

Novel Aromatic Polymers with Pendant Lithium Perfluoroalkylsulfonate or Sulfonimide Groups

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Received May 23, 2000

ABSTRACT: Styrenes with pendant lithium perfluoroalkyl ether sulfonate or sulfonimide groups readily homopolymerized and copolymerized with olefinic monomers to provide moderate to high molecular weight ionomers. Comonomers included styrene, methyl methacrylate, acrylonitrile, and acrylates. In addition, soluble polymers containing both mobile lithium ions and immobilized tetraalkylammonium cations were prepared. Cross-linked polymers were obtained by copolymerization of the functionalized styrenes with difunctional comonomers or by cocuring with an unsaturated elastomer. Polyesters with pendant lithium perfluoroalkylsulfonate groups were obtained by condensation polymerization of functionalized isophthalate monomers with bis(hydroxyethyl)terephthalate. Surprisingly, most of the ethylene glycol units in the polymers were converted into poly(ethylene glycol) segments during polymerization. Lithium ion conductivities of 10^{-4} – 10^{-3} S/cm were shown by selected polymers in solution or as solvent swollen films.

Introduction

Fluorinated ionomers have been of scientific and commercial interest for several decades.^{1,2} The best known examples are perfluorinated polymers prepared by copolymerization of tetrafluoroethylene with perfluorinated vinyl ethers, such as $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$, followed by hydrolysis of the sulfonyl fluoride groups. The perfluorinated backbone provides high chemical and thermal stability while the side chains function as exceptionally strong acids in their sulfonic acid form or as weakly coordinating anions in their conjugate base form. Current and potential applications include membranes for chloroalkali cells, batteries and fuel cells, and strong solid acid catalysts.^{3,4}

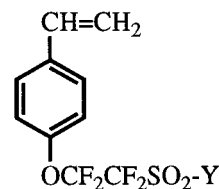
Perfluorinated polymers have special value in harsh environments, such as chloroalkali cells, due to their high stability. However, highly fluorinated polymers can be difficult to process. In addition, the perfluorinated vinyl ether monomers are costly, relatively unreactive during polymerization,² and can be polymerized only by a conventional free radical mechanism with a limited range of comonomers. Modern controlled polymerization techniques, such as living radical, anionic, or cationic, cannot be used with fluorinated vinyl ethers so polymer architectures are limited.

Partially fluorinated polymers with pendant fluoroalkylsulfonate groups have been reported. The polymer backbones include silicone⁵ and epoxy^{6,7} which provide materials with improved processability. However, the linkages between the fluoroalkylsulfonate groups and the polymer backbones are usually relatively sensitive alkyl ether or amide^{8,9} groups.

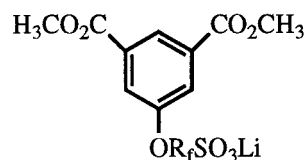
We considered that aromatic polymers with the fluoroalkylsulfonate groups attached to aromatic rings by robust ether linkages could offer better stability and synthetic versatility. Polystyrenes with pendant fluoroalkylsulfonate groups seemed of special interest because styrenes polymerize with many comonomers by anionic, cationic, coordination, and free radical processes and so can generate polymers with novel architectures. Other aromatic polymers with fluoroalkylsulfonate sub-

stituents, such as polyesters, -amides, or -imides, might also offer unusual properties.

We now report that the novel styrenes **1**, with a pendant fluoroalkylsulfonate group, and **2**, with the even more weakly coordinating bis(fluoroalkylsulfonimide) group,^{10,11} readily homo- and copolymerize under conventional free radical conditions to form soluble polymers with moderate to high molecular weights. Insoluble copolymers were obtained by using difunctional comonomers or by cocuring **1** or **2** with an unsaturated elastomer. In addition, copolyesters with pendant perfluoroalkylsulfonate groups were prepared from bis(hydroxyethyl)terephthalate, ethylene glycol, and the new isophthalate monomers **3** or **4** by standard condensation polymerizations. Lithium ion conductivities were obtained on many of the polymers in solution or as solvent swollen films.



1. Y = OLi
2. Y = N(Li)SO₂CF₃



3. R_f = CF₂CF₂
4. R_f = CF₂CFHOCF₂CF(CF₃)OCF₂CF₂

Experimental Section

Materials. Monomers **1**–**4** were prepared as described.¹² Styrene, acrylonitrile, methyl methacrylate, butyl acrylate, and

ethylhexyl acrylate were obtained from the Aldrich Chemical Co. and were passed through short columns of basic alumina and vacuum distilled immediately before use. Methyl acrylate, poly(ethylene glycol), ethyl ether methacrylate (average M_n 246), poly(ethylene glycol) diacrylate (average M_n 575), and anhydrous DMF were obtained from Aldrich and used as received. Polymer grade ethylene glycol and bis(hydroxyethyl) terephthalate were obtained from DuPont and used as received. Ammonium persulfate (Aldrich), Vazo 52 (2,2'-azobis-(2,4-dimethylpentanenitrile) (DuPont), benzoyl peroxide (Aldrich), ethylene carbonate (Aldrich, 98%), dimethyl carbonate (Alfa Aesar, 99%), and propylene carbonate (E. M. Industries, Selectipur) were used as received.

Techniques. Proton and fluorine NMR spectra were obtained on a Bruker DRX 500 instrument. Carbon NMR spectra were obtained on a Varian 400 MHz Unity instrument using an inverse gate pulse for both H and F to suppress the nuclear Overhauser effect. The recycle time was 12.7 s. A Brookhaven Instrument BI-200SM light scattering goniometer was used for light scattering measurements with an argon ion laser at wavelength 488 nm and power of 200 mW. Polyester viscosities were determined in mixtures of methylene chloride and trifluoroacetic acid on a Viscotek Y900 instrument. SEC molecular weight determinations were done on a triple-detector instrument using Waters Alliance 2690 pumps, Shodex GPC HFIP800P and GPC HFIP80M columns in series, Viscotek T-60A dual laser light scattering/viscosity detectors, and Waters 410 refractive index detector. Calculations were done using Viscotek TriSEC v. 3.0 software. Column temperatures were 35 °C, and flow rates were 1.0 mL/min. DSC and TGA measurements were done on a TA5000 thermal analysis system, DSC model #2910 autosampler, and TGA model #2950 autosampler.

Homopolymerization of 1. Monomer **1** (12.24 g, 0.04 mol) was dissolved in 75 mL of deionized water. This solution was concentrated under vacuum to remove about 60 mL of water to eliminate organic solvents complexed to the salt. Deionized water (40 mL) was added, and this solution was deoxygenated by two freeze, evacuate, thaw cycles. Ammonium persulfate (0.018 g, 0.00008 mol) was added, and the solution was again deoxygenated by freeze, evacuate, and thaw cycles. The solution under argon was then heated in a 61–63 °C oil bath for 26 h. The solution was cooled to room temperature and transferred to 3500 MW cutoff dialysis tubing and dialyzed against three changes of 1 L deionized water over several days. The aqueous solution in the dialysis tubing was concentrated on a rotary evaporator, and the residue was dried at 100 °C and 0.1 mm giving 9.33 g (76%) of faintly yellow solid homopolymer of **1**. $^1\text{H NMR}$ (δ , D_2O): 1.50 (bs, 3H), 6.5 and 7.0 (bs, 5H). $^{19}\text{F NMR}$ (δ , D_2O): -82.02 (2F), -117.58 (2F). M_w , determined by light scattering in water containing 0.25% LiCl, was 1.6×10^5 . A film of the polymer cast from water followed by air-drying was light amber and self-supporting but brittle.

Anal. Calcd for $\text{C}_{10}\text{H}_7\text{O}_4\text{F}_4\text{SLi} \cdot 1.67\text{H}_2\text{O}$: C, 35.73; H, 3.08; F, 22.61; Li, 2.06; S, 9.54. Found: C, 35.72; H, 3.17; F, 19.43; Li, 2.27; S, 10.03.

Homopolymerization of 2. During purification, **2** (17.4 g) was dissolved in ether in the air, and hexane was added to precipitate a gummy solid. It was recognized from the solubility characteristics and loss of olefinic resonances in the proton NMR spectrum that the monomer had polymerized. The solid was dissolved in 50 mL of deionized water and was dialyzed for several days against 2×2 L of deionized water in a 3500 MW cutoff dialysis tube. The solution in the tube was concentrated and dried at 100 °C and 0.1 mm pressure to give 10.9 g (63%) of off-white solid homopolymer of **2**. $^1\text{H NMR}$ (δ , CD_3OD): 1.50 (broad, 3H), 6.5 and 6.9 (broad, 5H). $^{19}\text{F NMR}$ (δ , CD_3OD): -78.81 (3F), -79.47 (2F), -114.8 (2F).

