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Synthesis of Sulfonated Polysulfone-*block*-PVDF Copolymers: Enhancement of Proton Conductivity in Low Ion Exchange Capacity Membranes

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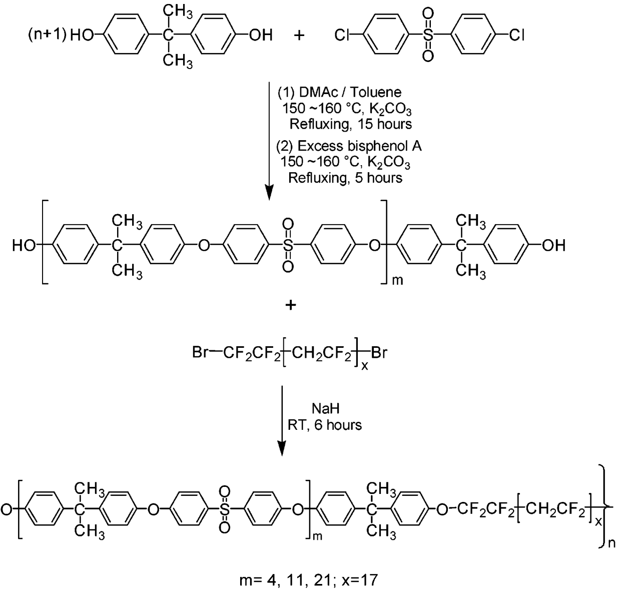
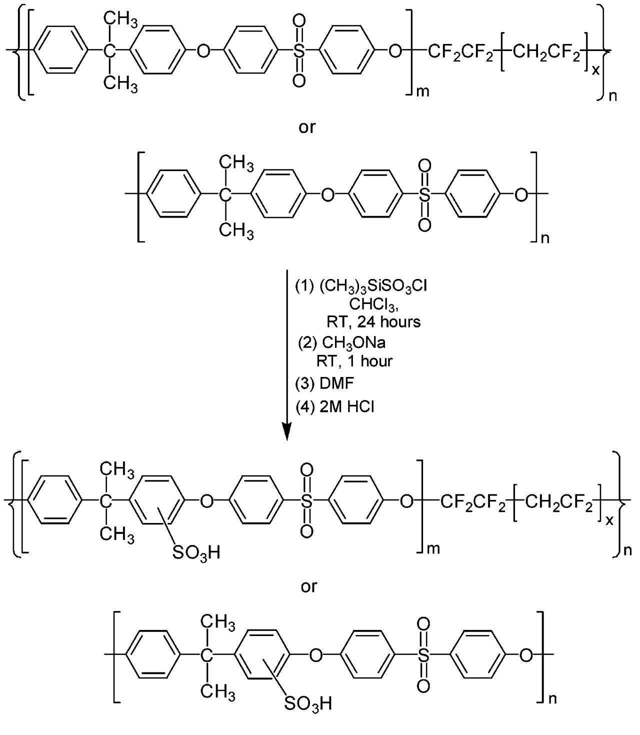
The study of proton conducting polymers is of interest due to their application in proton exchange membrane (PEM) fuel cells. Although much attention continues to be paid to perfluorosulfonate ionomer (PFSI) membranes,[1−3] their high cost and difficult synthesis and processing[4−6] have led to researchers investigating proton conducting polymers membranes based on acid complexes of basic polymers,[7,8] sulfonated polyarylenes,[9−12] grafted sulfonated polystyrene,[13,14] and organic−inorganic hybrids.[15,16] The morphology of these polymers is expected to play an important role in determining the membranes' mechanical strength, water uptake, proton conductivity, and electroosmotic drag. In PFSI membranes, for example, a "channel-like" network of ions accounts for high proton conductivity, despite their relatively low IEC.[17] However, Nafion, when dissolved and recast into membranes, can exhibit an ionic conductivity up to 4 orders of magnitude lower, affirming the importance of polymer morphology.[18] The development of model polymers that can assist the understanding of morphological formation and its role on membrane properties is both a challenge and opportunity.

