Synthesis of Polyphosphazenes with Sulfonimide Side Groups

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Introduction. Proton conductive polymers are attractive materials for a wide variety of applications.[1] Over the past two decades, the potential use of these materials in devices for power generation, namely polymer electrolyte fuel cells (PEFCs), has received considerable attention.[2−5] However, the range of candidates for use as membrane materials in PEFCs is significantly limited by a number of demanding membrane requirements including good chemical and mechanical stability, high ionic conductivity, and low reactant permeability (i.e., hydrogen or methanol and oxygen). For the most part, research to date has mainly focused on sulfonic acid functionalized polymers, in particular, the perfluorosulfonic acid membranes typified by Nafion.[6]

Attractive alternatives to sulfonic acid containing materials are those containing sulfonimide groups. The high acid strength of sulfonimide acids has been well documented,[7] and DesMarteau and co-workers have been preparing perfluorinated polymeric membranes containing these acid groups since the early 1990s.[8,9] Quite recently, sulfonimide-functionalized polymers containing aromatic units have been developed. In 2000, Feiring and co-workers reported the synthesis of a novel styrene monomer bearing a pendent sulfonimide group and described its homopolymerization and copolymerization with a variety of olefinic monomers as potential electrolytes for lithium battery applications.[10,11] DesMarteau and co-workers have also described the synthesis of various trifluorovinyl aromatic ether monomers bearing both pendent sulfonimide groups and sulfonimide groups incorporated into the monomer main chain.[12,13] These monomers undergo thermal cyclopolymerization to yield perfluorocyclobutane aromatic polyethers and are quite interesting materials as potential fuel cell membranes.[14]

In the present work we describe the synthesis of a sulfonimide bearing phenolic compound and its use in the classical macromolecular substitution approach to produce a phosphazene (−P=N-backbone) polymer bearing pendent sulfonimide groups. Membranes were cast from 1,4-dioxane and were characterized before and after cross-linking with respect to their proton conductivity, water swelling, and thermal properties. A blended membrane of the sulfonimide functionalized polymer with poly(vinylidene fluoride) was also evaluated. These polymers appear to be excellent candidates for use as proton-conducting membranes in fuel cell applications.

Results and Discussion. a. Incorporation of Acid Groups into Polyphosphazenes. The incorporation of carboxylic,[15,16] phosphonic,[17] and sulfonic acids[18,19] into polyphosphazenes has been examined previously, and polyphosphazenes bearing phosphonic and sulfonic acid groups have been shown to be promising as fuel cell membrane materials, particularly for use in direct methanol fuel cells (DMFCs).[20−22] These polymers are obtained through the synthesis of poly(aryloxyphosphazenes) that are appropriate for further modification by relatively harsh reagents (e.g., SO_3) to incorporate the acidic functionalities. This method of synthesis limits the potential choice of side groups and thus the degree of tailorability in these systems, generally considered one of the main advantages to the polyphosphazene platform.[23] It is thus desirable to have the acid functionality already incorporated into a side group that can then easily be reacted with **1** or partially substituted derivatives of **1**. However, sodium salts of difunctional reagents (e.g., *p*-hydroxybenzenesulfonic acid) are, in general, not suitable reagents for reaction with unsubstituted or partially substituted poly(dichlorophosphazene) due to the tendency of both functional sites to produce polymer cross-links and insoluble products.[18] The sulfonimide side group $NaOC_6H_4SO_2NNaSO_2CF_3$ (**2a**) synthesized in this work is unique in that the sulfonimide functionality is essentially nonnucleophilic and thus permits its use in the classical macromolecular chlorine replacement of at least a partially substituted poly(dichlorophosphazene) and, potentially, the ability to easily tune final polymer properties through the choice of the cosubstituents.

b. Synthesis of Sulfonimide Side Group $NaOC_6H_4SO_2NNaSO_2CF_3$ (2a). The synthesis of the sulfonimide side group is outlined in Scheme 1. Reaction of *p*-methoxybenzenesulfonyl chloride (**3**) with trifluoromethanesulfonamide and triethylamine in anhydrous acetone afforded the triethylammonium sulfonimide **4** in ∼90% yield. Cation exchange with sodium methoxide in methanol gave the sodium sulfonimide **5**. The methyl ether group of **3** was then cleaved by treatment with sodium ethanethiolate in refluxing DMF over 3 h and gave the sodium sulfonimide-bearing sodium phenolate **2a**, which was isolated as the phenol **2b** in 80% yield.

c. Reaction of 2a with a Partially Substituted Chlorophosphazene Polymer. The synthesis of the sulfonimide-functionalized polymer **6** is outlined in Scheme 2. Poly(dichlorophosphazene) was treated with sufficient sodium 4-methylphenoxide to displace ∼50% of the initial chlorine atoms (polymers **6a**). A suspension of **2a** in THF with tetrabutylammonium bromide as a phase-transfer agent was then added, and the reaction mixture was refluxed for 48 h. The remaining chlorine atoms in polymer **6b** were then displaced by treatment with 4-methylphenoxide in a sealed autoclave at 150 °C for 30 h. The sulfonimide groups on the polymers were then converted to their acid form by multiple precipitations into concentrated HCl. Purification was accomplished by dialysis and precipitation into pentane to give polymer **6** ($M_w = 34\,000$, PDI = 2.1).