Anal. Calcd for $\text{C}_{11}\text{H}_7\text{F}_7\text{S}_2\text{O}_5\text{NLi} \cdot 2\text{H}_2\text{O}$: C, 27.92; H, 2.34; N, 2.96; F, 28.10; Li, 1.47; S, 13.55. Found: C, 27.98; H, 2.37; N, 2.97; F, 26.65; Li, 1.40; S 13.84.

Copolymerization of 1 and Styrene. A polymer tube was charged with 4.59 g (0.015 mol) of **1**, 8.0 mL of DMF, 8.84 g (0.085 mol) of styrene, and 0.05 g of benzoyl peroxide. The solution was frozen, evacuated, purged with argon, and thawed

several times and heated under argon in a 60 °C oil bath for 66 h. After cooling to room temperature, the solid mass was dissolved in 50 mL of DMF and precipitated into excess ether. The ether was decanted, and the gummy residue was washed with hexane and dried at 100 °C and 0.5 mm giving 11.8 g (88%) of white copolymer. A clear, colorless film could be cast from a mixture of THF with 2% DMF. $^1\text{H NMR}$ (δ , DMF- d_7): 1.65 and 2.0 (broad), 6.8 and 7.2 (broad). $^{19}\text{F NMR}$ (δ , DMF- d_7): -80.9 (2F), -116.4 (2F). $^{13}\text{C NMR}$ (δ , DMF- d_7): 118.3 and 114.09 (CF_2 's), 147.77 (aromatic C next to O), 146.05 (aromatic C substituted by CH), 122.09 (aromatic C ortho to O), 128.7–128.2 (remaining aromatic C), 40.97 (CH) and 42–48 (CH_2). From integration of appropriate resonances in the F and H decoupled ^{13}C spectrum, the polymer contained 88% styrene and 12% of functionalized styrene. DSC showed a T_g at 136 °C on second heat.

Anal. Found: C, 71.52; H, 5.81; F, 8.76; Li, 0.72; S, 3.55.

Copolymerization of 2 and Styrene. The above procedure was followed using 4.37 g (0.01 mol) of **2**, 9.36 g (0.09 mol) of styrene, 8.0 mL of DMF, and 0.048 g of benzoyl peroxide. Polymerization was conducted for 96 h. The solid mass was dissolved in additional DMF and filtered. The polymer was precipitated into 1 L of ice water, filtered, and dried at 96 °C and 0.05 mm giving 8.38 g (68%) of copolymer. $^1\text{H NMR}$ (δ , DMF- d_7): 1.65 and 2.0 (broad), 6.8 and 7.2 (broad). $^{19}\text{F NMR}$ (δ , acetone- d_6): -78.8 (3F), -79.7 (2F), -115.4 (2F). DSC showed a T_g at 108 °C on second heat.

Anal. Found: C, 70.31; H, 6.07; N, 1.75; F, 8.69; S, 4.63; Li, 0.44.

From the elemental analysis for percent carbon, the polymer composition was 89% styrene and 11% **2**.

Copolymerization of 1 and Methyl Methacrylate. A polymer tube was charged with 3.06 g (0.01 mol) of **1**, 9.0 g (0.09 mol) of methyl methacrylate, and 0.05 g of Vazo 52. The solution was frozen, evacuated, purged with argon, and thawed several times. The polymer tube was sealed and heated in a 50 °C oil bath for 22 h. After cooling to room temperature, the solid was dissolved in 250 mL of acetone with warming and filtered. The acetone was evaporated, and the solid polymer was dried at 100 °C and 0.05 mm giving 11.6 g of product. $^1\text{H NMR}$ (δ , acetone- d_6): 0.6–3.0 (m), 3.65 (s), 6.8–7.5 (m). From integration of the appropriate peaks, the polymer contained 88 mol % methyl methacrylate and 12 mol % of **1**. $^{19}\text{F NMR}$ (δ , acetone- d_6): -80.9 (2F), -116.6 (2F). A clear, flexible film of the polymer could be cast from acetone solution.

Anal. Found: C, 54.39; H, 6.77; F, 4.86; Li, 0.50; S, 2.62.

Copolymerization of 2 and Methyl Methacrylate. The above procedure was followed using 4.36 g of **2** in place of **1**, giving 12.4 g (93%) of polymer. $^1\text{H NMR}$ (δ , acetone- d_6): 0.6–3.1 (m), 3.65 (s), 6.9–7.7 (m). From integration of the appropriate peaks, the polymer contains 88 mol % methyl methacrylate and 12 mol % of **2**. $^{19}\text{F NMR}$ (δ , acetone- d_6): -78.8 (s, 3F), -79.7 (m, 2F), -115.5 (s, 2F). DSC showed a T_g at 150 °C on second heat.

Anal. Found: C, 49.77; H, 6.06; N, 1.03; F, 9.93; S, 5.08; Li, 0.50.

Copolymerization of 1 and Acrylonitrile. The above procedure was followed using 3.06 g (0.01 mol) of **1**, 10 mL of DMF, 4.77 g (0.09 mol) of acrylonitrile, and 0.050 g of Vazo 52. The solid product was dissolved in 50 mL of DMF, filtered, and precipitated into a large excess of ether. After drying at 100 °C and 0.05 mm, 7.59 g (97%) of white polymer was isolated. $^1\text{H NMR}$ (δ , DMF- d_7): 2.30 (b), 3.32 (b), 7.3–7.5 (b) plus absorptions suggesting small amounts of DMF. By integration of the aromatic versus the aliphatic peaks, the polymer contained 12 mol % **1** and 88 mol % acrylonitrile. DSC showed a T_g at 73 °C on second heat.

Anal. Found: C, 54.72; H, 4.51; N, 15.55; F, 8.36; Li, 0.81; S, 4.04.

Copolymerization of 1 and Methyl Acrylate. In a glovebox, 2.8 g (0.0091 mol) of **1**, 7.2 g (0.0827 mol) of methyl acrylate, 35 mg (1.41×10^{-4} mol) of Vazo 52, and 20 mL of DMF were combined in a Schlenk flask. The flask contents were stirred to dissolve, placed under argon, and heated at 35 °C for 48 h. The polymer was dissolved in DMF/acetone and

precipitated into water. The polymer was redissolved in acetone and precipitated once into hexane and twice into water. The final polymer was dried under vacuum at 70 °C to give 4.85 g (49%) of copolymer. Films were prepared by dissolving 0.5 g of polymer in acetone and casting the solution into a 5.5 cm diameter Teflon Petri dish. ¹⁹F NMR (δ , acetone-*d*₆): -82.4 (2F), -118.1 (2F). ¹³C NMR (δ , acetone-*d*₆): 174.9, 129.2, 122.1, 51.2, 41.3, 35.1 (b). ¹H NMR (δ , acetone-*d*₆): 7.2 (b), 3.6, 2.9, 2.8, 2.1, 3.5, 2.4 (b), 1.9 (b), 1.7 (b), 1.7–1.5 (b). Proton NMR indicated 4 mol % ionomeric groups based on integration of aromatic signal and methyl group signal of the methyl acrylate. Molecular weight (SEC, HFIP + 0.01 M Na triflate): $M_n = 5.7 \times 10^4$, $M_w = 2.0 \times 10^5$, $M_w/M_n = 3.6$.

Anal. Found: C, 53.16, 53.13, 52.78; H, 6.77, 6.79, 6.36; F, 3.24, 3.07, 4.81; Li, 0.28, 0.47, 0.38; S, 1.91, 1.98, 2.39. Elemental analysis indicated 5–6 mol % **1** in the polymer.

Copolymerization of 1 and Butyl Acrylate. The above procedure was followed using 3.74 g (0.0122 mol) of **1**, 6.26 g (0.0489 mol) of butyl acrylate, and 45 mg (1.81×10^{-4} mol) of Vazo 52. Polymerization was at 45 °C for 24 h. The polymer was dissolved in acetone/THF and precipitated into water. The polymer was then precipitated from THF into water and into hexane and from acetone into hexane and dried to obtain 4.8 g (48%) of copolymer. Films could be cast by dissolving 0.5 g of polymer in THF and casting the solution into a 5.5 cm diameter Teflon Petri dish. ¹⁹F NMR (δ , acetone-*d*₆): -82.4 (2F), -118.1 (2F). ¹³C NMR (δ , acetone-*d*₆): 175.5, 130.3, 123.1, 65.3, 42.8, 36.6 (b), 31.9, 20.3, 14.5. ¹H NMR (δ , acetone-*d*₆): 7.1 (b), 4.1, 3.9 (b), 3.2, 3.1, 2.4, 1.9–1.2, 0.9. TGA (N₂, 10 °C/min): onset of decomposition at 275 °C. DSC (N₂, -100 to 225 °C, 10 °C/min): no T_m detected. Molecular weight (SEC, HFIP + 0.01 M Na triflate): $M_n = 9.8 \times 10^5$, $M_w = 1.4 \times 10^6$, $M_w/M_n = 1.4$. The polymer was not totally soluble in this solvent, so a dn/dc value of 0.173 was used.

