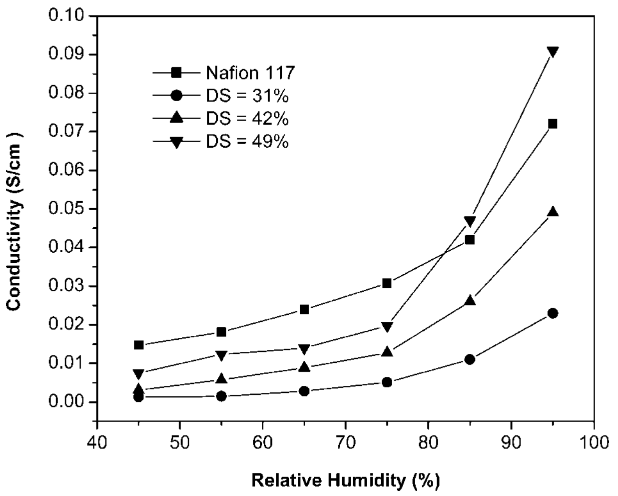

Figure 8. Proton conductivity versus the relative humidity for S-PS-*b*-PVDF-*b*-PS and Nafion 117 membranes.

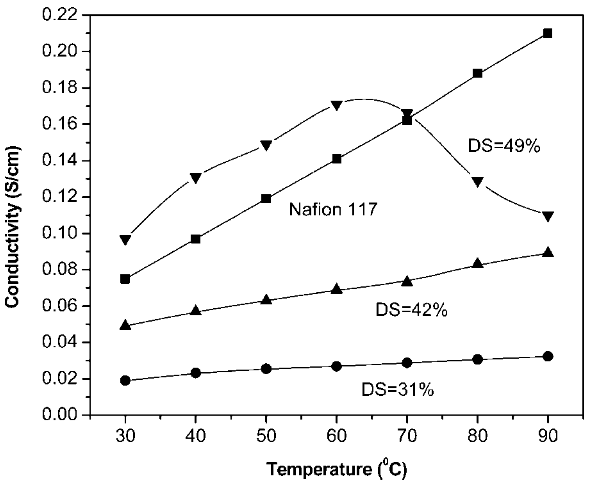

Figure 9. Variation of proton conductivity measured under the condition of 95% relative humidity as a function of temperature for S-PS-*b*-PVDF-*b*-PS and Nafion 117 membranes.

sessing similar IECs (0.93–1.24 mmol/g).[47,48] Table 1 lists λ (i.e., $[H_2O]/[SO_3^-]$, the average number of water molecules per sulfonic acid group) for the membranes with different DS. For S-PS-*b*-PVDF-*b*-PS, the conductivity increases significantly with λ from 5 to 15 and decreases as λ is further increased from 15 to 68. These λ values are lower than those in previously reported PEMs in which conductivity saturates when λ reaches about 40.[25,45] This implies that the copolymers are less compatible with water presumably because of a larger volume faction of hydrophobic fluoropolymers in the structures, which is consistent with their lower water uptake relative to other ionic polymers.

Figure 8 compares the proton conductivity against the relative humidity (RH) of the membranes. Different from Nafion 117 whose conductivity increases steadily as RH increases, the conductivity of the S-PS-*b*-PVDF-*b*-PS films shows relatively little variation over a rather wide range of RH, and it rapidly increase at RH higher than 75%. An optimal conductivity value of 0.091 S/cm, higher than that of Nafion (0.072 S/cm), was observed at 95% RH and 30 °C for S-PS-*b*-PVDF-*b*-PS with a DS of 49%. This value is also much higher than the conductivity (0.062 S/cm) measured under the fully hydrated state, where the higher water content dilutes the proton concentration in the membrane.

The dependence of conductivity on temperature under 95% RH is depicted in Figure 9. The conductivity of the copolymer membrane with a DS of 49% was found to maximize between 60 and 70 °C. At temperature below 60 °C, the conductivity increases with temperature. The increase in conductivity is attributed to the effect of temperature in overcoming the activation barriers for proton motion. Above 70 °C, due to dehydration of the membrane, the number of hydronium ions as proton carriers decreases, thus resulting in a sharp decrease of the proton conductivity. In contrast, as observed in Nafion 117 and many other PEM materials,[49,50] for the membranes with DS of 31 and 42%, increase of temperature results in a concomitant increase in conductivity. Especially, the membrane containing a DS of 31% displays proton conductivity less dependent on the temperature. This striking behavior is believed to correlate with the membranes containing well-connected ionic channels and low concentration of the ions, in which high mobilities of the carrier ions counteract each other and lead to a nearly constant value of proton conductivity.[51]

Conclusions

A series of novel triblock copolymers containing sulfonated polystyrenes have been synthesized from a chain-end-functionalized PVDF that is used as a macroinitiator in controlled radical polymerization of styrene. One major advantage of preparing the chain-end-functionalized fluoropolymers by using the functionalized BPO over conventional preparation by telomerization is significantly improved molecular weights of the resulting polymers, which ensures essential mechanical properties for durable and ductile films and offers a library of self-assembled microstructures with tunable ionic domains for systematic structure–property studies. In addition, as an efficient initiator for the polymerization of a broad range of fluorinated alkenes,[33,52] the functional BPO would also enable the preparation of a variety of fluoropolymer-containing structures for PEM applications. These studies are currently underway.

It has been found that the prepared block copolymers display variable phase-separated domains that depend strongly on the DS. As observed in AFM and TEM studies, the hydrophilic ionic clusters coalesce into larger channel structures when DS > 23%, coinciding with sharp increases of water uptake and proton conductivity. The proton con-

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ductivity increases significantly when the IEC is increased from 0.5 to 1.5 mmol/g. An optimal conductivity value of 0.091 S/cm was observed at 95% RH and 30 °C for the membrane with a DS of 49%. The copolymer membrane also shows the maximum proton conductivity between 60 and 70 °C.

Acknowledgment. We thank Miss Jianer Bao, Prof. Digby Macdonald, and Prof. Michael Hickner for their invaluable help with conductivity measurements. This work was supported in part by the National Science Foundation (CAREER DMR-0548146).

CM071626S