

Synthesis of Comb Polysiloxane Polyelectrolytes Containing Oligoether and Perfluoroether Side Chains

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Comb polyelectrolytes consisting of a polysiloxane backbone with tetraglyme and lithium-sulfonate terminated perfluoroether side chains have been synthesized. Both types of side chains were independently prepared with allyl functionality and attached to poly(methylhydrosiloxane) by hydrosilylation. Several methods are described to form lithium sulfonate from sulfonate esters. Spectroscopic and thermal characterizations of the resulting polyelectrolyte are described.

Introduction

Polysiloxanes are attractive as polymer backbones for comb polyelectrolytes because the highly flexible $[Si-O]_n$ units result in glass transition temperatures as low as $-100^{\circ}C$. These polymers have little or no crystallinity, which would be detrimental to ion transport. Another benefit of the siloxanes is that each monomer unit provides two sites for cross-links or functional side chains through bond formation with silicon.

A common method for synthesizing comb polysiloxanes is to functionalize a pre-made polymer, such as poly(methylhydrosiloxane), PMHS, which is commercially available. Although polymers such as PMHS are restricted to only one side chain per repeat unit, the relatively high molecular weight of the resulting functionalized polymer electrolyte often imparts better mechanical properties than that of those synthesized by polymerizing a functionalized monomer.^{1,2}

The most common technique to functionalize poly(hydro)siloxanes is a platinum-catalyzed hydrosilylation reaction,³ involving the addition of a carbon=carbon double bond to a hydrosilane unit under relatively mild conditions.⁴ Karstedt's catalyst, Pt(0) tetramethyldivinyldisiloxane,^{5,6} was used in the hydrosilylation reactions because of its high activity and low incidence of side reactions.^{7,8}

In previous work, polymer–salt complexes have been reported between alkali metal salts and linear copoly-

mers of poly(dimethyl siloxane) and poly(ethylene oxide).^{9–11} Alkali metal salts also have been complexed with comb polysiloxanes that are monofunctionalized^{12,13} or bifunctionalized^{14,15} with poly(ethylene oxide) side chains. Similar comb polysiloxanes have been utilized in the synthesis of polyelectrolytes containing lithiumalkylsulfonate-terminating oligoether side chains.^{16,17} Polyelectrolytes are useful owing to their inherent cation transference number of 1. Theoretical studies indicate that anion mobility may considerably influence ion pairing in polyelectrolytes.^{18,19} Cation mobility in polyelectrolytes may be significantly hindered by ion pairing between the cations and the immobile anions. Yeh et al. sought to decrease ion pairing and improve cation mobility in comb polysiloxane polyelectrolytes by the introduction of bulky anions.^{20,21} They obtained high sodium and potassium ion conductivities, but found that the lithium ion conductivity was nearly 2 orders of magnitude lower. Macrocycles have been introduced to Yeh's materials to probe ion interactions,²² but there has been relatively little development of polysiloxane polyelectrolytes with high lithium ion conductivity.

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These systems would be interesting for electrochemical applications owing to the inherently high energy density of lithium batteries. The present research was designed to decrease ion pairing, and thereby increase conductivity, in comb polysiloxane polyelectrolytes that contain weakly basic terminal anions. The synthetic procedures for these polyelectrolytes are described. Cation conductivities for the systems specified here have been measured to reach a maximum of 2.5×10^{-6} S/cm at room temperature and are reported in detail elsewhere.²³

Experimental Section

Materials. Tetrafluoro-2-(tetrafluoro-2-iodoethoxy)ethane-sulfonyl fluoride (**1**) was provided by Professor Shisheng Zhu. It was distilled under reduced pressure and stored over activated 4-Å molecular sieves. The chemical purity of **1** was confirmed by comparison of the FT-IR, ¹H NMR, and ¹⁹F NMR spectra to those supplied by the Aldrich Chemical Co. All other reagents were purchased from the Aldrich Chemical Co. and, unless otherwise noted, were used without further purification. Because **1** is light sensitive and extremely moisture-sensitive it was shielded from bright light and handled under dry nitrogen.

Characterization. ¹³C, ¹H, and ¹⁹F NMR spectra were obtained on a Varian 400 MHz spectrometer. For most samples, CDCl₃ was used as the solvent and TMS was the internal reference for ¹H NMR. CFCl₃ was the external reference for ¹⁹F NMR. Polysiloxane samples were analyzed in CDCl₃ and residual CHCl₃ was used as the internal reference.²⁴ Polyelectrolytes with high lithium ion concentrations (<30 EO:Li) were found to be insoluble in chloroform, so these samples were analyzed in deuterated acetone.

Infrared spectra were acquired on a Bio-Rad FTS-60 spectrometer on neat samples prepared in an inert atmosphere glovebox and contained between KBr or CaF₂ plates. FT-IR spectra were used to check the dryness of polysiloxane polyelectrolytes. Raman spectra were acquired on a Bio-Rad FT-Raman spectrometer on samples under N₂ in sealed capillary tubes.

Differential scanning calorimetry data were collected on ca. 5-mg samples of thoroughly dried polyelectrolytes using a Perkin-Elmer Pyris 1 differential scanning calorimeter fitted with a liquid nitrogen cooling apparatus. The temperature was varied between -110 and 140 °C at 5 heating rates from 5 to 30 °C/min, and the reported *T_g* values were obtained by extrapolating the halfway point of the transition curves to zero heating rate.

Preparation of Alkyl and Phenyl Alkanesulfonates (3). *ICF₂CF₂OCF₂CF₂S(O)₂O-R*. In an N₂-purged glovebox, 0.1 mol of the alcohol reagent (**2**, previously dried over activated 4-Å molecular sieves) and 40 mL of triethylamine (distilled from CaH₂) were added to a flask fitted with a pressure-equalizing addition funnel. When the highly deactivated alcohol 4-nitrophenol was used the proton-transfer rate was slow. The reaction is facilitated by a high dielectric solvent, so a mixture of 25 mL of triethylamine and 45 mL of acetonitrile (distilled from CaH₂) was employed. The reaction solution was chilled in an ice bath, and 0.05 mol of **1** was added dropwise with stirring. The distribution of products was found to be very sensitive to the reaction conditions. Fast addition of **1** or early removal of the ice bath resulted in a loss of up to 40% of the reagents to sideproducts, so the flask was allowed to warm to room temperature only after it was maintained in the ice bath for 8 h. Under these optimized conditions, less than 2% of the reagents was lost to sideproducts. After 24–48 h of stirring at room temperature, a dark solution resulted and the ¹⁹F NMR peak at δ45 (sulfonyl fluoride) was no longer present.