d. Membrane Characterization for Polymer 6. Membranes of polymer **6** were solution cast from diox-

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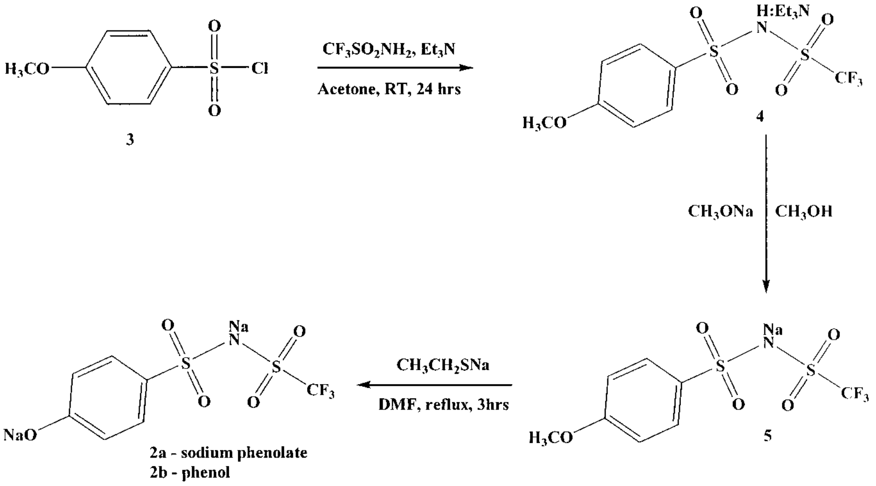
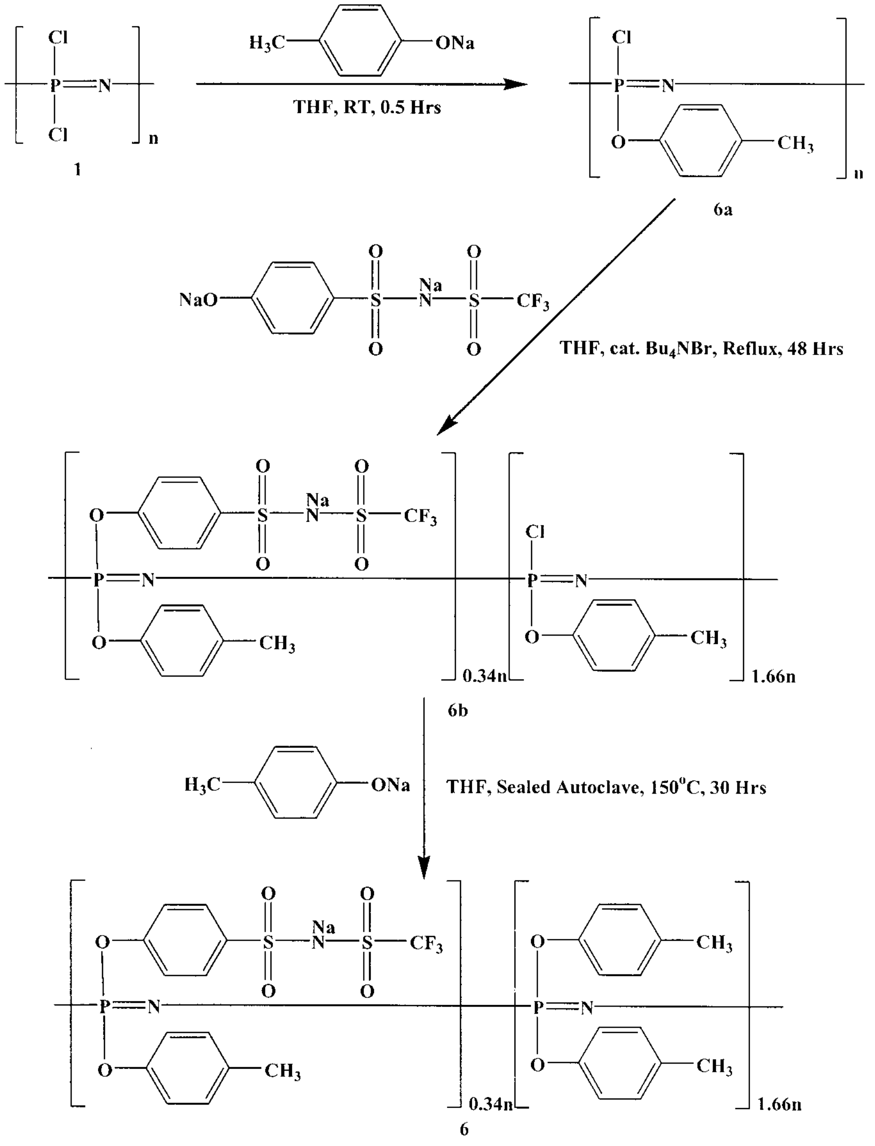
Scheme 1. Synthesis of the Sulfonimide Side Group $NaOC_6H_4SO_2NNaSO_2CF_3$ (2a)



