1692 *Macromolecules* **2010**, *43*, 1692–1694
DOI: 10.1021/ma902716x

Macromolecules
COMMUNICATION TO THE EDITOR

Synthesis of Proton Conductive Polymers with High Electrochemical Selectivity

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Received December 9, 2009
Revised Manuscript Received January 15, 2010

High-performance membranes with controllable transport and separation properties play a vital role in advanced energy and environmental systems.[1] For instance, proton/methanol selectivity is a critical aspect in the design of new polymer electrolyte membranes (PEMs) for direct methanol fuel cells (DMFCs).[2] One of the main barriers to fully realizing the potential of DMFCs is the methanol permeability of the PEMs. The crossover of methanol through the anode and electrolyte membrane to the cathode leads to low cell voltage and reduced fuel efficiency.[3] Nafion, the benchmark PEM for DMFCs, is known to have undesirably high methanol permeability.[4] Extensive research has been directed to the development of new PEM materials that are less permeable to methanol.[5] New membranes with low methanol crossover have been realized by using non-fluorinated PEMs, by the incorporation of nanoparticles composed of silica, metal oxide, proton conducting inorganic materials, clays, or metallic nanoparticles into Nafion and other PEMs, and by other strategies such as cross-linking and polymer blends.[6] In many cases, current strategies to decrease methanol permeability in PEMs are accompanied by a corresponding significant decrease in proton conductivity. A broadly accepted figure-of-merit to capture the vital material parameters important for DMFC is the electrochemical selectivity, defined as the ratio of proton conductivity over methanol permeability.[7] The simultaneous decrease in both methanol permeability and proton conductivity has little impact on the resulting selectivity of the membrane. The electrochemical selectivity relative to Nafion is less than 10 for most PEMs with sufficient proton conductivities (i.e., >0.01 S/cm).[5]

In this Communication, we report a remarkable electrochemical selectivity achieved in the cross-linked polymer membrane based on chain-end-functionalized fluoropolymers containing perfluorosulfonic acid side chains. Cross-linking has shown to be a promising approach to restricting the water adsorption of PEMs, thereby decreasing their methanol permeability.[8] Cross-linking reactions have been performed through reaction with the sulfonic acid groups to form inter/intrachain bridges.[9] Departing from the previous approaches, this study is based on selective placement of cross-linkable groups at both ends of the polymer chains for the formation of proton conductive networks with controlled molecular structures. It is envisioned that the cross-linking through the chain end groups would help to retain the continuity of transport channels of the linear polymer to a large extent. Furthermore, this end-linking approach keeps the main chain structures of fluoropolymer intact and thus preserves their unique physical properties, such as excellent chemical and thermal stability and strong acidity of perfluorosulfonic acid, which are highly desirable for PEM fuel cells.

As shown in Scheme 1, the copolymer of vinylidene fluoride (VDF) and perfluoro(4-methyl-3,6-dioxane-7-ene) sulfonyl fluoride (PFSVE) was prepared via a radical polymerization using 4-*tert*-butoxycarbonylaminobenzoyl peroxide as the initiator.[10] As the termination in radical polymerization of fluorinated alkenes proceeds exclusively through radical coupling,[11] the functional groups in the initiator are transferred to the polymer chain ends after polymerization. Indeed, the ^{1}H NMR spectra of the prepared P(VDF−PFSVE) clearly showed the signals at 1.58, 7.54, and 8.17 ppm corresponding to the protons from *tert*-butyl and phenyl groups, respectively. Removal of the protecting *tert*-butoxycarbonyl groups in the copolymer using iodotrimethylsilane yielded the copolymer terminated with amino groups, evidenced by complete disappearance of the peaks from *tert*-butyl protons at 1.58 ppm and emergence of a singlet at 6.19 ppm attributed to amines in the ^{1}H NMR spectrum. Figure 1 shows the ^{19}F NMR spectrum of P(VDF−PFSVE) and the assignment of the peaks are summarized in Table 1. The chemical composition of P(VDF−PFSVE) was calculated according to the following equation:

$$\text{PFSVE mol \%} = \frac{I_1/7}{(I_2+I_3+I_4+I_5+I_6+I_8+I_9+I_{11})/2} \times 100\%$$

It was found that the prepared P(VDF−PFSVE) contained 91.5 mol % VDF and 8.5 mol % PFSVE. The weight-average molecular weight of the polymer, determined by gel permeation chromatography equipped with light scattering detectors in DMF, was around 34 kDa with a polydispersity of ~1.7.

