COMMUNICATION

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Synthesis of Polyphosphazenes with Sulfonimide Side Groups

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Supporting Information

Experimental Section

Materials. Trifluormethanesulfonamide, 98+% was obtained from TCI and used as received. 4-methoxybenzenesulfonyl chloride, 99%, 4-methylphenol, 99%; 3-methylphenol, 99%, tetra(*n*-butyl)ammonium bromide, 99%; sodium hydride 95%; sodium methoxide, 0.5M in methanol; sodium ethanethiolate, tech., 80%; 1-4-dioxane, 99.8% (anhydrous); *N,N*-dimethylformamide (DMF), 99%; *N,N*-dimethylacetamide (DMAC), 99% and poly(vinylidene fluoride) (PVDF), M_w = 530,000; were obtained from Aldrich and used as received. Methylene chloride, chloroform, methanol, ethyl acetate (anhydrous), pentane, and hydrochloric acid (36.5-38%), were obtained from EM Science and used as received. Tetrahydrofuran (THF) was obtained from EM Science and distilled from sodium benzophenone ketyl prior to use. Acetone was obtained from EM Science and distilled from $CaSO_4$ prior to use. Triethylamine was obtained from Acros and distilled from CaH_2 prior to use. Hexachlorocyclotriphosphazene was

obtained from Ethyl Corp./Nippon Fine Chemical Co. and recrystallized from heptane and sublimed at 40 °C (0.05 mm Hg) prior to use. Poly(dichlorophosphazene) (**1**) was obtained by ring-opening polymerization of hexachlorocyclotriphosphazene.[1,2] Nafion 117, produced by E.I. du Pont de Nemours & Co., Inc., was obtained from Aldrich. Samples of Nafion 117 were pretreated as described elsewhere.[3] All reactions were carried out under an atmosphere of dry argon.

Equipment. ^{1}H (360MHz) and ^{31}P (146 MHz) NMR spectra were obtained using a Bruker AMX-360 spectrometer, ^{13}C (126 MHz) spectra were obtained using a Bruker AMX-500 spectrometer. ^{19}F spectra (282 MHz) were obtained using a Bruker DPX-300. The ^{31}P, ^{13}C, and ^{19}F spectra were proton decoupled. ^{31}P NMR spectra were referenced to external 85% H_3PO_4 with positive shifts recorded downfield from the reference. ^{1}H and ^{13}C NMR spectra were referenced to external tetramethylsilane. ^{19}F NMR spectra were referenced to external trichlorofluoromethane. All NMR spectra were obtained in d_8-THF with chemical shifts recorded in ppm and coupling constants recorded in Hz.

Molecular weights were estimated using a Hewlett-Packard HP1090 gel permeation chromatograph equipped with a HP-1047A refractive index detector. The samples were eluted with a 0.1% by weight solution of tetra(*n*-butyl)ammonium nitrate in THF. The GPC system was calibrated with polystyrene standards (Polysciences). Elemental analyses were preformed by Quantitative Technologies of Whitehouse, New Jersey.

Methods. Ion-exchange capacities (IEC) were determined by placing a known weight (approximately 0.1 g) of dry polymer in the acid form in 50 mL 2M aqueous NaCl. The sample was swirled intermittently for 48 hours. Three 10 mL aliquots were

then removed and titrated with 0.01 M NaOH to a methyl red endpoint. The IEC was then taken as the average IEC of the three samples calculated using the following equation:

$$\text{IEC} = \frac{(\text{x mL}_{\text{NaOH}}) \times (0.01\ \text{M}_{\text{NaOH}}) \times (5)}{\text{g}_{\text{dry weight}}} = \text{meq/g}$$

The proton conductivity in water-equilibrated membranes was determined using a four-electrode electrochemical impedance spectroscopy (EIS) method.[4] Equilibrium water swelling for all membranes was measured at room temperature as the weight percent water per dry membrane weight in a fully equilibrated membrane.

Synthesis of sulfonimide side group $NaOC_6H_4SO_2NNaSO_2CF_3$, 2a. Triethylamine (40.0 mL, 0.29 mol) was slowly added dropwise via addition funnel to a solution of 4-methoxybenzenesulfonyl chloride (**3**; 25.0 g, 0.12 mol) and trifluoromethanesulfonamide (20 g, 0.13 mol) in 250 mL freshly distilled acetone and solution stirred at room temperature for 48 hours. The resulting mixture was concentrated via reduced pressure rotary evaporation. To the residue was added 250 mL 1.0 M HCl and the solution extracted with three 250 mL portions methylene chloride. The organic extracts were combined, dried over anhydrous sodium sulfate, and solvent removed via reduced pressure rotary evaporation followed by further drying at < 0.1 mmHg for 72 hours to give 45.5 g (~90% based on **3**) of a brown oil which was the triethylammonium salt **4**. ^{1}H NMR (δ, d_8-THF) 1.23 (t, 9H, CH_3), 3.15 (q, 6H, CH_2), 3.70 (s, 3H, CH_3O), 6.83 (d, 2H, aromatic), 7.71 (d, 2H, aromatic), 8.10 (s, 1H, NH). This salt was dissolved in 150 mL methanol and treated with 148 mL of 0.5 M sodium methoxide in methanol. After stirring for 20 minutes, the solution was evaporated via reduced pressure rotary evaporation leaving a tan solid. The solid was redissolved in 100