The reaction mixture was then quenched in 100 mL of deionized water, producing two liquid phases. HCl (1 M) was slowly added to the two-phase system until the aqueous phase became acidic, indicating that all of the triethylamine was complexed with either HF or HCl. The organic phase was extracted with 3 × 75 mL of hexane. The hexane fractions were combined and washed with 2 × 100 mL of deionized H₂O, followed by 3 × 100 mL portions of 10% KOH solution in deionized H₂O. The hexane solution was washed with 4 × 100 mL deionized H₂O, until the aqueous fraction was neutral. The organic phase was dried with MgSO₄, filtered, and hexane evaporated at 40 °C. Further purification was achieved by fractional distillation under vacuum. About 5% loss in yield occurred during purification.

2,2,3,3,4,4,5,5-Octafluoropentyl Tetrafluoro-2-(tetrafluoro-2-iodoethoxy)ethanesulfonate (3/R₁). **3/R₁** was prepared according to the general procedure for **3** in high yield based on **1**, as determined in-situ by ¹⁹F NMR spectroscopy. Density 1.96 g/mL. ¹H NMR δ 6.03 (triplet of triplets, 1, *J* = 52 Hz, 5 Hz), 4.82 (t, 2, *J* = 12 Hz). ¹⁹F NMR δ -65.97 (t, 2, *J* = 6 Hz), -82.79 (t, 2, *J* = 13 Hz), -85.91 (septet, 2, *J* = 6 Hz), -114.34 (s, 2), -120.63 (quintet, 2, *J* = 11 Hz), -125.35 (s, 2), -130.01 (m, 2), and -137.69 (doublet of quintets, 2, *J* = 52 Hz, 3 Hz).

Neopentyl Tetrafluoro-2-(tetrafluoro-2-iodoethoxy)ethanesulfonate (3/R₂). **3/R₂** was prepared according to the general procedure for **3** in high yield based on **1**, as determined in-situ by ¹⁹F NMR spectroscopy. ¹H NMR δ 4.14 (s, 2), 0.95 (m, 9). ¹⁹F NMR δ -65.70 (m, 2), -82.86 (m, 2), -85.89 (m, 2), and -115.13 (m, 2).

Phenyl Tetrafluoro-2-(tetrafluoro-2-iodoethoxy)ethanesulfonate (3/R₃). **3/R₃** was prepared according to the general procedure for **3** in high yield based on **1**, as determined in-situ by ¹⁹F NMR spectroscopy. bp 72 °C (0.05 Torr). ¹H NMR δ 7.45 (m, 5). ¹⁹F NMR δ -65.39 (s, 2), -82.17 (t, 2, *J* = 19 Hz), -85.71 (s, 2), and -113.26 (s, 2).

4-Nitrophenyl Tetrafluoro-2-(tetrafluoro-2-iodoethoxy)ethanesulfonate (3/R₄). **3/R₄** was prepared according to the general procedure for **3** in high yield based on **1**, as determined in-situ by ¹⁹F NMR spectroscopy. The crude ester, a dark orange solid, decomposes rapidly at elevated temperatures. Purification was accomplished by crystallizing the product out of hexanes to yield a light yellow powder. IR (neat) 1535 and 1349 cm⁻¹ (NO₂) and 603 cm⁻¹ (C—I). ¹H NMR δ 8.37 (d, 2, *J* = 9 Hz), 7.49 (d, 2, *J* = 9 Hz). ¹⁹F NMR δ -65.0 (t, 2, *J* = 6 Hz), -81 (t, 2, *J* = 12 Hz), -85.0 (septet, 2, *J* = 6 Hz), and -112 (s, 2).

2,4-Difluorophenyl Tetrafluoro-2-(tetrafluoro-2-iodoethoxy)ethanesulfonate (3/R₅). **3/R₅** was prepared according to the general procedure for **3** in high yield based on **1**, as determined in-situ by ¹⁹F NMR spectroscopy. Density 1.63 g/mL. ¹H NMR δ 7.34 (triplet of doublets, 1, *J* = 9 Hz, 5 Hz), 7.01 (triplet of doublets, *J* = 9 Hz, 3 Hz), 6.94 (triplet of triplets, *J* = 8 Hz, 2 Hz). ¹⁹F NMR δ -65.87 (t, 2, *J* = 6 Hz), -82.34 (t, 2, *J* = 12 Hz), -85.92 (septet, 2, *J* = 6 Hz), -108.08 (quintet, 1, *J* = 7 Hz), -113.61 (s, 2), -121.95 (sextet, 1, *J* = 7 Hz).

Preparation of Alkyl and Phenyl 4-(Prop-1-ene)-tetrafluoro-2-(tetrafluoro-2-ethoxy)ethanesulfonates (4). *CH₂CHCH₂CF₂CF₂OCF₂CF₂S(O)₂O-R*. AIBN (0.0015 mol) and 60 mL of hexane were transferred to a flame-dried Schlenk flask, which was then immersed in an ice bath, and dry N₂ was bubbled through the mixture for 30 min. To this solution 0.02 mol allyltributyltin (purged with N₂) and 0.01 mol **3** were added by syringe under a N₂ atmosphere. The flask was partially evacuated, sealed, and transferred to an oil bath at 65 °C. The solution was stirred for 8 h and then allowed to cool to room temperature. Completion of the reaction was indicated by a shift in the ¹⁹F NMR peak from δ-66 (I-CF₂-) to δ-118 (Allyl-CF₂-).