Anal. Found: C, 54.34, 54.19; H, 6.95, 6.91; F, 9.46, 9.31; Li, 0.71, 0.80; S, 4.40, 4.47.

Copolymerization of 2 with Butyl Acrylate. In a glovebox, 2.75 g (0.0063 mol) of **2**, 7.25 g (0.057 mol) of butyl acrylate, and 45 mg (1.81×10^{-4} mol) of Vazo 52 were combined in a Schlenk tube and stirred to dissolve. The flask was placed under argon and heated at 40 °C for 24 h, followed by 45 °C for 24 h. The resultant polymer was dissolved in THF and precipitated into water (3 \times). The polymer was then dissolved in THF and precipitated twice into hexane. The polymer was dried under vacuum to give 2.4 g (24%) of polymer. Films were cast by dissolving 0.5 g of polymer in 1:1 THF/acetone and casting the solution into a 5.5 cm diameter Teflon Petri dish. A small amount of gelled material was present which did not dissolve. NMR spectra refer to the soluble fraction. ¹⁹F NMR (δ , THF-*d*₈): -80.4 (3F), -81.4 (2F), -117.2 (2F). ¹³C NMR (δ , THF-*d*₈): 175.1, 130.1, 122.7, 64.9, 42.6, 36.1, 31.8, 20.2, 14.3. ¹H NMR (δ , THF-*d*₈): 7.1 (b), 4.0, 3.1, 2.0–3.0 (b), 1.1–1.8 (b), 0.8. The ratio of aromatic to methyl peak of butyl acrylate indicates approximately 15 mol % ionomeric monomer incorporated. TGA (N₂, 10 °C/min): onset of decomposition at 275 °C. DSC (N₂, -100 to 250 °C, 10 °C/min): no T_m detected. Molecular weight (SEC, HFIP + 0.01 M Na triflate): $M_n = 2.0 \times 10^5$, $M_w = 8.9 \times 10^5$, $M_w/M_n = 4.4$.

Anal. Found: C, 52.49, 52.24; H, 6.90, 6.84; N, 1.19, 1.19; F, 10.02, 9.83; S, 4.82, 4.93; Li, 0.48, 0.51. Elemental analysis indicated 12 mol % incorporation of the ionic monomer.

Copolymerization of 1 with Ethylhexyl Acrylate. In a glovebox, 1.56 g (0.0051 mol) of **1** was dissolved in 20 mL of DMF and added to 8.44 g (0.046 mol) of ethylhexyl acrylate in a Schlenk tube, followed by the addition of 48 mg (1.93×10^{-4} mol) of Vazo 52. The flask was placed under argon and heated at 40 °C for 24 h. The resultant polymer was dissolved in additional THF and precipitated into water, followed by two precipitations from THF into hexane. The polymer was dried under vacuum at 65 °C, giving 3.2 g (32%) of copolymer. Films could be melt pressed by placing the polymer between Teflon sheets, preheating 2 min at 150 °C, pressing at 2000 lb/in.², and then cooling under pressure. The polymer picks up moisture rapidly from air and becomes a gum. Films could also

be solution cast by dissolving 0.5 g of polymer in 15 mL of THF and casting the solution into a 5.5 cm diameter Teflon Petri dish. ¹⁹F NMR (δ , acetone-*d*₆): -84.4 (2F), -120.0 (2F). ¹H NMR (δ , THF-*d*₈): 7.1 (b), 3.95 (b), 3.8 (b), 2.9, 2.3 (b), 1.8–2 (b), 1.5–1.7 (b), 1.4, 1.2 (b), 0.9. Ratio of aromatic styrene signal to a methyl signal from the ethylhexyl acrylate indicated approximately 10 mol % incorporation of **1**. ¹³C NMR (δ , THF-*d*₈): 172.4, 127.4, 120.3, 40.1, 37.4, 28.9, 27.5, 22.7, 12.1, 8.2. TGA (N₂, 10 °C/min): onset of decomposition at 250 °C. DSC (N₂, -100 to 200 °C, 10 °C/min): no T_m detected. Molecular weight (SEC, solvent HFIP + 0.01 M Na triflate): $M_n = 1.4 \times 10^5$, $M_w = 3.2 \times 10^5$, $M_w/M_n = 2.3$.

Anal. Found: C, 65.62, 65.51; H, 9.48, 9.69; F, 3.82; Li, 0.34; S, 1.86.

Terpolymerization of 1 with Styrene and Acrylonitrile. A polymer tube was charged with 3.06 g (0.011 mol) of **1** and 8 mL of DMF. The solution was placed under vacuum for 1 h at room temperature to remove volatile impurities. Styrene (5.41 g, 0.052 mol), acrylonitrile (2.01 g, 0.038 mol), and benzoyl peroxide (0.048 g) were added. The solution was frozen, evacuated, purged with argon, and thawed several times and then heated under an argon atmosphere in a 60 °C oil bath for 22 h. After cooling to room temperature, the solid mass was dissolved in DMF, filtered, and poured slowly into excess ether. The sticky precipitate was dried under vacuum at 95 °C to give 10.7 g (100%) of white polymer. ¹H NMR (δ , THF-*d*₈): 1.70–2.2 (br), 6.8 and 7.05 (br) and 2.0 (br). ¹⁹F NMR (δ , THF-*d*₈): -81.5 (2F), -117.2 (2F); IR 2237 cm⁻¹(CN). ¹³C NMR (δ , DMF-*d*₇): 118.3 and 114.09 (CF₂'s), 122.08 (aromatic carbon ortho to O and CN from acrylonitrile), 147.77 (aromatic carbon adjacent to O), 146.0 to 140 (quaternary carbons), 128.4 to 127.1 (remaining aromatic carbons), 38.83 (aliphatic CH from styrenes) 28.5 to 26.6 (aliphatic CH from acrylonitrile), and 43 to 40 (CH₂). From integration of the carbon NMR spectrum, the polymer contained 52 mol % styrene, 39 mol % acrylonitrile, and 9 mol % **1**. DSC showed a T_g at 134 °C on second heat.

Anal. Found: C, 69.03; H, 6.00; N, 6.37; F, 6.59; S, 2.95; Li, 0.52.

Terpolymerization of 1 with Styrene and Butyl Acrylate. The above procedure was followed using 3.06 g (0.01 mol) of **1**, 6.55 g (0.063 mol) of styrene, and 3.46 g (0.027 mol) of butyl acrylate. The crude product, dissolved in DMF, was precipitated by adding to excess ice water in a blender. After drying in a vacuum oven at 50 °C, 7.10 g (54%) of polymer was obtained. ¹H NMR (δ , DMF-*d*₇): 1.05 (br) 1.3–2.6 (br), 3.8 (br), 6.95 and 7.40 (br). ¹⁹F NMR (δ , DMF-*d*₇): -81.0 (2F), -116.6 (2F). ¹³C NMR (δ , DMF-*d*₇): 118.4 and 114.1 (CF₂'s), 122.2 (aromatic carbon ortho to O), 148.5 (aromatic carbon adjacent to O), 143.0 to 146.9 (quaternary carbons), 125.0 to 130.0 (remaining aromatic carbons), 38.85 (aliphatic CH from styrenes), 42 to 48 (CH₂ from styrenes), 175.9 (ester carbonyl), 64.06 (OCH₂), 14.06 (CH₃), 19.75 and 13.03 (remaining CH₂'s from ester). From integration of the carbon NMR spectrum, the polymer contained 66 mol % styrene, 27 mol % butyl acrylate, and 7 mol % **1**.

Anal. Found: C, 73.55; H, 7.32; F, 4.21; Li, 0.38; S, 1.97.

Copolymerization of 1, 2, and Butyl Acrylate. In a glovebox, 1.0 g (0.00327 mol) of **1**, 1.43 g (0.0033 mol) of **2**, 7.56 g (0.059 mol) of butyl acrylate, and 45 mg (1.81×10^{-4} mol) of Vazo 52 were combined in a Schlenk tube and stirred to dissolve. The flask was placed under argon and heated at 40 °C for 24 h, followed by 45 °C for 24 h. The resultant polymer was dissolved in acetone/THF and precipitated into water (2 \times). The polymer was then dissolved into acetone/THF (3:1) and precipitated into hexane (2 \times). The polymer was dried under vacuum at 60 °C to give 3.3 g (33%). Films could be obtained by dissolving 0.5 g of polymer in 20 mL 3:1 acetone/THF and casting the solution into a 5.5 cm diameter Teflon Petri dish. TGA (N₂, 10 °C/min): onset of decomposition at 300 °C. DSC (N₂, -100 to 250 °C, 10 °C/min): no T_m detected. ¹⁹F NMR (δ , THF-*d*₈): -80.2 (3F), -81.2 (2F), -82.6 (2F), -117.1 (2F), -118.4 (2F). ¹⁹F NMR integration indicated equal amounts of **1** and **2**. ¹³C NMR (δ , THF-*d*₈): 175.0, 64.9, 42.5, 36.2 (b), 31.9, 20.2, 14.3. ¹H NMR (δ , THF-*d*₈): 7.1, 4.0, 2.9,

2.3, 1.8, 1.7–1.2 (b), 0.9. ¹H NMR integration indicated 7 mol % ionomeric content based on integration of aromatic signal to methyl signal of butyl acrylate. Molecular weight (SEC, solvent HFIP + 0.01 M Na triflate) $M_n = 7.7 \times 10^4$, $M_w = 6.4 \times 10^5$, $M_w/M_n = 8.4$. The polymer was not totally soluble so a dn/dc value of 0.173 was used.