The cross-linked network was formed via thermal condensation between the amine end groups of P(VDF−PFSVE) and a curing agent, 1,3,5-benzene triisocyanate. FTIR shown in Figure 2 confirmed the formation of urea linkages by appearance of the characteristic urea bands at 3348 cm^{-1} (N−H stretching vibration), 1632 cm^{-1} (C−N stretching), and 1546 cm^{-1} (N−H bending) and absence of the absorbance at 2267 cm^{-1} assigned to isocyanate groups in the cross-linked membrane. Hydrolysis of the sulfonyl fluoride groups to the ammonium salt was achieved in triethylamine methanol/water solution, and the sulfonic acid form of the polymer was obtained by ion-exchange with HCl aqueous solution. The chemical transformation was verified by disappearance of the characteristic bands of $-SO_2F$ groups at 1462 cm^{-1} (S═O stretching vibration) and 816 cm^{-1} (S−F stretching vibration) and appearance of a broad peak attributed to acid groups at 3000−3300 cm^{-1} in the FTIR spectrum of the membrane after hydrolysis. The band at 1632 cm^{-1} was found to remain in the spectra of the acid form membrane, suggesting that the urea linkages were kept intact during hydrolysis.

The onset decomposition temperature of the cross-linked membrane evaluated by thermal gravimetric analysis is 265 °C, which is comparable with Nafion (~275 °C). Oxidative stability of the cross-linked membrane was tested by immersing membrane samples in Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 60 °C for 1 h. Hydrolytic stability was estimated by soaking the membrane at 80 °C in deionized water for 2 weeks. It was found that the cross-linked membrane remained intact and retained more than 95% of their original weight after the tests, indicating its excellent thermal, hydrolytic, and oxidative

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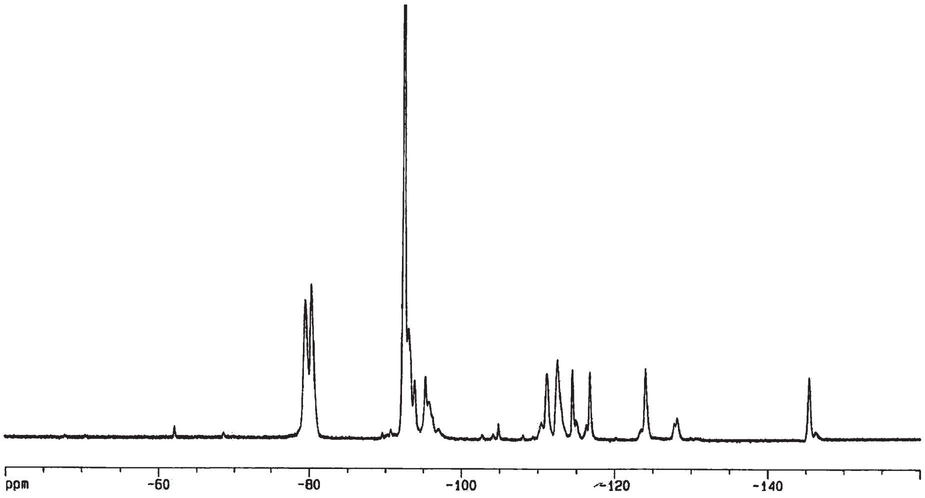
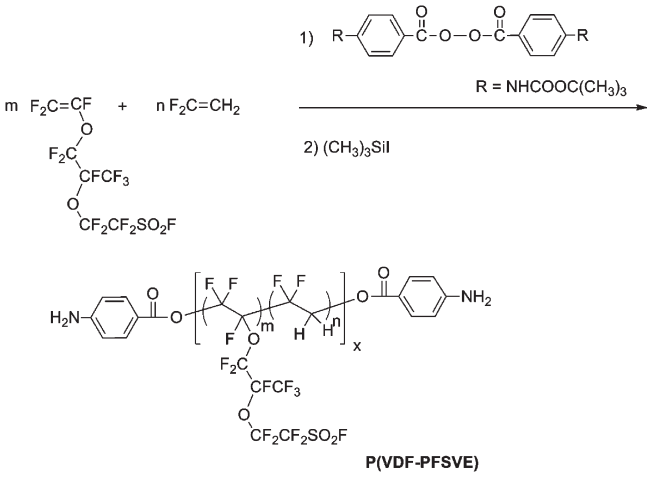