The hexanes were removed by rotary evaporation at 50 °C. The product was then added to a concentrated aqueous solution of 0.015 mol potassium fluoride dihydrate in a Teflon container and thoroughly agitated to convert ISnBu₃ to FS-

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$n\text{Bu}_3$.³⁰ The resulting white precipitate formed an emulsion, which was broken up with 20 mL of acetone, filtered, and washed with acetone, which was then removed from the filtrate under vacuum at 40 °C. Diethyl ether (75 mL) was then added and potassium fluoride was extracted with 3 × 100 mL of deionized water. The organic fraction was dried over MgSO_4 and filtered. Ether was then removed from the filtrate under vacuum at 40 °C, resulting in two immiscible phases. ^1H and ^{19}F NMR indicate the presence of both allyltributyltin and **4** in each phase. The two components were separated and purified using dry flash chromatography.³¹ The separation was monitored with ^1H and ^{19}F NMR, and thin-layer chromatography. Allyltributyltin has an $R_f = 0.72$ in hexanes on silica. The silica column was eluted in 75-mL fractions with hexanes until allyltributyltin was removed. The eluent was then changed to 10 vol % ether in hexanes. The product-containing fractions were combined, dried over MgSO_4 , and filtered, and the solvent was removed at 50 °C under vacuum. The resulting clear, colorless liquid was stored under N_2 over activated 4-Å molecular sieves. About 15% loss in yield occurred during purification.

2,2,3,3,4,4,5,5-Octafluoropentyl 4-(prop-1-ene)-tetrafluoro-2-(tetrafluoro-2-ethoxy)ethanesulfonate (4/R₁). **4/R₁** was prepared according to the general procedure for **4** in high yield based on **3**, as determined in-situ by ^{19}F NMR spectroscopy. ^1H NMR δ 6.04 (triplet of triplets, 1, $J = 52$ Hz, 5 Hz), 5.78 (m, 1), 5.33 (d, 1, $J = 9$ Hz), 5.32 (d, 1, $J = 19$ Hz), 4.82 (t, 2, $J = 12$ Hz), 2.81 (triplet of doublets, 2, $J = 18$ Hz, 7 Hz). ^{19}F NMR δ -82.71 (t, 2, $J = 13$ Hz), -87.72 (septet, 2, $J = 6$ Hz), -114.40 (s, 2), -117.61 (s, 2), -120.54 (quintet, 2, $J = 11$ Hz), -125.24 (s, 2), -129.90 (m, 2), and -137.56 (doublet of quintets, 2, $J = 52$ Hz, 3 Hz).

Neopentyl 4-(prop-1-ene)-tetrafluoro-2-(tetrafluoro-2-ethoxy)ethanesulfonate (4/R₂). **4/R₂** was prepared according to the general procedure for **4** in high yield based on **3**, as determined in-situ by ^{19}F NMR spectroscopy. ^1H NMR δ 5.69 (m, 1), 5.21 (m, 2), 2.81 (m, 2). ^{19}F NMR δ -83.15 (m, 2), -88.44 (m, 2), -117.92 (m, 2), and -118.42 (m, 2).

Phenyl 4-(prop-1-ene)-tetrafluoro-2-(tetrafluoro-2-ethoxy)ethanesulfonate (4/R₃). **4/R₃** was prepared according to the general procedure for **4** in high yield based on **3**, as determined in-situ by ^{19}F NMR spectroscopy. $R_f = 0.15$ (hexanes on silica). ^1H NMR δ 7.45 (m, 5), 5.77 (m, 1), 5.30 (m, 2), 2.80 (triplet of doublets, 2, $J = 18$ Hz, 8 Hz). ^{19}F NMR δ -82.40 (t, 2, $J = 13$ Hz), -87.83 (t, 2, $J = 13$ Hz), -113.59 (s, 2), and -117.66 (t, 2, $J = 18$ Hz).

4-Nitrophenyl 4-(prop-1-ene)-tetrafluoro-2-(tetrafluoro-2-ethoxy)ethanesulfonate (4/R₄). **4/R₄** was prepared according to the general procedure for **4** in high yield based on **3**, as determined in-situ by ^{19}F NMR spectroscopy. ^1H NMR δ 8.35 (d, 2, $J = 9$ Hz), 7.49 (d, 2, $J = 9$ Hz), 5.77 (m, 1), 5.33 (d, 1, $J = 8$ Hz), 5.32 (d, 1, $J = 18$ Hz), 2.82 (triplet of doublets, 2, $J = 18$ Hz, 7 Hz). ^{19}F NMR δ -82.38 (t, 2, $J = 12$ Hz), -87.68 (t, 2, $J = 12$ Hz), -113.00 (s, 2), and -117.54 (t, 2, $J = 18$ Hz).

2,4-Difluorophenyl 4-(prop-1-ene)-tetrafluoro-2-(tetrafluoro-2-ethoxy)ethanesulfonate (4/R₅). **4/R₅** was prepared according to the general procedure for **4** in high yield based on **3**, as determined in-situ by ^{19}F NMR spectroscopy. Density 1.48 g/mL. ^1H NMR δ 7.34 (triplet of doublets, 1, $J = 9$ Hz, 5 Hz), 7.01 (triplet of doublets, $J = 9$ Hz, 3 Hz), 6.94 (triplet of triplets, $J = 8$ Hz, 2 Hz), 5.77 (m, 1), 5.31 (d, 1, $J = 10$ Hz), 5.30 (d, 1, $J = 17$ Hz), 2.82 (triplet of doublets, 2, $J = 18$ Hz, 7 Hz); ^{19}F NMR δ -82.36 (t, 2, $J = 12$ Hz), -87.81 (t, 2, $J =$

Table 1. Percent Yield Data Resulting from Preparation of the Lithium Salt from Several Perfluoroalkylsulfonate Esters^a

	LiBr ^b	LiOH ^c
4-methoxyphenyl triflate ^d	3 ^e	2
1-naphthyl triflate ^d	0	94
4/R₁	100	
4/R₂	100	
4/R₃		0
4/R₄	0	100
4/R₅	0	100

^a Yields are based on the formation of the desired product as determined by ^{19}F NMR. For the sake of accurate comparison, possible reductions in overall yield due to purification were not taken into account. **4/R_x** refers to the compound **4** in Scheme 1 with the corresponding protecting group, R_1 – R_5 . ^b The appropriate sulfonate reagent was added to a solution of up to 6 equiv of LiBr in 2-benzophenone and allowed to reflux for 48 h. ^c The appropriate sulfonate reagent was added to a solution of 6 equiv of LiOH in THF and allowed to reflux for 48 h. ^d These commercially available compounds were used to approximate **4** with 4-methoxyphenyl or 1-naphthyl protecting groups. ^e No reaction after 48 h. 3% free triflate was detected after 5 days of reflux.

13 Hz), -108.15 (quintet, 1, $J = 7$ Hz), -113.76 (t, 2, $J = 3$ Hz), -117.57 (t, 2, $J = 18$ Hz), -122.03 (sextet, 1, $J = 7$ Hz).