Anal. Found: C, 58.24, 58.52; H, 8.32, 8.12; N, 0.48, 0.41; F, 5.69, 5.89; Li, 0.33, 0.35; S, 3.70, 3.47.

Copolymerization and Cross-Linking of 1, Poly(ethylene glycol) Ethyl Ether Methacrylate, and Poly(ethylene glycol) Diacrylate. Poly(ethylene glycol) ethyl ether methacrylate (8.79 g, 3.6×10^{-2} mol) and monomer 1 (1.21 g, 4.0×10^{-3} mol) were premixed.

Film A: A 3.33 g aliquot of the monomer mixture was placed in a vial with 0.038 g (6.6×10^{-5} mol) of poly(ethylene glycol) diacrylate and 16 mg (6.45×10^{-5} mol) of Vazo 52 and stirred to dissolve.

Film B: A 3.33 g aliquot of the monomer mixture was placed in a vial with 0.076 g (1.32×10^{-4} mol) of poly(ethylene glycol) diacrylate and 16 mg (6.45×10^{-5} mol) of Vazo 52 and stirred to dissolve.

Film C: A 3.15 g aliquot of the monomer mixture was placed in a vial with 0.15 g (2.61×10^{-4} mol) of poly(ethylene glycol) diacrylate and 16 mg (6.45×10^{-5} mol) of Vazo 52 and stirred to dissolve.

The mixtures were poured into small Teflon casting dishes and heated between 35 and 40 °C on a hot plate under a nitrogen atmosphere for 5 h, left at room temperature overnight, and then heated at 37 °C for 6 h. The films were insoluble, soft, and flexible. The films were dried at 75 °C under vacuum. Acetone extracts of the thinner films showed no monomer signals by ¹³C NMR. Trace monomer was detected in thicker films. TGA (N₂, 10 °C/min): onset of decomposition 225 °C (A, B) and 200 °C (C). DSC (N₂, -100 to 200 °C, 10 °C/min): no T_m detected.

Anal. Found: Film A: C, 56.49; H, 8.17; F, 2.87; S, 0.74; ash, 1.74; Li, 0.22. Film B: C, 56.45; H, 8.16; F, 2.33; S, 0.50; ash, 1.83; Li, 0.23. Film C: C, 56.79; H, 8.24; F, 2.44; S, 0.57; ash, 1.83; Li, 0.23.

Copolymerization and Cross-Linking of 2 and Poly(ethylene glycol) Ethyl Ether Methacrylate and Poly(ethylene glycol) Diacrylate. In a glovebox, 8.36 g (0.033 96 mol) of poly(ethylene glycol) ethyl ether methacrylate, 1.64 g (0.00376 mol) of 2, and 5 mL of DMF were combined in a vial and stirred to mix. Three films with different amounts of cross-linker were made as described below:

Film 1: 4.33 g (3.33 g of monomers, 1 g of DMF) of the monomer mixture was placed in a vial with 0.036 g (6.26×10^{-5} mol) of diacrylate. Vazo 52 (16 mg, 6.45×10^{-5} mol) was added and stirred to dissolve.

Film 2: 4.33 g (3.33 g of monomers, 1 g of DMF) of the monomer mixture was placed in a vial with 0.071 g (1.24×10^{-4} mol) of diacrylate and 16 mg (6.45×10^{-5} mol) of Vazo 52 and stirred to mix.

Film 3: Approximately 3.8 g of the monomer/DMF mixture, 0.14 g (2.44×10^{-4} mol) of diacrylate, and 16 mg (6.45×10^{-5} mol) of Vazo 52 were placed in a vial and stirred to mix.

The mixtures were pipetted onto Teflon-coated glass and warmed on a slide heater at 39 °C for 6 h, cooled to room temperature overnight, and then heated at 40 °C for 8 h. Flexible films were formed. TGA (N₂, 10 °C/min): onset of decomposition at 200 °C for all three films. DSC (N₂, -100 to 200 °C, 10 °C/min): no T_m detected.

Anal. Found. Film 1: C, 54.29; H, 7.72; N, 0.55; F, 4.02; S, 1.29; Film 2: C, 54.20; H, 7.68; N, 0.57; F, 4.40; S, 1.29; Film 3: C, 54.46; H, 7.75; N, 0.57; F, 3.84; S, 1.06. Elemental analysis indicated approximately 9 mol % of monomer 2 incorporated.

Synthesis of (ar-Vinylbenzyl)trimethylammonium 2-(4-Ethenylphenoxy)tetrafluoroethanesulfonate (5). Monomer 1 (3.06 g, 0.01 mol) was dissolved in 10 mL of deionized water. To this was added a solution of 2.12 g (0.01 mol) of (ar-vinylbenzyl)trimethylammonium chloride (Aldrich, mixture of meta and para isomers) in 10 mL of deionized water. An oily gum precipitated instantly which turned into a crystalline solid

on further stirring. The solid was collected, washed with 20 mL of water, and dried at 40 °C under vacuum to give 4.52 g (95%) of the title salt which was soluble in THF, DMF, and methanol. ¹H NMR (δ , CD₃OD): 3.08 (s, 9H), 4.50 (s, 2H), 5.25 (d, 1H), 5.35 (d, 1H), 5.5 (d, 1H), 5.88 (d, 1H), 6.60–6.80 (2dd, 2H), 7.23 (d, 2H), 7.55 (m, 6H). ¹⁹F NMR (δ , CD₃OD): -81.07 (2F), -116.66 (2F).

Anal. Calcd for C₂₂H₂₅F₄NO₄S: C, 55.57; H, 5.30; N, 2.95; S, 6.74; F, 15.98. Found: C, 54.27; H, 5.09; N, 2.83; S, 7.19; F, 15.79.

Synthesis of (ar-Vinylbenzyl)trimethylammonium N-(Trifluoromethanesulfonyl)-2-(4-ethenylphenoxy)tetrafluoroethanesulfonimide (6). Monomer 2 (8.75 g, 0.02 mol) was dissolved in 20 mL of deionized water and cooled in an ice water bath. To this was added a solution of 4.24 g (0.02 mol) (ar-vinylbenzyl)trimethylammonium chloride (Aldrich, mixture of meta and para isomers) in 20 mL of deionized water. A clear gum was immediately deposited. The aqueous solution was decanted, and the gum was washed with water. Drying under vacuum at 30 °C occurred with severe foaming. The product was dissolved in 50 mL of methanol, filtered into a 300 mL round-bottom flask, and concentrated on a rotary evaporator to a clear syrup which was dried for 16 h at 30 °C and 0.05 mm. The product weighed 11.5 g (95%). ¹H NMR (δ , CD₃OD): 3.1 (s, 9H), 4.47 (s, 2H), 5.25 (d, 1H), 5.35 (d, 1H), 5.76 (d, 1H), 5.87 (d, 1H), 6.68–6.81 (2dd, 2H), 7.20 and 7.50 (AB quartet, 4H), 7.42–7.50 (m, 4H). ¹⁹F NMR (δ , CD₃OD): -78.91(3F), -79.77 (2F), -115.27 (2F).

Copolymerization of 1, 5, and Methyl Methacrylate.

A polymer tube was charged with 3.06 g (0.01 mol) of 1, 2.38 g (0.005 mol) of 5, and 20 mL of DMF. This solution was placed under pump vacuum until about 1 mL of solvent had evaporated to remove traces of methanol from the salts. Methyl methacrylate (8.5 g, 0.085 mol) and 0.05 g Vazo 52 were added, and the solution was subjected to three freeze, evacuate, and thaw cycles. It was then heated for 20 h in an oil bath at 50 °C. The solution was cooled, diluted with 80 mL of DMF, and poured into water. This gave a gel that could not be filtered. The solvents were removed at 49 °C and full pump vacuum to give 16.5 g of residue. This material was washed with 2 × 100 mL of water, agitating for several hours with each portion. The water-insoluble material was dried under high vacuum at 48 °C, giving 9.92 g of polymer. This material was soluble in methanol, acetone, DMF, and DMSO, and a clear brittle film could be cast from DMF. From the ¹³C NMR spectrum of the polymer in DMF, it was calculated that it contained 81 mol % MMA units, 14 mol % OCF₂CF₂SO₃⁻ units, and 5 mol % CH₂NMe₃⁺ units from integration of peaks at 17 ppm (MMA methyl), 118.4 + 122.3 ppm (CF₂), and 68.8 ppm (CH₂N).