mL methanol and evaporated via reduced pressure rotary evaporation followed by drying at < 0.1 mmHg for 72 hours to give the sodium salt **3**. This solid was dissolved in 800 mL DMF and sodium ethanethiolate (30.0 g, 0.29 mol for 80%) added. The reaction was brought to reflux for three hours, after which the bulk DMF was removed via vacuum distillation. The remaining residue was further concentrated under vacuum at ~35°C for 48 hours. The residue was then dissolved in 250 mL distilled water and 250 mL saturated sodium chloride added. The aqueous solution was then extracted with two 500 mL portion THF that were discarded. The aqueous solution was then treated with 25 mLs concentrated HCl to pH = 3 (to convert the sodium phenolate **2a** to the phenol **2b**) and extracted with three 250 mL portions THF. The organic extracts were then dried over anhydrous sodium sulfate and concentrated via reduced pressure rotary evaporation. The solid residue was dissolved in ethyl acetate and the solution filtered to remove insoluble products. Final purification was afforded by precipitation of **2b** as a fine white powder from ethyl acetate by the addition of chloroform. **2b** was then collected via filtration and dried at < 0.1 mmHg over 7 days at ~65°C to give 28.2 g (80 % yield based on **4**). The overall isolated yield based on reactant **3** was ~70 %. ^{1}H NMR (δ, d_8-THF) 6.78 (d, 2H, aromatic), 7.74 (d, 2H, aromatic), 8.87 (s, 1H, phenol proton). ^{19}F NMR (δ, d_8-THF) –81.32 (s, CF_3). ^{13}C NMR (δ, d_8-THF) 114.7 (aromatic), 120.8 (q, $^{1}J_{CF}$ = 323 Hz, CF_3), 128.5 (aromatic), 136.1 (aromatic-S), 160.7 (aromatic-O). MS (ESI) m/e 304 (M-1).

Synthesis of polymer 6. 4-methylphenol (3.73 g, 0.035 mol) was dissolved in 10 mL THF and added dropwise to a suspension of sodium hydride (0.83 g, 0.035 mol) in 60 mL THF. **2b** (4.06 g, 0.012 mol) was dissolved in 50 mL THF and added dropwise to a

suspension of sodium hydride (0.30 g, 0.012 mol) and tetra(*n*-butyl)ammonium bromide (0.4 g) in 50 mL THF and let to stir over 16 hours. The sodium 4-methylphenoxide was added dropwise to a stirring solution of poly(dichlorophosphazene) (**1**) (4.0 g, 0.035 mol) in 400 mL THF and stirred for 30 minutes. The sodium phenoxide solution of **2b** was then added dropwise and the reaction heated to reflux for 48 hours. 4-methylphenol (7.45 g, 0.069 mol) was dissolved in 10 mL THF and added dropwise to a suspension of sodium hydride (1.57 g, 0.065 mol) in 40 mL THF. The polymer solution was then cooled to room temperature and transferred to an autoclave. The sodium 4-methylphenoxide solution was added and the autoclave sealed and heated to 150 °C. After 30 hours the autoclave was cooled to room temperature and the contents concentrated via rotary evaporation till viscous. The polymer was precipitated into 6 M aqueous HCl and allowed to air dry in a fume hood. The polymer was then reprecipitated from dioxane into concentrated HCl and allowed to air dry. This precipitation was repeated 3 times. After the final precipitation the polymer was placed in distilled water and soaked for 16 hours. The polymer was then dried under vacuum over 24 hours. The polymer was dissolved in a 50/50 (v/v) solution of dioxane/methanol, placed in 12-14K dialysis tubing, and dialyzed against a 50/50 (v/v) solution of dioxane/methanol. At 24-hour intervals the dialysis solution was changed to 75/25 dioxane/methanol, dioxane, and dioxane. The polymer solution was vacuum filtered, concentrated via reduced pressure rotary evaporation until viscous, precipitated into pentane, and dried at < 0.1 mmHg over at least 48 hours to yield 8.65 g (77% based on **1**) of a tan solid. ^{1}H NMR (δ, d_8-THF) 2.10 (s, 3H x 0.83, CH_3) 6.4-7.1 (multiple peaks, 4H x 0.83 + 2H x 0.17, aromatic), 7.45 (s, 2H x 0.17, aromatic), 8.0-12.0 (concentration dependent, broad, s, 1H x 0.17, NH).

^{19}F NMR (δ, d_8-THF) –78.24 (s, CF_3). ^{31}P NMR (δ, d_8-THF) –23 to –16 (broad multiple peaks, phosphazene phosphorus). ^{13}C NMR (δ, d_8-THF) 21.0, 120.3 (q, $^1J_{CF}$ = 322 Hz), 121-123 (multiple peaks), 129-131 (multiple peaks), 133-135 (multiple peaks), 135.1, 149-151 (multiple peaks), 157.2. M_w = 34,000 with PDI = 2.1. Elemental analysis: found (calculated based on 17% sulfonimide side group); C, 50.56 (51.53); H, 3.70 (4.12); N, 5.55 (5.75); S, 6.28 (6.68); P, 9.61 (9.49); F, 6.09 (5.94); Cl, <0.10 (0.00); Na, 307 ppm (0 ppm).

Membrane casting. Membranes of polymer **6** were solution-cast from 1,4-dioxane as ~10% solutions (w/v) onto a poly(propylene) plate and the solvent allowed to evaporate at room temperature and pressure over 48 hours. The membranes were then dried under vacuum at ~50°C for an additional 48 hours. Cross-linked versions of these membranes were obtained by ^{60}Co gamma-radiation. Blended membranes of 75% polymer **6** (w/w) and 25% PVDF (w/w) were solution-cast from DMAC as ~10% solutions (w/v) onto a poly(propylene) plate and dried in a vacuum oven under vacuum at room temperature for 24 hours followed by drying at ~65°C for an additional 72 hours. The membranes were then soaked in water for at least 24 hours, with the water replaced intermittently, followed by drying at <0.1 mmHg over 48 hours.

References

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