Preparation of 4-(Prop-1-ene)-tetrafluoro-2-(tetrafluoro-2-ethoxy)ethanesulfonic acid, lithium salt (5). $\text{CH}_2\text{CHCH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{S(O)}_2\text{O}^- \text{Li}^+$. In a 100-mL flask fitted with a condenser, 8 mmol of **4** was added to 40 mmol LiOH and 50 mL of THF. The mixture was refluxed overnight and then cooled to room temperature. Much of the excess LiOH was removed from the resulting slurry by filtration. THF was removed on a rotary evaporator and replaced by 40 mL of pentane to form a light yellow precipitate, which was filtered off. Pentane was removed on a rotary evaporator and replaced by 40 mL of hexane to precipitate the product. Minor losses in yield occurred during purification. Table 1 lists the success of reaction for several protecting groups. When the lithium salt of the sulfonate group was prepared, up to 100% of the phenol byproduct was also converted to the lithium salt, as indicated by ^1H and ^{19}F NMR spectroscopy. ^1H NMR δ 5.78 (m, 1), 5.33 (d, 1, $J = 9$ Hz), 5.32 (d, 1, $J = 19$ Hz), 2.80 (triplet of doublets, 2, $J = 18$ Hz, 7 Hz). ^{19}F NMR δ -83.2 (s, 2), -88.5 (s, 2), -117.8 (s, 2), -118.1 (s, 2).

3-(Methoxytriethoxy)-prop-1-ene (6). $\text{CH}_2\text{CHCH}_2(\text{OCH}_2\text{CH}_2)_3\text{OCH}_3$. Dropwise addition of 100 mL of tri(ethyleneglycol)monomethyl ether (103 g, 0.625 mole, previously dried over activated 4-Å molecular sieves) to a magnetically stirred slurry of 24.6 g NaH (1.03 mole) in 150 mL of tetrahydrofuran (THF, freshly distilled from Na-benzophenone) under dry N_2 resulted in evolution of H_2 and formation of $\text{NaO}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$. After gas evolution ceased, the flask was cooled to 0 °C and 80 mL of allyl chloride (75 g, 0.98 mol) was added dropwise. The flask was allowed to warm to room temperature, stirred overnight, and then chilled in an ice bath. Dropwise addition of 80 mL of 2-propanol in dry THF (1:1) eliminated the excess NaH. The solution was allowed to warm to room temperature and stirred for 2 h. The resulting slurry was filtered three times through Celite to remove precipitated NaCl. It was then concentrated on a rotary evaporator, resulting in a thick yellow liquid that was purified by distillation under reduced pressure. ^1H NMR δ 5.90 (m, 1), 5.20 (multiplet of quartets, 2), 3.96 (doublet of quartets, 2), 3.57 (m, br, 10), 3.47 (m, 2), 3.33 (s, 3).

Co-functionalization of Poly(methyl(hydro)siloxane) with 3-(Methoxytriethoxy)-prop-1-ene and 2,2,3,3,4,4,5,5-Octafluoropentyl 4-(prop-1-ene)-tetrafluoro-2-(tetrafluoro-2-ethoxy)ethanesulfonate (8). Precisely weighed (ca. 1.0 g, 0.016 mole) amounts of poly(methylhydrosiloxane) (**7**, $n = \sim 35.1$; previously dried over activated 4-Å molecular sieves) were transferred under a flow of dry N_2 into purged, flame-dried Schlenk flasks along with 20 mL of dry toluene and 30 μL of Karstedt's catalyst. The desired amount of **4/R₁** (dried over activated 4-Å molecular sieves) was precisely weighed and

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added by syringe. Dry air was bubbled through the solution for fifteen minutes to introduce a catalytic amount of oxygen. The reaction mixture was then sealed and heated to 80 °C with stirring until the reaction was complete (ca. 30 h). The extent of side chain attachment was determined by ¹⁹F NMR, and completion of the reaction was verified by loss of the ¹H NMR allyl peaks at δ 5.78, δ 5.33, and δ 5.32.

A quantity of **6** was then added in up to 15% molar excess of the calculated remaining methylhydrosiloxane repeat units. The solution was bubbled with dry N₂ for 30 min, partially evacuated, resealed, and heated to 80 °C for 48 h with magnetic stirring. Toluene was then removed on a rotary evaporator at 70 °C. Nearly complete functionalization of the polymer was determined by the significant reduction of the FT-IR band at 2161 cm⁻¹, and loss of the ¹H NMR peak at δ 4.7. Residual silane content in the purified product was determined to be no greater than 3% in all cases by ¹H NMR end-group analysis. Residual platinum content in most samples was determined to be no greater than 10% of the content of lithium ions by weight, and to have no significant effect on the impedance of the samples. When a greater quantity of platinum was added, samples were filtered through a dry flash column consisting of 11 g of activated carbon sandwiched between two layers of 4 g of Celite. The column was washed with 2 \times 40 mL of toluene before applying the sample in a solution of 20 mL of toluene, and it was eluted with toluene. This process was monitored by ¹H and ¹⁹F NMR. Fractions were collected and volatiles were removed under vacuum at 70 °C, to produce a clear golden product.

[OSi(CH₃)(CH₂CH₂CH₂CF₂CF₂OCF₂CF₂SO₃CH₂CF₂CF₂CF₂CF₂H)(OSi(CH₃H)]_n. ¹H NMR δ 6.11 (t, 1, J = 56 Hz), 4.85 (s, 2), 4.64 (s, br, n*x), 2.00 (m, br, 2), 1.57 (m, br, 2), 0.55 (m, br, 2), 0.06 (m, br, 3). ¹⁹F NMR δ -82.46 (m, br, 2), -87.90 (m, br, 2), -114.16 (m, br, 2), -118.51 (m, br, 2), -120.20 (m, br, 2), -124.94 (m, br, 2), -129.50 (m, br, 2), -137.27 (m, br, 2).

*[OSi(CH₃)(CH₂CH₂CH₂(OCH₂CH₂)₃OCH₃]_n**. ¹H NMR δ 3.64 (m, br, 12), 3.36 (m, br, 5), 1.57 (m, br, 2), 0.46 (m, br, 2), 0.03 (m, br, 3).