Anal. Found: C, 52.98; H, 6.26; F, 7.56; Li, 0.45; S, 3.66.

Copolymerization of 2, 6, and Methyl Methacrylate.

A 50 mL polymer tube was cooled in ice water and charged with 2.19 g (0.005 mol) of 2 and 10 mL of ice water. After the salt dissolved, a solution of 1.06 g (0.005 mol) of (ar-vinylbenzyl)trimethylammonium chloride in 10 mL of ice water was added, resulting in immediate precipitation of a sticky gum. The water was decanted, and the gum was stirred with 10 mL of ice water with a spatula. The gum (6) was dried briefly under pump vacuum and then dissolved in 20 mL of DMF. Monomer 2 (4.37 g, 0.01 mol) was added, followed by 8.5 g of methyl methacrylate and 0.05 g of Vazo 52. The solution was deoxygenated by four freeze/pump/thaw cycles and then heated in an oil bath for 22 h at 50 °C. An additional 20 mL of DMF was added, and the mixture was warmed to give a clear solution. Polymer was precipitated by adding the DMF solution to excess ether. The precipitate was washed in a blender with ether and then dried at 100 °C and 0.1 mm to give 14.86 g of white solid. NMR showed that the solid still contained DMF so it was reprecipitated from acetone into ether and dried, giving 12.45 g (78%) of white solid. ¹H NMR (δ , acetone-*d*₆): 0.6–3.8 (multiplets), 4.60 (bs), 7.2–7.5 (b). By integration of the aliphatic versus benzyl versus aromatic peaks, calculate the polymer contains 9.8 mol % of 2, 4.6 mol % of 6, and 85.5 mol % of MMA. ¹⁹F NMR (δ , acetone-*d*₆): -78.69(3F), -79.47 (2F), -115.30 (2F). A film cast from acetone was clear and stiff.

Table 1. Soluble Copolymers of **1** and **2**^a

entry	monomers (mol %)	solvent	initiator	polymer		
				yield (%)	composition (mol %)	$M_n \times 10^{-4} (M_w/M_n)$
1	1 (15), Sty (85)	DMF	Bz ₂ O ₂	88	1 (12), Sty (88) ^b	2.4 (1.6) ^e
2	1 (10), MMA (90)	none	Vazo 52	96	1 (12), MMA (88) ^c	13.3 (8.9) ^e
3	1 (10), AN (90)	DMF	Vazo 52	97	1 (12), AN (88) ^c	
4	1 (10), MA (90)	DMF	Vazo 52	49	1 (4), MA (96) ^c	5.7 (3.6) ^f
5	1 (20), BuAc (80)	none	Vazo 52	48	1 (20), BuAc (80) ^c	98.1 (1.4) ^f
6	1 (10), EHMA (90)	DMF	Vazo 52	32	1 (10), EHMA (90) ^c	14.0 (2.3) ^f
7	1 (11), Sty (52), AN (38)	DMF	Bz ₂ O ₂	100	1 (9), Sty (52), AN (39) ^b	
8	1 (10), Sty (63), BuAc (27)	DMF	Bz ₂ O ₂	54	1 (7), Sty (66), BuAc (27) ^b	
9	2 (10), Sty (90)	DMF	Bz ₂ O ₂	68	2 (11), Sty (89) ^d	
10	2 (10), MMA (90)	none	Vazo 52	93	2 (12), MMA (88) ^c	
11	2 (10), BuAc (90)	none	Vazo 52	24	2 (15), BuAc (85) ^c	20.4 (4.4) ^f
12	1 (5), 2 (5), BuAc (90)	none	Vazo 52	33	1 + 2 (7), BuAc (93) ^c	7.7 (8.4) ^f

^a Abbreviations: Bz₂O₂ (benzoyl peroxide); MMA (methyl methacrylate); AN (acrylonitrile); MA (methyl acrylate); BuAc (butyl acrylate); EHMA (ethylhexyl acrylate); Sty (styrene). ^b By ¹³C NMR analysis. ^c By ¹H NMR analysis. ^d From elemental analysis for % C. ^e GPC using THF + 2% DMF. ^f SEC using hexafluoro-2-propanol + 0.01 M sodium trifluoromethanesulfonate.

Table 2. Hydrin T Elastomer Cured with **1** or **2**

entry	1	2	3	4	5	6	7	8	9
Hydrin T (g)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
1 (g)	1.0	2.0		2.5	2.5	2.5			
2 (g)			2.0				2.5	2.5	2.5
Bz peroxide (g)	0.2	0.2	0.2	0.2	0.3	0.4	0.2	0.3	0.4
DMF (mL)	50	50	50	50	50	50	50	50	50
film weight (g)	1.33	1.73	1.71	1.84	1.95	2.02	1.80	1.96	2.00
THF extraction									
swollen wt (g)	5.63	8.22	9.83	9.55	7.77	6.45	12.01	15.23	8.68
wt % increase	323	375	475	419	299	219	567	677	334
THF soluble (g)	0.15	0.22	0.32	0.15	0.17	0.16	0.32	0.57	0.52
wt % soluble	11.0	12.7	18.7	8.2	8.7	7.9	17.8	29.1	26.0
anal.: F	4.03	6.61	8.58	7.10	7.05	7.06	7.40	5.77	4.33
anal.: Li	0.36	0.51	0.42	0.67	0.62	0.65	0.40	0.27	0.25
anal.: S	1.94	3.00	3.96	3.47	2.69	3.17	3.76	3.24	3.14
EW ^a	1649	1067	1619	922	1190	1011	1705	1975	2038
$\sigma (\times 10^4) S/cm^b$	0.27		1.6	1.36	1.27	1.22		1.92	1.57

^a Equivalent weight calculated from elemental analysis for % S. ^b Conductivity of propylene carbonate swollen films.

Anal. Found: C, 48.79; H, 5.52; N, 2.06, F, 12.22, Li, 0.40; S, 6.30.

Cocuring of **1** with Hydrin T (Typical Procedure).

Monomer **1** (1.0 g), Hydrin T (5.0 g), and 50 mL of DMF (50 mL) were mixed in a glass jar on rollers until the solution was homogeneous. Benzoyl peroxide (0.2 g) was added, and mixing was continued for 2 h. A portion (15 mL) of this solution was poured into each of three casting molds (Teflon, 2.44 in. square). The molds were placed in a vacuum oven under nitrogen purge at room temperature overnight and then heated to 70 °C for 48 h under vacuum with a slight nitrogen purge. The resulting films were readily peeled from the mold and were slightly yellow, highly flexible, tough, and without visible phase separation. One film was weighed and immersed in THF for 24 h at room temperature. The film was observed to swell to several times its size but retained its shape. It was removed from the THF, patted dry with paper towels, and weighed to determine percent swelling. The percent swelling data were calculated on the basis of the weight of dry film. After drying, the film returned to its original size. The THF solution was concentrated on a rotary evaporator to determine percent extractable. Equivalent weights were calculated from elemental analysis for percent sulfur. Results are summarized in Table 2.

Polymerization of 3 and Bis(hydroxyethyl)terephthalate (9). A 500 mL round-bottom flask with mechanical stirrer and distillation head was charged with 28.5 g (0.0712 mol) of **3** and 20 g of ethylene glycol. The flask was immersed in a tin/bismuth alloy bath and preheated to 200 °C, and the contents were stirred until a homogeneous solution was formed. The stirring was halted, and 54.8 g (0.216 mol) of bis-(hydroxyethyl)terephthalate (**9**) and 0.02 g of titanium(IV) isopropoxide were added. The system was flushed with nitrogen by alternatively evacuating and filling to 1 atm several

times. The stirrer speed was set to 50 rpm, and the bath temperature was increased to 240 °C over 1 h, resulting in a slow distillation. The bath temperature was gradually increased to 250 °C, and the system pressure decreased to 160 mTorr over 3.75 h with continuing collection of distillate. The stirring torque increased from 24 to 180 during this period. The mixture was allowed to cool to room temperature, and 82.1 g of solid and 19.2 g of distillate were isolated. The solid was dissolved in γ -butyrolactone, and the solution was filtered and added to excess ether to precipitate a gum. The gum was dried at 135 °C and 0.05 mm pressure. It was dissolved in about 1 L of acetone, and the solution was concentrated to 500 mL and added in small portions to excess ether. The precipitated polymer was dried at room temperature and 0.05 mm giving 63.8 g of polymer **10** (Table 3, entry 1). Intrinsic viscosity (1:1 CH₂Cl₂:CF₃COOH) = 0.286; T_g (DSC) = 84 °C. ¹H NMR (acetone-*d*₆) shows peaks at δ 8.5, assigned to one proton from the sulfonate-substituted aromatic groups, and 8.0, assigned to two protons from the sulfonate-substituted groups plus four protons from the terephthalate units. By integration, the ratio of these groups is calculated to be 1:3, in excellent agreement with the starting material ratio. See Results and Discussion section for description of remaining proton NMR. ¹⁹F NMR (acetone-*d*₆) shows peaks of equal area at δ -81.2 and -116.7.