Recently, the study of phase separation in well-defined polymers bearing different graft chain lengths of styrenesulfonic acid units emphasized how the formation of ionic networks modifies water sorption and substantially improves proton conductivity.[19−21] Block copolymerization is another route to achieve phase-separated morphologies, as is polymer blending, but in general, morphologies obtained using block copolymers can be more precisely controlled, and on a much smaller dimensional scale than blends.[22] Furthermore, in block copolymers, the physicochemical properties of individual blocks can be realized in a single polymer structure.[23] There are several reports of proton conducting membranes based on poly(styrenesulfonic acid)-containing block copolymers, including partially sulfonated polystyrene-*b*-poly(ethylene-*r*-butylene)-*b*-polystyrene (SSEBS)[24−27] and partially sulfonated polystyrene-*b*-polyisobutylene-*b*-polystyrene (S-SIBS),[28] and while these provide important insights into structure−property relationships the benzylic carbon−hydrogen bonds of the poly(styrenesulfonic acid) are susceptible to chemical attack and rapid degradation, which limits their employment in fuel cells.[29] It is, therefore, desirable to explore the design and synthesis of novel block polymers to further examine the relationship between polymer structure, morphology, and proton conductivity.

Scheme 1. Synthetic Scheme for Bisphenol A Polysulfone-*b*-PVDF Copolymers



Scheme 2. Sulfonation of Bisphenol A Polysulfone and Bisphenol A Polysulfone-*b*-PVDF Copolymer



Recently, we synthesized a series of block copolymers containing bisphenol A polysulfone and poly(vinylidene fluoride) (PSF-*b*-PVDF) by polycondensation of α,ω-dihydroxybisphenol A polysulfone precursors and α,ω-dibromopoly(vinylidene fluoride), as shown in Scheme 1.[30] In this Communication, we report post-sulfonation of selected block copolymers and compare their physico-chemical properties to sulfonated bisphenol A polysulfone homopolymers. The effect of incorporating high surface energy fluoropolymer blocks on film morphology and proton conductivity are examined for a wide range of IEC membranes.

Sulfonation of bisphenol A polysulfone homopolymer (PSF) and PSF-*b*-PVDF block copolymer was carried out with $(CH_3)_3SiSO_3Cl$, as depicted in Scheme 2, using

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Table 1. Sulfonation of PSF and Properties of SPSF

sample	γ[a]	IEC (mmol/g) titration	IEC (mmol/g) NMR[b]	DS titration	DS NMR[b]	water uptake (%)	λ[c]	$\sigma \times 10^3$ (S/cm)[d]
1	1.4	0.83	0.81	0.41	0.40	15	10.0	0.817
2	1.7	1.07	1.19	0.53	0.59	21	10.9	1.85
3	2.0	1.25	1.33	0.61	0.65	25	11.1	4.38
4	2.2	1.43	1.44	0.70	0.71	30	11.7	9.89
5	2.6	1.55	1.65	0.76	0.81	36	12.9	22.5
6	2.8	1.67	1.79	0.82	0.88	48	15.9	30.4
7	3.4	1.81	1.79	0.89	0.88	60	18.4	39.8
8	3.9	2.02	2.04	0.99	1.00	76	20.9	52.4

[a] [Sulfonation agent]/[repeating unit]. [b] Calculated according to ref 32. [c] $\lambda = [H_2O]/[SO_3H]$. [d] 30 °C, 95% RH.

Table 2. Sulfonation of PSF-*b*-PVDF and Properties of SPSF-*b*-PVDF

sample	γ[a]	IEC (mmol/g) titration	IEC (mmol/g) NMR[b]	DS titration	DS NMR[b]	water uptake (%)	λ[c]	$\sigma \times 10^3$ (S/cm)[d]
1	0.9	0.78	0.65	0.40	0.34	14	9.9	3.88
2	1.2	1.14	0.97	0.59	0.50	21	10.2	4.63
3	1.5	1.30	1.26	0.67	0.65	25	10.6	6.58
4	2.0	1.43	1.33	0.74	0.68	30	11.7	12.4
5	2.9	1.62	1.49	0.84	0.77	38	13.0	31.4
6	3.5	1.85	1.73	0.95	0.89	53	15.9	35.4
7	4.0	2.18	2.06	1.12	1.06	77	19.6	55.1

[a] [Sulfonation agent]/[repeating unit of polysulfone block]. [b] Calculated from the weight content of polysulfone block and ^{1}H NMR according to ref 32. [c] $\lambda = [H_2O]/[SO_3H]$. [d] 30 °C, 95% RH.