Deprotection of the Sulfonate Group to Form the Lithium Salt (9). In a N₂-purged glovebox, anhydrous lithium bromide beads were weighed to milligram precision in a 1:1 molar ratio to the perfluoroether side chain on the polymer. The beads were dissolved in 20 mL of 2-butanone and added to the polymer. The reaction flask was partially evacuated and then stirred for 48 h at 75 °C. The extent of deprotection was determined by ¹⁹F NMR. Solvent and low-molecular-weight byproducts were removed at 80 °C under vacuum. BrCH₂(CF₂)₄H and residual 3-(methoxytriethoxy)-prop-1-ene were removed by repeated extraction with hexane. A high yield of the lithium salt was determined by ¹⁹F NMR in-situ, but some loss of product occurred during extraction.

[OSi(CH₃)(CH₂CH₂CH₂CF₂CF₂OCF₂CF₂SO₃⁻ Li⁺)(OSi(CH₃H)]_n. ¹H NMR δ 4.80 (s, br, n*x), 2.21 (m, br, 2), 1.64 (m, br, 2), 0.71 (m, br, 2), 0.20 (m, br, 3). ¹⁹F NMR δ -83.99 (m, br, 2), -89.74 (m, br, 2), -119.27 (m, br, 2), -119.40 (m, br, 2).

*[OSi(CH₃)(CH₂CH₂CH₂(OCH₂CH₂)₃OCH₃]_n**. ¹H NMR δ 3.60 (m, br, 10), 3.50 (m, br, 3), 3.45 (m, br, 2), 3.31 (m, br, 2), 1.66 (m, br, 2), 0.61 (m, br, 2), 0.17 (m, br, 3).

Results and Discussion

Synthesis. Several comb polyelectrolytes, depicted in Figure 1, were synthesized from polymethylhydrosiloxane by hydrosilylation reactions. Changes in the etheric oxygen-to-lithium ratio (EO/Li) were accomplished by altering the relative concentration of the perfluoroether and tetraglyme side chains. The large number of electron-withdrawing fluorine groups in proximity to the terminal sulfonate group should reduce the anion basicity. The ether linkage within the perfluorinated side

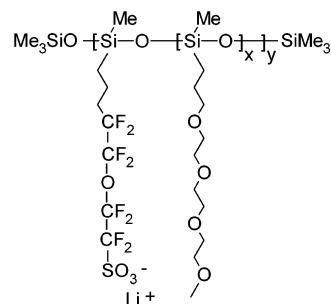


Figure 1. A comb polyelectrolyte with a polysiloxane backbone to impart flexibility. The short, completely amorphous oligoether side chains provide cation coordination sites. The perfluoroether side chain provides a very weakly basic terminal anion with some expected local mobility independent of the segmental motions of the polymer backbone.

chain may help to introduce flexibility and increase the dielectric constant. The ratios of the tetraglyme side chains to the perfluoroether side chains are high enough to ensure a favorable dielectric constant for the polymer matrix. The oligoether length was chosen to achieve an amorphous phase through the range of investigated temperatures. Similar polymer–salt complexes based on PMHS display crystallization at temperatures as high as -7 °C when the poly(ethylene oxide) side chains include 7 etheric oxygens.¹⁴

The target oligoether side chain and perfluorosulfonate side chain were synthesized with terminal allyl groups to facilitate hydrosilylation of the side chains to the polysiloxane backbone. Attempts to react vinyl-terminated perfluoroalkyl molecules with PMHS resulted in poor yields.

3-(Methoxytriethoxy)-prop-1-ene was prepared in a one-pot synthesis from tri(ethyleneglycol)monomethyl ether by reacting an alkoxide of the reagent with allyl chloride.²⁵ Similar reactions for tetrafluoro-2-(tetrafluoro-2-iodoethoxy)ethane-sulfonyl fluoride, **1**, using allyl alcohol have yields reported to be as low as 50%.^{26,27} A simpler method for introducing allyl functionality to the perfluoroether compound involves an AIBN-initiated radical reaction with allyltributyltin,^{28,29} which proceeds quickly in the presence of terminal chloride and iodide groups. Conversion of the tributyltin iodide byproduct to tributyltin fluoride, which is insoluble in most solvents, facilitated purification.³⁰ Excess allyltributyltin, residual tributyltin iodide, and other impurities were removed using dry flash chromatography.³¹

Tetrafluoro-2-(tetrafluoro-2-iodoethoxy)ethanesulfonate fluoride, **1**, was the precursor for the perfluoroether side chain. The multistep alteration of **1** to the perfluoroether side chain is detailed in Scheme 1. The sulfonyl fluoride group was converted to a sulfonate ester to avoid reaction of the sulfonyl halide with moisture. The sulfonate ester protecting group allowed the formation of the lithium salt under a range of conditions.

The addition of an alcohol-functionalized compound to sulfonyl fluoride provides a convenient route to formation of a sulfonate ester.^{32–34} This reaction involves a proton transfer facilitated by triethylamine.³⁵

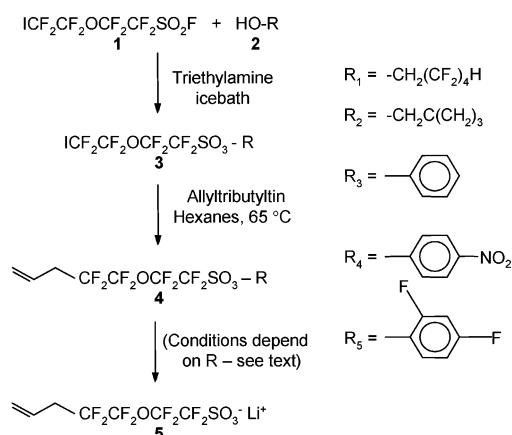
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Scheme 1



Scheme 2



Triethylamine serves the additional function of absorbing the caustic byproduct, hydrogen fluoride, as it is generated. Each molecule of triethylamine may form a complex with up to three molecules of HF.³⁶ This complexation of HF helps to prevent erosion of the glass reaction flask and it simplifies the purification of the product, **3**, as shown in Scheme 2.

In comparison to pure triethylamine, the complex between triethylamine and HF has low solubility in nonpolar solvents, and favorable solubility in polar solvents. A similar effect is seen with 1:1 complexes involving triethylamine and hydrochloric acid.³⁶ The addition of excess HCl to the quenched reaction ensures that all of the triethylamine reacted with either HF or HCl. This facilitated separation of triethylamine from **3**. Several combinations of solvents for this separation are cited in the literature, of which the most common pair is water and diethyl ether.³⁷⁻³⁹ In the present investigation, extraction with hexanes from water provided an efficient high yield purification of **3**.