Figure 1. ^{19}F NMR spectrum of P(VDF−PFSVE).

Table 1. Chemical Shifts and Assignments of the ^{19}F NMR Peaks of P(VDF−PFSVE)

chemical shift (ppm)	sequence	integral
−77.0 to −80.0	$-\mathrm{OCH}F_2\mathrm{CF(C}F_3\mathrm{)OC}F_2\mathrm{CF_2SO_2F}$	I_1
−92.4 to −93.65	$-\mathrm{CH_2CF_2-CH_2C}F_2\mathrm{-CH_2CF_2-}$	I_2
−93.8	$-\mathrm{CF_2CF(OR_FSO_2F)-CH_2C}F_2\mathrm{-CH_2CF_2-}$	I_3
−94.8 to −95.8	$-\mathrm{CF_2CH_2-CH_2C}F_2\mathrm{-CH_2CF_2-}$	I_4
−96.0	$-\mathrm{CF_2CF(OR_FSO_2F)-CH_2C}F_2\mathrm{-CH_2CF_2-}$ $\mathrm{CF_2CF(OR_FSO_2F)-}$	I_5
−110.2 to −110.8	$-\mathrm{CH_2C}F_2\mathrm{-CF_2CF(OR_FSO_2F)-}$	I_6
−112.3	$-\mathrm{OCHF_2C}F_2\mathrm{SO_2F}$	I_7
−114.8	$-\mathrm{CH_2CF_2-CH_2C}F_2\mathrm{-CF_2CH_2-}$	I_8
−116.5	$-\mathrm{CF_2CH_2-CH_2C}F_2\mathrm{-CF_2CH_2-}$	I_9
−123.2	$-\mathrm{C}F_2\mathrm{C}F\mathrm{(OR_FSO_2F)-}$	I_{10}
−127.8	$-\mathrm{CF_2CF(OR_FSO_2F)-C}F_2\mathrm{CH_2-}$	I_{11}
−145.9	$-\mathrm{OCHF_2C}F\mathrm{(CF_3)OCF_2CF_2SO_2F}$	I_{12}

Scheme 1. Synthesis of P(VDF−PFSVE) Copolymer



stabilities. The ion exchange capacity (IEC) was determined by titration of the sulfonic acid groups with 0.02 M NaOH aqueous solution using phenolphthalein as an indicator. The water uptake of the membrane was calculated as the percentage increase from the dry sample to the membrane that has been equilibrated in water overnight at 30 °C. Compared with Nafion 117 film that has an IEC of 0.91 mequiv/g and a water uptake of 29 wt %, the cross-linked membrane with a similar IEC value of 0.84 mequiv/g exhibited a much lower water uptake of 14 wt %. Accordingly, Nafion 117 has a hydration number λ, i.e., the average number of water molecules per sulfonic acid groups, of 17.1, which is much higher than the cross-linked membrane with a λ of 8.9.

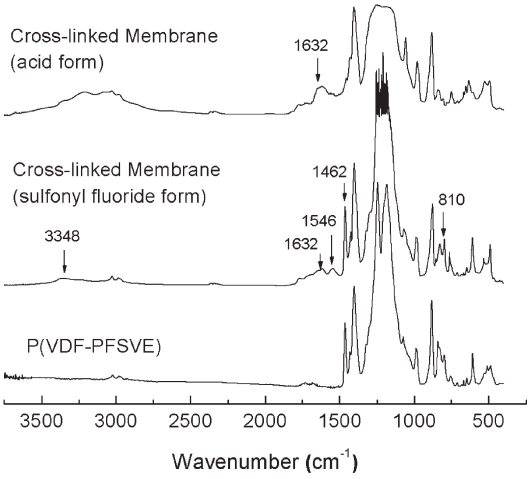


Figure 2. FTIR spectra of P(VDF−PFSVE) and the cross-linked membrane.