previously reported conditions.[31] The number-average molecular weights of the polysulfone and PVDF blocks were 9500 and 1200 Da, respectively. Briefly, trimethylsilyl chlorosulfonate was added to the polymer solution in $CHCl_3$, and the mixture stirred for 24 h at room temperature. Excess sodium methoxide was added in order to cleave the silyl sulfonate intermediate and obtain the sodium sulfonate form, which was dissolved in DMF and precipitated as its acidic form in 2 M HCl. Films were cast from DMF solutions, dried at room temperature for 2 days, and soaked in 2 M HCl solution for 48 h to ensure the acidic form. Details of IEC and water uptake measurement have been previously reported.[20] A Hewlett 8753A network analyzer was used to measure impedance spectra in the frequency range of 300 kHz to 1 GHz. The relative humidity was controlled with an ESPEC temperature and humidity chamber, model SH-240. Molar ratios of sulfoning agent to polymer were varied to obtain polymers bearing different degrees of sulfonation. Compositions of sulfonated homopolymers (SPSF) and block copolymers SPSF-*b*-PVDF, their water uptake (22 °C), and conductivity data (at 30 °C, 95% RH) are listed in Tables 1 and 2, respectively.

The degree of sulfonation (DS) of the homopolymer and copolymer was readily controlled by the ratio of sulfonating agent to polysulfone repeat unit and varied between ~0.4 and 1. Analysis by titration and NMR gave consistent results. IEC values varied between ~0.8 and ~2.0 mmol/g for the homopolymer and between ~0.8 and ~2.2 mmol/g for the block copolymer. Water uptake varied from 15% to 76%, and 14 to 77%, for the corresponding homopolymers and copolymers, while λ values ($\lambda = [H_2O]/[SO_3H]$) were 10−18 and 10−20, respectively. The λ values are smaller than observed for Nafion 117 but similar to other polyarylenes for the range of IEC examined. Overall, the two series possessed similar ranges of IEC, water uptake, and λ and varied only in the absence or presence of fluoropolymer blocks.

The difference in proton conductivity between SPSF and SPSF-*b*-PVDF polymers of similar IEC is illustrated in Figure 1. The plot indicates that in the low IEC regime SPSF1-*b*-PVDF copolymers exhibit higher proton conductivity than the homopolymers. For lowest IEC polymer, this conductivity is enhanced by a factor of 4. This enhancement was maintained when the temperature was raised to 80 °C (at 95% RH)—data not shown. As the IEC increases the conductivity increases, but the difference in conductivity between the two series diminishes. Above 1.4 mmol/g the conductivities of the two series are similar. In comparing low IEC copolymers and homopolymers, we note that for a given degree of sulfonation the IEC values are similar, as are water contents and λ values. Thus, differences in proton conductivity are not associated with differences in λ, which can exert a strong influence.[33]

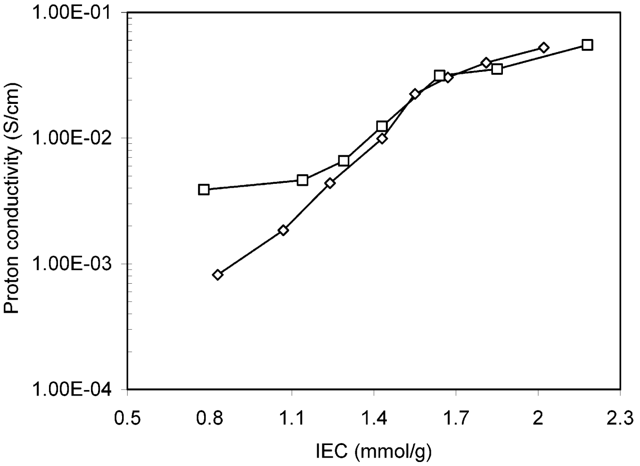

Figure 1. Dependence of proton conductivity on IEC for SPSF (diamond) and SPSF-*b*-PVDF (square) membranes (30 °C, 95% RH).

TEM analysis was performed on ~100 nm thick slices of ultramicrotomed Ag^+ stained SPSF and SPSF-*b*-PVDF membranes (Figure 2). Dark regions are assigned to localized domains of ionic $-SO_3Ag$ and lighter regions to nonionic. Parts a and b of Figure 2 show TEMs for high IEC membranes: SPSF (1.55 mmol/g) and SPSF-