The use of a high-dielectric cosolvent such as acetonitrile increased the rate of proton transfer for the reaction described in Scheme 2.⁴⁰⁻⁴² The reaction is usually exothermic, and so the reaction vessel was contained in an ice bath to minimize byproduct formation at higher temperatures. Thoroughly dry reagents were used to prevent hydrolysis of the sulfonyl fluoride.

A convenient approach for deprotecting a perfluorosulfonate group to yield the lithium salt involves the use of LiBr in 2-butanone. This reaction has been shown to be effective with 2,2-dimethyl propane, **R**₂.^{43,44} As indicated in Table 1, LiBr was not effective in displacing

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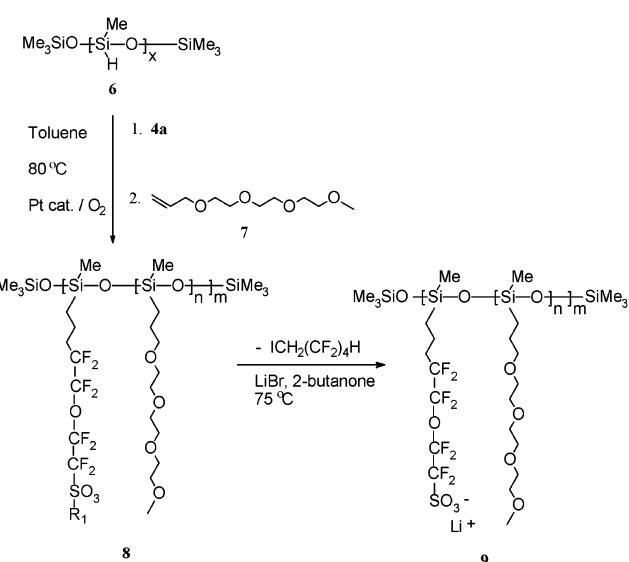
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Scheme 3



aryl protecting groups. When **R**₂ was used as the protecting agent the deprotection and purification during the final step were difficult to verify in-situ by standard techniques. In contrast, the protecting group **R**₁ resulted in a product yield of 100% as well as a simple and quantifiable means of monitoring the protecting group using ¹⁹F NMR analysis. For these reasons **R**₁ was used as the protecting group for all of the polyelectrolytes discussed in this work.

Two additional methods were explored for preparing the lithium salt of the aryl-protected sulfonate group. The first alternate approach involved an adaptation of the Stille palladium-catalyzed coupling reaction using organotrihalides.⁴⁵⁻⁴⁷ Although the Stille reaction is fundamentally a coupling reaction, the lithium salt of a perfluorosulfonate group is often a byproduct.⁴⁵ Stille reported high yields of the coupling reaction for triflates of substituted phenyl groups.⁴⁶ Yields greater than 50% were not obtained in the present research for the protecting groups listed in Table 1.

In the second alternate method for preparing the lithium salt of the aryl-protected sulfonate group an excess of LiOH in THF was employed. Nucleophilic attack by hydroxide results in formation of the initial alcohol used in Scheme 1. The reaction was found to be complementary to reactions involving LiBr, as shown in Table 1. Because of the susceptibility of siloxane bonds to nucleophilic attack, this method was employed prior to attaching the side chains to the polymer. The purified lithium salt of the side chain, **5**, was obtained, but it was found to be only partially soluble in the solvents required for the hydrosilylation reaction. Attempts to perform the hydrosilylation in high yields with the lithium salt were unsuccessful.

The side chains **4** (with protecting group **R**₁) and **7** were synthesized and purified, and then covalently bound to polymethylhydrosiloxane by the hydrosilylation reaction as shown in Scheme 3. The manufacturer

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of PMHS confirmed that the method of production results in a polymer consisting of only methylhydro-siloxane repeat units, so no dimethylsiloxane or dihydro-siloxane repeat units should be present.⁴⁸ MALDI MS experiments were performed with the PMHS precursor and an *a*-cyano-4-hydroxycinnamic acid matrix. A strong peak at ~ 1524 Da and minor repeat peaks every 60 Da indicated an average backbone repeat unit number of $n \approx 23$. ¹H NMR end-group analysis of an aliquot of PMHS purified through repeated fractional precipitations with hexanes from methanol^{49,50} confirmed an average backbone repeat unit number between 20 and 25. ¹H NMR end-group analysis of the final product also suggested a similar number of repeat units. On the basis of this value for n , the sizes of the final polyelectrolytes were calculated to be in the 6000–8000 Da range.

The reaction between PMHS and the allyl-functionalized perfluoroether was promoted by dry air and it went to completion within 24 h, as determined by ¹⁹F NMR. Oxygen predisposes the Pt/SiH complex to nucleophilic attack,⁵¹ and thereby counteracts the influence of electron-withdrawing fluorine groups adjacent to the olefin.⁵² Oxygen also facilitates the formation of platinum colloids,⁵³ which are essential in the catalytic cycle proposed by Lewis.^{54,55} Furthermore, oxygen deters undesirable platinum colloid agglomeration.^{56,57} The formation of platinum colloids is indicated by a yellow solution color whereas the presence of platinum colloid aggregates shifts the solution color to dark brown or black. Platinum colloid aggregates were removed by filtering the final product through activated carbon.

A 40-hour reaction period provided 97% side chain hydrosilylation of the polymer, as determined by ¹H NMR end-group analysis. Complete functionalization of PMHS was never attained, even under conditions of high temperatures, excess reagents, or long reaction times. The incomplete functionalization was indicated by the presence of a silane peak at 2160 cm^{-1} in the infrared spectrum.⁴⁹ The slow reaction rate of the last few silane groups is attributed primarily to steric factors.