Scheme 2. Reaction of 2a with Partially Substituted Chlorophosphazenes



ane to produce free-standing films when dry. The flexibility of films increases significantly with hydration. Characterization data for membranes of polymer **6** are given in Table 1. The experimentally measured ion-exchange capacity (IEC) of polymer **6** was 0.99 mequiv/g, which translated to an acid content of ~32% per polymer repeat unit. This was in good agreement with the acid content calculated from the ^{1}H NMR spectrum (~34%). The equilibrium water swelling of an un-cross-linked membrane was measured at 119% (based on

Table 1. Membrane Data

membrane	membrane thickness (cm)	IEC (mequiv/g)	water swelling (% H_2O/dry wt)	proton conductivity (S/cm)	cross-linking (Mrad)
6	0.013	0.99	119	0.049	0
6	0.011	0.99	73	0.071	20
6	0.009	0.99	42	0.058	40
PVDF/**6** blend	0.015		41	0.060	0
Nafion 117	0.020	0.91	30	0.100	0

membrane dry weight). As seen in Table 1, cross-linking via γ radiation had a significant effect on membrane swelling, resulting in a 40% and 65% reduction in water uptake after exposure to 20 and 40 Mrad radiation dosages, respectively. The water swelling of the un-cross-linked membrane was significantly higher than the value reported for an un-cross-linked, sulfonated polyphosphazene membrane (42% for IEC = 0.96 mequiv/g).[24] The higher swelling of the polyphosphazene sulfonimide membrane, when compared to the sulfonated polyphosphazene membrane, is not overly surprising. Previous work by DesMarteau and co-workers had shown that a sulfonyl imide ionomer that is structurally similar to Nafion 117 with a similar IEC had an equilibrium water swelling of 116% compared to the value reported for Nafion 117 of 31%.[25]

Proton conductivities in fully hydrated membranes of polymer **6** were measured at room temperature via a four-electrode electrochemical impedance spectroscopy method.[26] As shown in Table 1, it was clear that, after cross-linking with 20 Mrad radiation, the conductivity increased significantly from 0.049 to 0.071 S/cm. This may result from the acid groups being kept in close proximity to each other due to the polymer cross-links. While further cross-linking had a significant effect on water swelling, the effect on the proton conductivity was not as dramatic. The slight decrease in conductivity observed could be due to either restricted polymer mobility or insufficient hydration due to the decreased water content. These values compared favorably with those reported for a cross-linked, sulfonated polyphosphazene membrane (0.04 S/cm).[21]

e. Membrane Characterization for Polymer 6 Blended with PVDF. Pintauro and co-workers have found substantial improvements in the mechanical properties of sulfonated polyphosphazene membranes when blended with poly(vinylidene fluoride).[27] Membranes of polymer **6** blended with PVDF in a 75/25% w/w ratio were fabricated by solution-casting from DMAC. The blended membranes were translucent when dry and transparent when hydrated, indicating true blend formation rather than a phase-separated mixture. Initial characterization by differential scanning calorimetry also supports this conclusion and will be included in a future detailed report on the blending of the new sulfonimide polymers. As shown in Table 1, blending of the sulfonimide polymer with PVDF gave similar results to those found for the pure sulfonimide membrane after a cross-linking dosage of 40 Mrad. However, the blended membranes appeared to have significantly improved mechanical properties. The measured proton conductivity also compared favorably to that reported for a cross-linked membrane that consisted of 75% sulfonated polyphosphazene (IEC = 1.8 mequiv/g) blended with 25% of a copolymer of vinylidene fluoride and hexafluoropropylene (0.014 S/cm).[27]

Conclusions. A method for the synthesis of the sulfonimide containing side group, $HOC_6H_4SO_2NNaSO_2CF_3$, for incorporation into phosphazene polymers has been developed. This side group was used to prepare a sulfonimide-functionalized phosphazene polymer with an ion-exchange capacity of 0.99 mequiv/g. The initial membranes fabricated from this polymer were found to have good proton conductivities and moderate water swelling, depending on cross-link density. A blend of the sulfonimide polymer with PVDF has improved mechanical properties, low water swelling, and good proton conductivity. An advantage of this synthesis protocol is the freedom to tune the polymer composition and properties by variations in the choice of cosubstituent and the side group ratios. These polymers are currently being evaluated as membrane materials for fuel cell applications. Ongoing studies with this synthetic route will examine (1) a variety of cosubstituents, (2) blends with a variety of polymers, including PVDF, (3) thermal properties of the resulting polymer systems, (4) the development of membrane electrode assembly fabrication procedures, and (5) evaluation in a fuel cell test unit.

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Supporting Information Available: Text detailing the synthesis, ion exchange, purification, and characterization of the products discussed. This material is available free of charge via the Internet at http://pubs.acs.org.

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