Anal. Found: C, 51.43; H, 4.18; F, 5.56; Li, 0.59; S, 3.10.

A second polymerization was conducted in similar fashion with a modified monomer ratio (Table 3, entry 3) and a polymerization time of 160 min.

Polymerization of 4 and Bis(hydroxyethyl)terephthalate (9). The above procedure was followed using 33.0 g (0.05 mol) of **4**, 20.3 g (0.08 mol) of **9**, 30.0 g of ethylene glycol, and 0.02 g of titanium(IV) isopropoxide. Final torque on the stirrer motor was 150. Isolated were 51.5 g of polymer and 27.5 g of distillate. The polymer was dissolved in acetone. This solution

Table 3. Polyester with Pendant Lithium Fluoroalkylsulfonate Groups.

entry	monomers (mole ratio)	polymer structure ^a	EW ^b	EW ^c	IV ^d	T _g (°C)
1	3 + 9 (1:3.0)	10 ($x = 3.0, a, b = 1.04$)	1158	1034	0.286	84
2	4 + 9 (1:1.6)	11 ($x = 1.72, a, b = 1.21$)	1127	1011	0.324	74
3	3 + 9 (1:2.0)	10 ($x = 2.23, a, b = 0.42$)	803	929	0.216	135
4	4 + 9 (1:0.63)	11 ($x = 0.73, a, b = 0.34$)	824	833	0.106	125

^a From ¹H NMR analysis; see Scheme 3 for definition of x , a , and b . ^b Equivalent weight calculated from polymer composition determined by NMR. ^c Equivalent weight calculated from elemental analysis for % S. ^d Intrinsic viscosity in 1:1 methylene chloride/trifluoroacetic acid.

was filtered and the filtrate added slowly to excess ether. The resulting stringy polymer was collected and dried, giving 31.8 g of off-white foam **11** (Table 3, entry 2). ¹H NMR was similar to that described above with integration of appropriate peaks, indicating a ratio of 1.7:1 for the terephthalate to sulfonate-substituted units. ¹⁹F NMR (δ , acetone-*d*₆): -78.5 to -79.7 (m, 5 F, CF₃ + CF₂), -81.7 to -86.7 (m, 4F, 2CF₂), -117.2 (s, 2F, 1CF₂), -144.1 to -145.1 (m, 2F, CF + CFH); intrinsic viscosity (1:1 CH₂Cl₂:CF₃COOH) = 0.324; T_g(DSC) 74 °C.

Anal. Found: C, 42.40; H, 3.32; F, 18.06; Li, 0.60; S, 3.17.

A second polymerization was conducted in similar fashion with a modified monomer ratio (Table 3, entry 4) and a polymerization time of 160 min.

Conductivity Measurements on a 1/Styrene Copolymer Film. A solution cast film of the 1/styrene copolymer was dried in a recirculating nitrogen oven at 110 °C for 48 h. The dried film was transferred to a sealed container while still warm and conveyed to a nitrogen-purged glovebox. The membrane was removed from the sealed container, allowed to come to room temperature, and cut into several 1.0 cm × 1.5 cm sections. A 1:1 (volume) mixture of ethylene carbonate and dimethyl carbonate was deposited by pipet on the top surface of a cooled 1.0 cm × 1.5 cm film specimen in an amount equal to 133% of the weight of the film sample. After 30 min, the ionic conductivity was measured.

Ionic conductivity was determined using the four-point probe technique.¹³ The method as described applies to aqueous electrolyte membranes and was modified for nonaqueous solvents by placing the apparatus in a sealed glovebox purged with dry nitrogen to minimize exposure to water. The method was also modified by substituting parallel linear Pt wire probes traversing the full width of the test specimen for the point probes employed in the published method. The solvent-treated film was blotted dry and positioned into the conductivity cell. Cell impedance was determined over the range 10–100 000 Hz, and the value with zero phase angle in the higher frequency range (usually 500–5000 Hz) was ascribed to the bulk sample resistance in ohms. The raw resistance value was then converted to conductivity, in S/cm, using the cell constant and liquid-swollen film thickness. The ionic conductivity was found to be 1.03 × 10⁻⁴ S/cm at 23 °C.

Ionic Conductivity on Ionomer Solutions. Polymer samples were weighed and dissolved in sufficient quantities to create 0.1 M solutions in propylene carbonate. The weight of polymer used was calculated on the basis of the measured equivalent weight, and the concentration is based on moles of lithium ions. Solutions were prepared in a nitrogen-purged glovebox and were heated in sealed glass vials to dissolve the polymers. Ionic conductivity was measured using a VWR Scientific EC Meter model 2052. The probe was rinsed with THF and dried between each measurement. Results are summarized in Table 4.

Results and Discussion

A. Polymer Synthesis. 1. Homopolymers of **1** and **2**.

The homopolymer of **1** was prepared in aqueous

Table 4. Lithium Ion Conductivity of Ionomers in Solution^a

entry	polymer composition	EW ^b	conductivity (mS/cm)
1	1 homopolymer	306	0.269
2	2 homopolymer	437	0.493
3	1 /styrene copolymer	814	0.359
4	2 /styrene copolymer	1373	0.528
5	1 /styrene/AN terpolymer	1137	0.305
6	1 /MMA copolymer	1206	0.187
7	2 /MMA copolymer	1170	0.304
8	7		0.247
9	8		0.473
10	10	1158	0.227
11	11	1127	0.295
12	10	803	0.254
13	11	824	0.391

^a Solutions are 0.1 M in propylene carbonate. ^b Equivalent weight

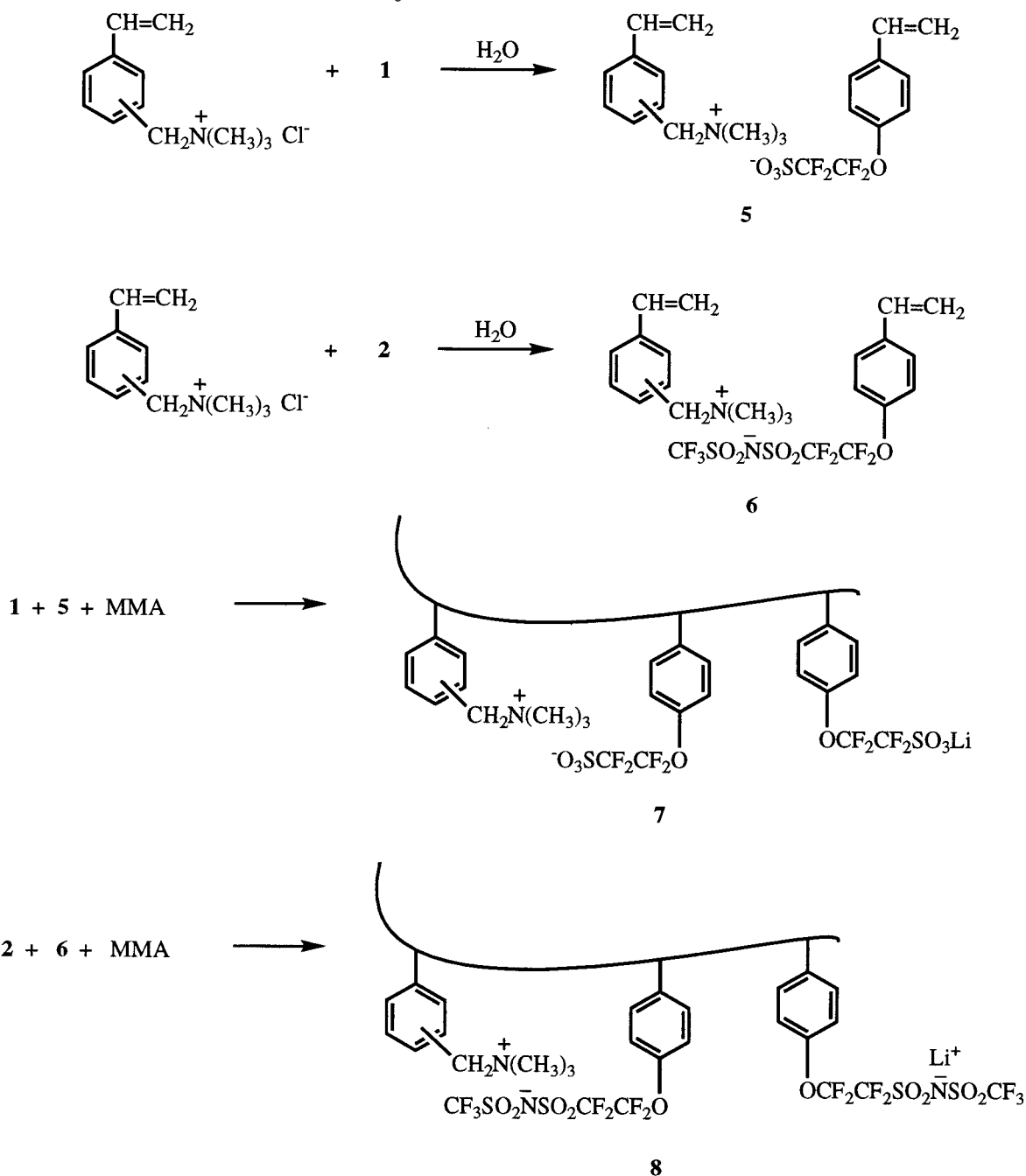
solution using ammonium persulfate initiator at 60 °C. Following dialysis to remove residual monomer and low MW impurities, it was isolated in 76% yield by evaporating the solvent under vacuum. Elemental analysis was consistent with a structure in which each lithium sulfonate unit is coordinated by 1.7 mol of water, and an M_w of 1.6 × 10⁵ was measured by light scattering in water. A self-supporting but brittle film could be cast from an aqueous solution.