Deprotection reactions with lithium bromide proceeded with little difficulty. High-purity anhydrous lithium bromide beads were added in increments until the total amount equaled the number of moles of perfluoroether side chain. The result of each addition was monitored by ¹⁹F NMR, and the percent yield determined in-situ corresponded to the calculated percent yield within the expected margin of error (typically 1 mg). Because minor losses of polymer were anticipated in samples that were filtered through activated carbon, an estimate was made of the total quantity of lithium bromide to be added. This estimate was refined by the

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Table 2. Glass Transition Temperatures for the Polyelectrolytes in Figure 1

Li/EO	EO/Li	T_g (K): Midpoint at 10 K/min	T_g (K): Midpoint extrapolated to 0 K/min
9a^a	0.00	∞	186
9b	0.019	54	200
9c	0.024	41	200
9d	0.030	33	203
9e	0.034	29	206
9f	0.056	18	214
9g	0.11	9.3	220
9h	0.14	7.1	236
9i	0.20	5.1	258

^a The labels 9a–f have been assigned for clarity in the related discussion and correspond to the polyelectrolyte, 9, in Scheme 2 at the indicated Li:EO ratios. T_g values were determined by DSC.

use of ¹⁹F NMR peak integrations following each incremental addition.

Characterization. ¹³C and ¹H NMR spectra of the compounds synthesized in the present work agree with those reported in the literature for similar compounds. ¹H NMR end-group analysis was used to determine the distribution ratio of the tetraglyme and perfluoroether side chains, as well as the residual silane content. The theoretical side chain distribution ratio was calculated from the amount of the starting materials, which often had a lower EO/Li ratio than expected. Some loss of product occurred during purification. The ¹H NMR spectra for **9d** (EO/Li 33:1; cf. Table 2) in Figure 2 contain peaks that are clearly resolved. Accurate and repeatable integration values were obtained by expanding the region of interest, as shown in the inset spectrum. Peak values are listed in the Experimental Section. Comparisons of peak H_a (δ 2.2) to peaks H_b and H_c (apparent as one singlet, δ 1.6) were used to determine the ratio of the tetraglyme and perfluoroether side chains. Calculations of the EO/Li ratio were also performed using NMR integrations of the other peaks. In each case the EO/Li ratio was found to be very close to the estimated ratio.

Residual silane protons on the polymer appear at δ 4.8, and they are present in less than 3% of the total number of side chains. The peak at δ 0.2 is composed of both the siloxymethyl repeat units (3^*n H/polymer, where n is the number of repeat units) and the terminal trimethylsiloxane peaks (18 H/polymer). Comparison of the integrated peak with the integrations of the other peaks indicates ~ 24 repeat units, which is very close to the average n of 23 obtained by MALDI MS reported above.

¹⁹F NMR solution spectroscopy was used to determine progress of the reaction and percent yield. ¹⁹F NMR also was used to determine removal of the protecting groups in the deprotection reaction.

FT-IR spectra were used to determine the residual silane groups (stretch 2160 cm^{-1}) in the final polyelectrolytes, and residual water when the polyelectrolytes were dried. As shown in Figure 3a, the CF₂ (asymmetric stretch $1350\text{--}1200\text{ cm}^{-1}$, symmetric stretch $1200\text{--}1080\text{ cm}^{-1}$), Si–R ($890\text{--}690\text{ cm}^{-1}$), and Si–O–Si (1080 , 1020 cm^{-1} , broad) stretching modes dominate the region between 1500 and 500 cm^{-1} . These bands make it difficult to detect lithium complexation of SO₃ groups and lithium complexation of PEO, as detected by

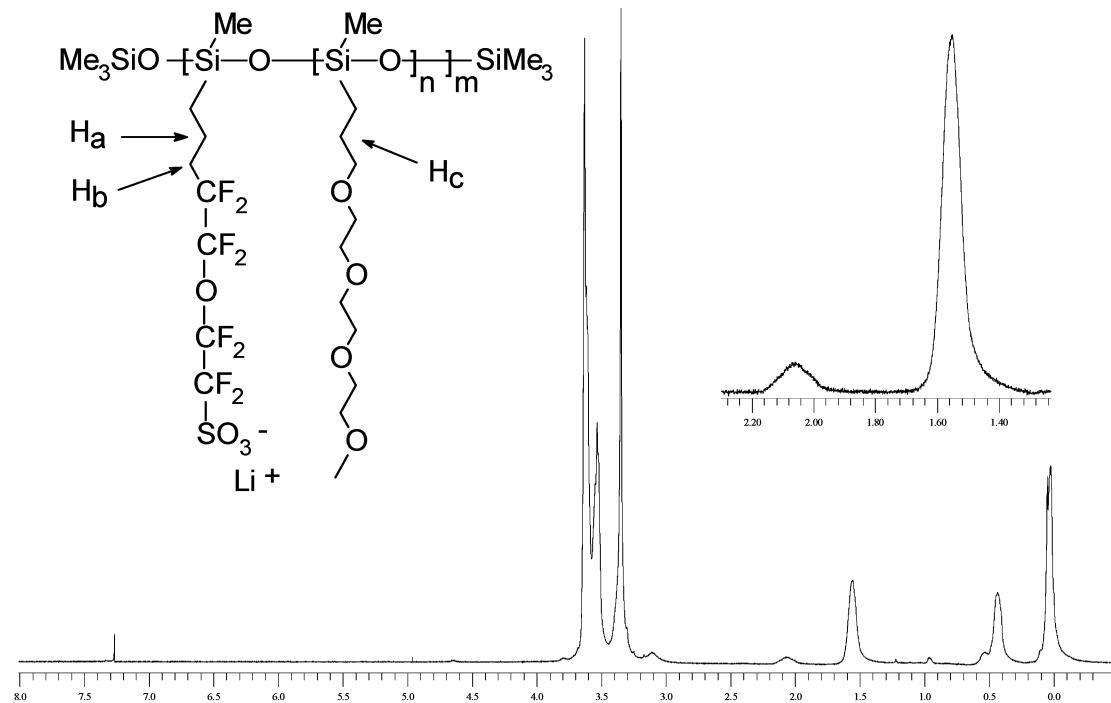


Figure 2. ^1H NMR spectrum of a typical polyelectrolyte in CDCl_3 . The EO/Li ratio is 33. The proximity of the singlet associated with H_a to the singlet formed by H_b and H_c allowed accurate determination of the ratio of side chains, and by extension the EO/Li ratio. The minor peak at δ 4.8 indicates residual silane protons, which were calculated to be no greater than 3% of the number of silane protons in the initial PMHS.