The proton conductivity measurements were conducted in water at 30 °C using a two-probe ac impedance method.[12] The methanol permeability was determined in a standard membrane-separated diffusion cell using 1 M methanol aqueous solution at 30 °C.[13] In accordance with water uptake and λ, the cross-linked membrane displayed a proton conductivity of 0.023 S/cm, while the conductivity of Nafion 117 was found to be 0.081 S/cm. Remarkably, the membrane exhibited methanol permeability of 1.89×10^{-9} cm^2/s, which is over 2 orders of magnitude lower than Nafion 117 with a methanol permeability of 1.92×10^{-6} cm^2/s. The selectivity of the cross-linked membrane is thus 288 times higher than that of Nafion 117. The lower methanol crossover of the cross-linked membrane has also been demonstrated in the preliminary membrane−electrode assembly (MEA) studies. The open-circuit voltages of the membrane under 3 M methanol/air conditions at 50 °C were found in a range of 0.80−0.85 V, which is greater than Nafion 117 (~0.65 V).

To rationalize the observed transport properties, the cross-linked membrane was examined by transmission electron microscopy (TEM) which can provide some valuable insights as to the ordering and size of ionic domains in membranes. For TEM measurements, polymer membranes were immersed in saturated lead acetate aqueous solution for 24 h and then washed thoroughly by

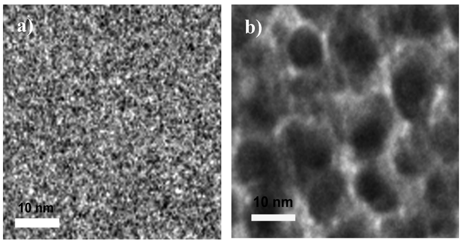


Figure 3. Cross-sectional TEM images of (a) the cross-linked membrane and (b) Nafion 117. The scale bar denotes 10 nm.

deionized water. After being dried in vacuum at 60 °C for 12 h, the membranes were cut by a microtome into 100 nm thick slices and put on copper grids. Figure 3 presents cross-sectional TEM images of the membranes stained with lead acetate. In the TEM images, the ionic domains appear as dark area due to their affinity with lead ions, and the white areas represent the hydrophobic regions of the polymer nanostructure. Nafion 117 membrane was also investigated by TEM for the purpose of comparison, in which phase-separated morphologies with the domain sizes at the scale of 5−10 nm have been clearly observed. The sizes of the ionic regions in the cross-linked membrane are markedly smaller than those of Nafion, e.g., an average of only 2−3 nm in the cross-linked membrane. Since the chemical structures of Nafion and the cross-linked membrane are similar, it is therefore confirmed that the formation of cross-linked structures restricts the size of hydrophilic domains and thus limits water absorption to yield smaller conduction channels. As methanol is a larger molecule with a smaller diffusion coefficient compared to water, the narrowing of the transport channels and reduced water content affects the diffusion of methanol much more significantly than proton transport in the cross-linked membrane;[13,14] this is likely responsible for the higher selectivity achieved in the cross-linked membrane.

In summary, we have developed a new method based on chain-end functionalization of perfluorosulfonic acid fluoropolymers for the preparation of cross-linked polymer electrolyte membranes. The resulting proton conductive network showed striking lower methanol permeability, while maintaining the proton conductivity at the same order of magnitude as Nafion. This unique transport feature gave rise to an unprecedented electrochemical selectivity that is over 10 times higher than those of the current proton conductive polymer membranes.[5] Considering the facile cross-linking conditions and controlled molecular structures, this strategy is expected to open up new opportunities in the development of high-performance polymer electrolyte membranes.

Acknowledgment. This work was supported by the National Science Foundation (CBET-0932740) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (48373-AC7).

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