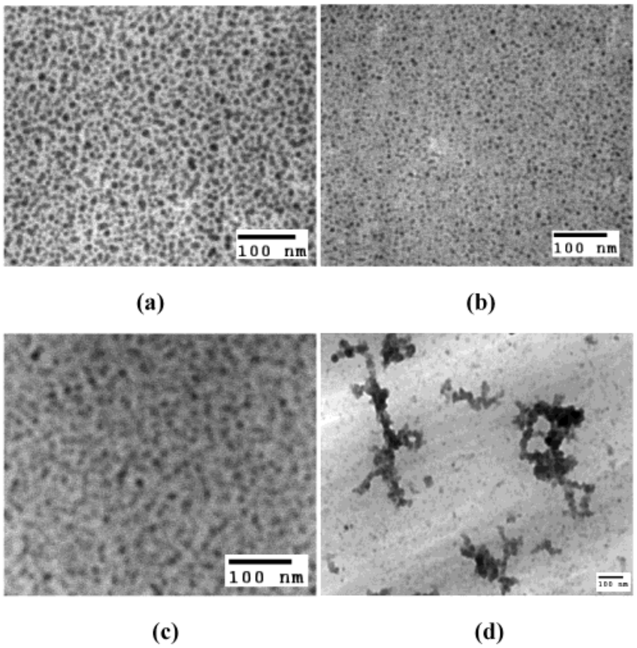

Figure 2. TEM micrographs of polymer membranes: (a) SPSF (IEC = 1.55); (b) SPSF1-*b*-PVDF (IEC = 1.62); (c) SPSF (IEC = 0.83); (d) SPSF1-*b*-PVDF (IEC = 0.78).

b-PVDF (1.62 mmol/g), respectively. Ionic aggregates are observed in both samples; however, the size of the aggregates is smaller for the block copolymer (∼7 nm vs ∼11 nm). Ionic aggregates are also observed for low IEC polymers (Figure 2c,d). Both SPSF and SPSF-*b*-PVDF exhibit ionic aggregates, but in addition, the block copolymer possesses larger regions of ionic aggregation. These large phase-separated features have precedence in the literature: for example, two types of microphase separation are reported present in perfluorinated ion exchange polymers: microphase separation and association of ionic groups, the latter forming ion multiplets or ion clusters.[34,35] In other work, on polymer blends of sulfonated polymers, they are simply referred to as being sulfonate-rich.[36] It appears in the present work these 50−200 nm size domains are the result of gross phase separation of ionic and nonionic regions. The enhancement in conductivity of the block copolymers is judged to be due to the presence of the fluoropolymer block, which promotes the formation of ionic aggregates and the formation of an ionic network—in an IEC domain where a percolation network is not saturated. Why the high IEC block copolymers did not exhibit a similar morphology is difficult to answer, but the presence or absence of these gross features is likely due to the delicate balance between hydrophilic and hydrophobic volume fractions, the ratio of block lengths, and the surface energy difference between the existing domains.[37,38] For higher IEC membranes, where the concentration of acidic sites is relative high, λ values much higher, and the network of ions fully formed, the presence or absence of the relatively small fluoropolymer segment has little effect on conductivity.

To gain more information on these low IEC polymers, we prepared a sulfonated bisphenol A polysulfone-*b*-poly(vinylidene fluoride) copolymer possessing a shorter polysulfone block (M_n = 4900 Da compared to the previous 9500 Da) and possessing an IEC of 0.75 mmol/g, i.e., similar to that of the lowest IEC polymers listed in Tables 1 and 2. This polymer possessed a degree of sulfonation of 0.42, water uptake of 14%, and a λ value of 10.4—all very similar to sample 1 (Table 2). However, the proton conductivity was found to be 1.0 mS/cm, i.e., ∼4 times smaller than sample 1 (Table 2) and similar to the sulfonated homopolymer (sample 1, Table 1). Inspection by TEM (not shown) shows the existence of small ionic aggregates but the absence of the larger phase-separated structures illustrated in Figure 2d.

It is tempting to speculate that the enhanced conductivity of the aforementioned block copolymers in the low IEC range is due to the presence of the microstructures observed in Figure 2d, as has been suggested for other polymer systems.[39] It may be that larger aggregates allow for higher localized λ values and hence transport protons more efficiently, but more evidence is required to support this. However, this speculation should be tempered by the fact that TEMs are, by necessity, observed under vacuum, with the membrane in its dry state; the nanostructure of membranes has been shown to undergo substantial change upon hydration.[40]

In conclusion, proton conductivity of sulfonated polysulfones possessing relatively lower IEC can be enhanced by block copolymerization with PVDF oligomer. It is speculated that this is due to greater phase separation, having size domains greater than typical ionic aggregation. It is predicted that proton conductivity of SPSF can be further enhanced in a wider range of IEC by incorporating longer blocks of PVDF; unfortunately, the radical telomerization method[30] used to prepare dibromo-telechelic PVDF oligomers limits the molecular weight to 1200 Da. Attempts to synthesize higher molecular weight PVDF oligomers and corresponding block copolymers are being pursued in order to further elucidate the role of phase-separated structures on proton conductivity.

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