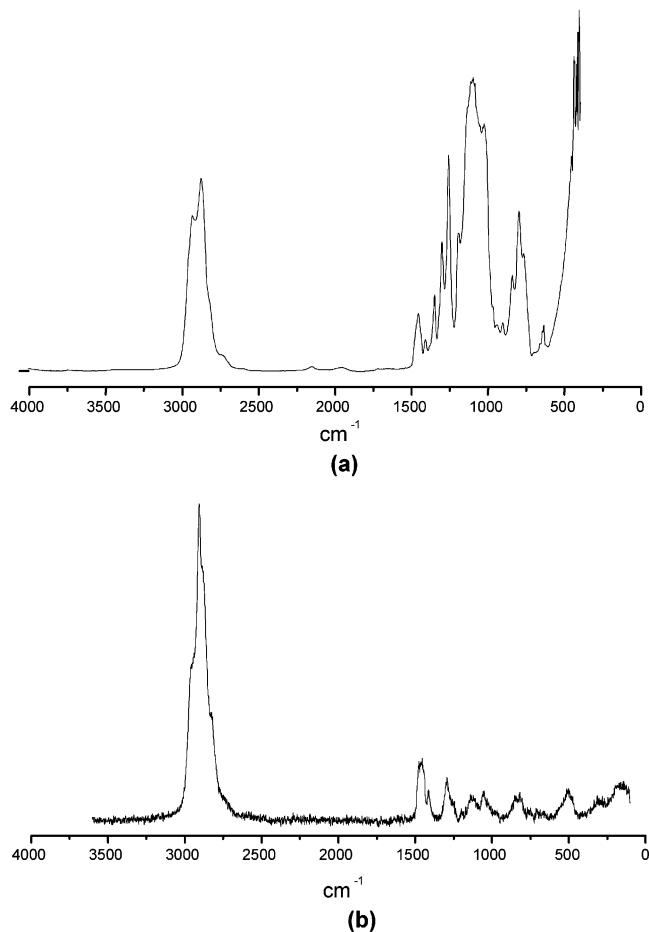


Figure 3. (a) FT-IR and (b) FT-Raman spectra of the polyelectrolyte described in Figure 2.

C–O–C stretching and bending modes within this region. The FT-Raman spectra, such as Figure 3b, did

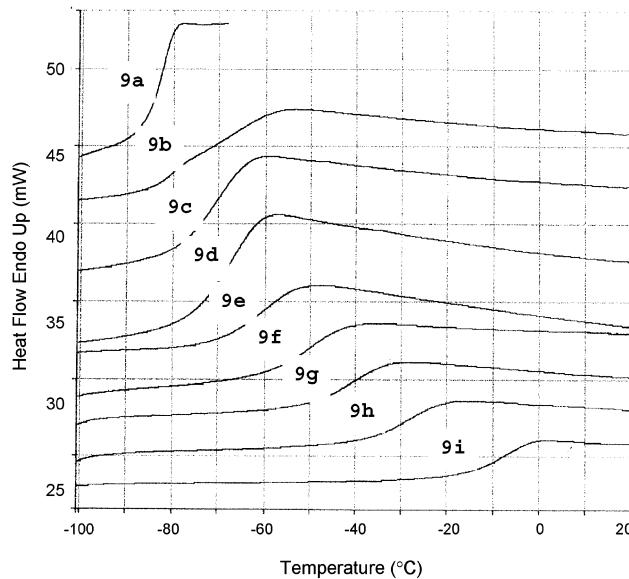


Figure 4. DSC scans at $30\text{ }^\circ\text{C}/\text{min}$ for **9a–i**.

not contain a peak at 867 cm^{-1} associated with an $\text{M}-\text{O}_n$ symmetric stretch “breathing mode” found in high-molecular-weight PEO complexes⁵⁸ and macrocyclic complexes⁵⁹ with alkali metal salts. The absence of this band may be due to the short oligoether side chain lengths, or more probably to the lowered symmetry expected around the lithium ions in the polyelectrolyte.

Table 2 lists the T_g values for eight polyelectrolytes studied plus the neat polysiloxane with only tetraglyme side chains. The glass transition temperature for each

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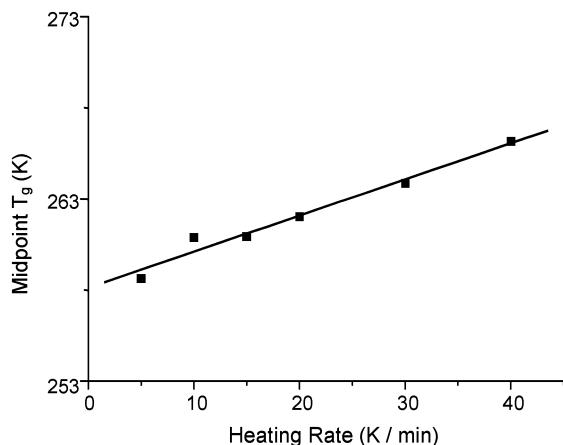


Figure 5. Extrapolation of the midpoint T_g at different scan rates to calculate the midpoint T_g at 0 K/min. The sample described is **9i**.

polyelectrolyte was measured below 0 °C. The T_g values were determined by three common methods using differential scanning calorimetry (DSC) data. Figure 4 compares the DSC traces at a heating rate of 30 °C/min over a limited temperature range for all reported samples. The fast scan rate accentuates thermal transitions and is shown for comparative purposes. Midpoint T_g values are reported in Table 2 for a scan rate of 10 K/min. Midpoint T_g values at 5 scan rates from 5 K/min to 30 K/min were extrapolated to determine the midpoint T_g at zero heating rate, as Figure 5 demonstrates for **9i**. A preliminary scan was taken for each sample

from -110 °C to 160 °C to detect possible melting points or secondary T_g transitions corresponding to the PEO side chain. The latter phenomenon was recently reported in comb polymer electrolytes with oligoether side chains.^{60,61} No secondary thermal transitions were observed for samples **9a–i**.

The polyelectrolytes corresponding to EO/Li ratios lower than 20:1 were found to be rubbery and to possess no perceptible fluidity at room temperature. EO/Li ratios higher than 30:1 resulted in poor mechanical properties, although this may be improved by cross-linking.⁶² The T_g for the ion-free polysiloxane, **9a**, is comparable to the T_g for similar compounds.^{13,15} The room-temperature conductivity was found to reach a maximum of 2.5×10^{-6} S/cm at 33:1 EO/Li. The conductivity data and methods are discussed in detail elsewhere.²³

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