A homopolymer of **2** was obtained by its unplanned polymerization during initial attempts at monomer purification. Dialysis in water was again used to remove residual monomer leading to isolation of the polymer in 63% yield. Elemental analysis was consistent with the presence of 2 mol of water per sulfonamide group. Because of limited supplies of **2**, deliberate synthesis and further characterization of this homopolymer was not attempted.

2. Soluble Copolymers. Copolymers of **1** and **2**, prepared by standard free radical polymerizations, are listed in Table 1. The salts **1** and **2** were soluble in methyl methacrylate and butyl acrylate so these copolymerizations were done without solvent whereas small amounts of DMF were added to the other copolymerizations to afford initially homogeneous solutions. Compositions of the styrene co- and terpolymers were determined by ¹³C NMR spectroscopy; the remaining polymers were analyzed by ¹H NMR. The monomer ratios for the terpolymers (entries 7 and 8) were azeotropic compositions (assuming that **1** behaves like styrene) to provide uniform products, and the polymer compositions were within 3 mol % of the initial monomer compositions. The copolymers were readily soluble in DMF and DMAc from which clear films could be cast. The styrene and acrylonitrile copolymers were brittle. The terpolymers showed better mechanical properties so that thin films could be handled gently without breaking. The methyl methacrylate and methyl acrylate copolymers gave thin films which were flexible and easy to handle. Copolymers with butyl or ethylhexyl acrylate were soft and gummy.

GPC molecular weights for several copolymers are reported in Table 1. Measurement on ionomers can be tricky, and the data must be interpreted with caution. In addition, variations in experimental procedure were employed so little significance is assigned at present to the differences among the copolymers. However, the results suggest that polymers of **1** and **2** can be obtained with moderate to quite high molecular weights.

Scheme 1. Synthesis of Mixed Cation Ionomers



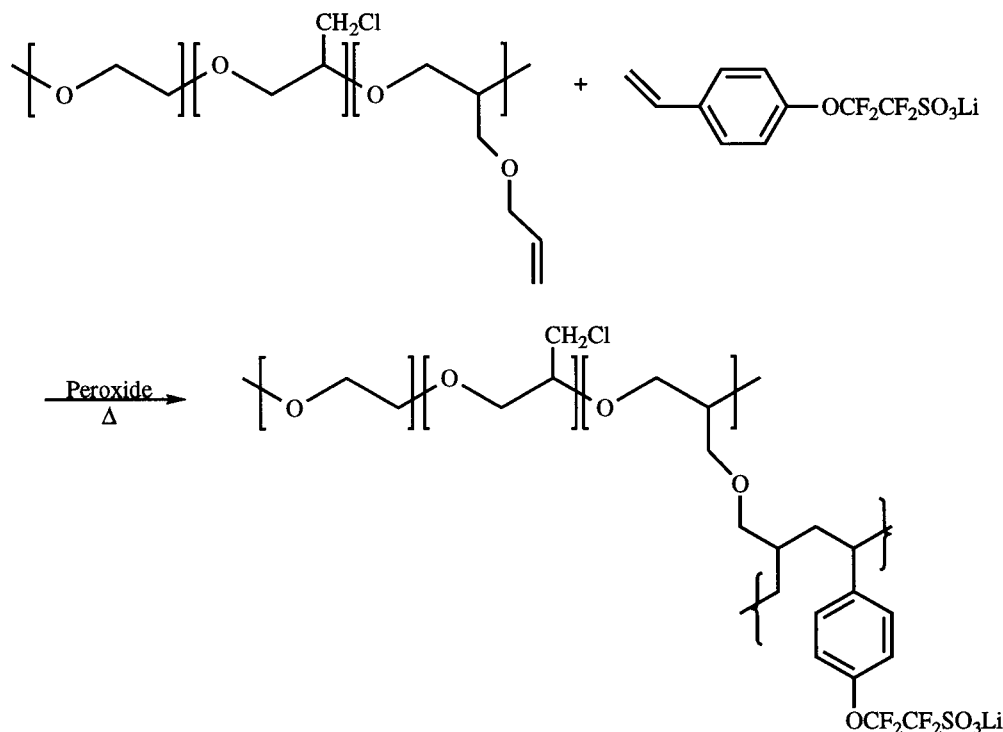
Monomers **1** and **2** were also used to generate ionic structures that contained both mobile Li^+ ions and immobilized tetraalkylammonium cations to determine the impact of additional ionic sites on the polymer backbone on Li^+ ion conductivity.¹⁴ These polymers create a new class of amphoteric ionomers having weakly coordinating fixed anion groups. Thus, salts **1** or **2** in water were added to aqueous solutions of commercially available (ar-vinylbenzyl)trimethylammonium chloride, resulting in immediate precipitation of gums. The product from **1** could be readily crystallized to a white solid which gave spectral and analytical data in good agreement with structure **5** (Scheme 1). The product from salt **2**, assigned as structure **6**, remained a gum and was used directly.

The salts **5** or **6** were mixed with their respective lithium salts **1** or **2** and methyl methacrylate in DMF in a 5:10:85 mole ratio and copolymerized using Vazo52

initiator. The products may be represented in cartoon form by structures **7** and **8**, although many of the styrenic units in the mixed salts may be bridging different polymer chains. Nevertheless, the products **7** and **8** were readily soluble in polar solvents such as methanol, acetone, and DMF. Proton NMR spectra showed no residual double bonds. Incorporations of the ammonium, sulfonate or sulfonimide, and MMA units were determined by proton or carbon NMR and were in good agreement with the monomer ratios.

3. Cross-Linked Addition Polymers. In addition to the soluble polymers, cross-linked films of poly(ethylene glycol) ethyl ether methacrylate and **1** or **2** were prepared using poly(ethylene glycol)diacrylate as cross-linking agent as described in the Experimental Section. The monomers and Vazo 52 initiator were mixed and poured into small Teflon casting dishes. Heating between 35 and 40 °C on a hot plate under a

Scheme 2. Cocuring of Hydrin T Elastomer and 1



nitrogen atmosphere gave films that were soft and flexible. Films prepared in a similar fashion using trimethylolpropane triacrylate and MMA as comonomers were brittle.

In another approach to cross-linked films, monomers **1** and **2** were cocured with Hydrin T elastomer. Hydrin T is a terpolymer of ethylene oxide, epichlorohydrin, and a few percent of allyl glycidyl ether as a cure site monomer.¹⁵ Heating with **1** or **2** in the presence of a peroxide initiator should cross-link the elastomer and tie the ionic group into the polymer backbone, as illustrated by the cartoon in Scheme 2.

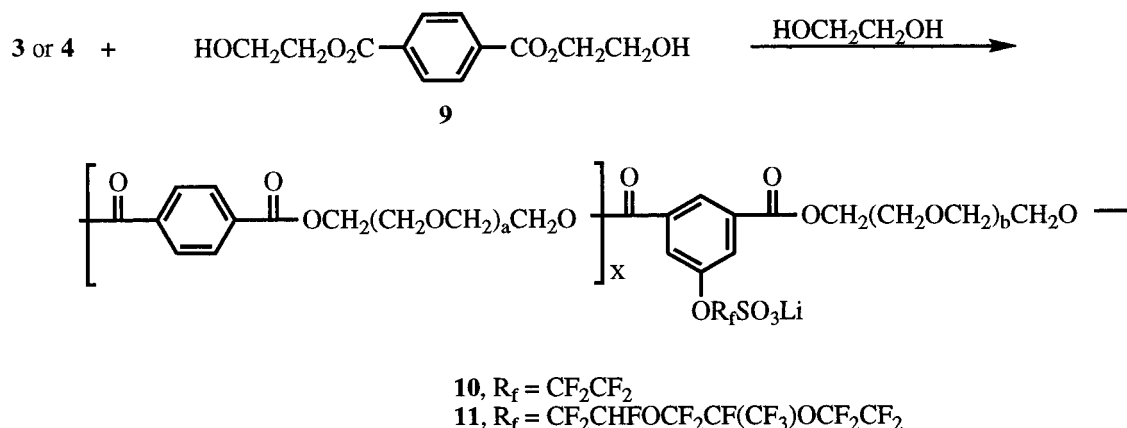
Visibly homogeneous solutions of Hydrin T and the lithium salts **1** or **2** were readily prepared in DMF. After adding a peroxide initiator, the solutions were cast into Teflon film holders and dried under vacuum at room temperature. The films were then cured by raising the temperature for 24 h in a vacuum oven under nitrogen. The resulting films could be easily peeled from the molds and were slightly yellow, visibly homogeneous, and quite tough. They could be elongated significantly by hand and returned to their original dimensions, like a typical cured elastomer. Properties of several films prepared using benzoyl peroxide initiator are summarized in Table 2. Initial tests revealed that this initiator gave superior results to dicumyl peroxide. The films were immersed in THF, a solvent for both the polymer and the ionic monomers, for 24 h at room temperature, resulting in a significant weight uptake (shown as wt % increase in the table). The swollen films remained intact and recovered their size and shape after drying. Evaporation of the THF solutions indicated the amount of material not incorporated into the network structure (indicated as wt % soluble in the table). Equivalent weights of the cross-linked elastomers were determined by elemental analysis for % S after extraction of soluble components and indicated significant incorporation of the ionic monomer. For reasons that

are not clear, incorporation of the sulfonamide monomer **2** was consistently inferior to sulfonate **1** as indicated by the higher percent extractables and higher equivalent weights observed with **2**.

4. Condensation Polymers. The isophthalate monomers with short (**3**) or longer (**4**) pendant lithium fluoroalkylsulfonate chains provide the opportunity to prepare various condensation polymers. We have initially explored polyester synthesis using bis(hydroxyethyl)terephthalate (**9**) as a comonomer. Two copolymers were prepared from each ionic monomer as indicated in Table 3, and the mole ratios of isophthalate to terephthalate units were selected so the resulting polymers from **3** and **4** would have approximately the same equivalent weights within each series. A standard condensation process was employed using excess ethylene glycol and titanium(IV) isopropoxide catalyst as described in the Experimental Section, although polymerization temperatures were limited to 250 °C because higher temperatures resulted in significant color formation. The products were dissolved in acetone and precipitated into excess ether, giving off-white stiff foams (Scheme 3). The polymers were soluble in acetone or DMF and insoluble in ether or toluene.

Proton NMR spectra of polymers **10** and **11** showed two well-resolved peaks in the aromatic region at about δ 8.5 and 8.0. The lower field peak was assigned to a single isophthalate proton whereas the upper field peak represented the remaining isophthalate protons plus the terephthalate protons. Integration of these peaks indicated terephthalate/isophthalate mole ratios in good agreement with feed ratios (Table 3). Polymer **11** showed a doublet at about 6.9 ppm, assigned to the H-CF group in the fluoroalkylsulfonate side chain which also showed the expected integral ratio. However, the upfield portions of the spectra for these polymers were not as expected. They showed expected absorptions in the region 4.3–4.9 for CO₂CH₂ protons but also showed

Scheme 3. Synthesis of Polyester Ionomers



substantial absorptions in the 3.5–4.0 region assigned to methylenes adjacent to ether oxygens. Repeated reprecipitations did not change the area ratios of these peaks. The additional methylene absorptions suggest that the glycol groups in the polymers had largely become poly(ethylene glycol) units with an average value for a and b in structures **10** and **11** of 1.04 and 1.21, respectively, in the first series of polymerizations (entries 1 and 2). Equivalent weights for polymers **10** and **11** were calculated from polymer compositions indicated by the NMR spectra and from the % S found by elemental analyses and showed reasonably good agreement. Glass transitions were apparent in the DSC at 84 and 74 °C, respectively. No melting transitions were observed. The intrinsic viscosities, measured in 1:1 methylene chloride/trifluoroacetic acid, indicated formation of moderately high molecular weight polymers.

The second series of polymerizations (Table 3, entries 3 and 4) was run using increased amounts of the functionalized monomer and shorter reaction times (160 vs 285 min). This provided polymers with lower equivalent weights and molecular weights as judged by viscosities. Again, there was good agreement between monomer feed ratios and polymer composition and the equivalent weights calculated from the NMR spectra and elemental analyses. NMR analyses also indicated substantial formation of polyether segments although less than in the first series of polymerizations. These polymers have higher glass transition temperatures than the first series, presumably due to their higher ionomer and/or lower polyether content.

Formation of ether units in polyester syntheses is well-known,¹⁶ but the amounts obtained here seem exceptional. It is likely that the lithium fluoroalkylsulfonates are catalysts for this transformation.

B. Lithium Ion Conductivity. Lithium ion conductivities were determined on several of the ionomers dissolved in propylene carbonate at 0.1 M, based on lithium ion concentration. Room temperature conductivities were generally in the range 0.1–0.6 mS/cm (Table 4). Conductivities from polymers containing the sulfonimide counterion (entries 2, 4, 7, and 9) were consistently and significantly higher than their sulfonate analogues in the nonaqueous solvent.¹⁷ The “dual cation” ionomers **7** and **8** (entries 8 and 9) show modestly improved conductivities as compared to their single cation analogues (entries 6 and 7). For the polyester-based ionomers, the polymers **11** with a longer chain separating the polymer backbone from the ionic group consistently gave higher conductivities than their

shorter chain analogues **10** at approximately the same equivalent weights.

Room temperature lithium ion conductivity was also measured on the **1**/styrene copolymer in film form, swollen with a limited (133 wt %) amount of a mixture of ethylene carbonate and dimethyl carbonate. Conductivity of the swollen film was 0.1 mS/cm. The copolymers of **1** with ethylhexyl acrylate and **2** with butyl acrylate gave similar conductivities when swollen with propylene carbonate (200 and 110% solvent uptake, respectively). Conductivities were also measured on several of the Hydrin T elastomer samples which had been cross-linked together with **1** or **2**. The data obtained on propylene carbonate swollen films are shown in Table 2. Again, the sulfonimide samples showed higher conductivity than their sulfonate analogues.

Conclusions

The styrene monomers **1** and **2** readily homopolymerize and copolymerize to provide soluble polymers with weakly coordinating perfluoroalkylsulfonate or sulfonimide groups and with a variety of equivalent weights and backbone structures. Ionomeric films which are insoluble but readily swellable in polar organic solvents can also be obtained using difunctional comonomers. Although detailed studies remain to be done, preliminary results suggest that **1** and **2** react as normal styrene monomers during polymerizations so that the large variety of polymerization processes known for styrene should be applicable to these monomers.

The ready preparation of polyesters from the isophthalate derivatives **3** and **4** indicate that these monomers should be useful for synthesis of many condensation polymers containing fluoroalkylsulfonate groups. The generation of polyether groups during the polyester synthesis, although not necessarily undesirable for conductivity applications, was unexpected and demands further investigation.

These ionomers show good lithium ion conductivity when dissolved or swollen with polar organic solvents with the sulfonimides showing significantly improved conductivity relative to their sulfonate analogues. Further modest improvements in conductivity are observed with ionomers having both free and attached counterions. It has also been demonstrated that the length of the fluoroalkyl chain attaching the sulfonate group to the polymer backbone can have a significant effect on ionic conductivity.

Acknowledgment. The authors gratefully acknowledge the careful experimental work done by B. E.

Fischel, M. Barker, and C. S. Naples and suggestions from M. E. Lewittes. R. R. Burch, P. E. O'Brian, and R. C. Schmeltzer provided invaluable assistance in conducting the condensation polymerizations. P. A. Ware, P. M. Cotts, D. E. Niehaus, and H. G. Barth provided great help in addressing the tricky problems of molecular weight determinations on ionomers. F. Davidson provided quantitative NMR analyses and interpretations for determination of polymer compositions. We thank Zeon Chemicals for providing a generous sample of Hydrin T elastomer and technical information regarding its handling and cross-linking.

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MA000893F