Li^+ Conductivity of Polysiloxane−Trifluoromethylsulfonamide Polyelectrolytes

David P. Siska and D. F. Shriver*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

Received May 23, 2000. Revised Manuscript Received September 7, 2001

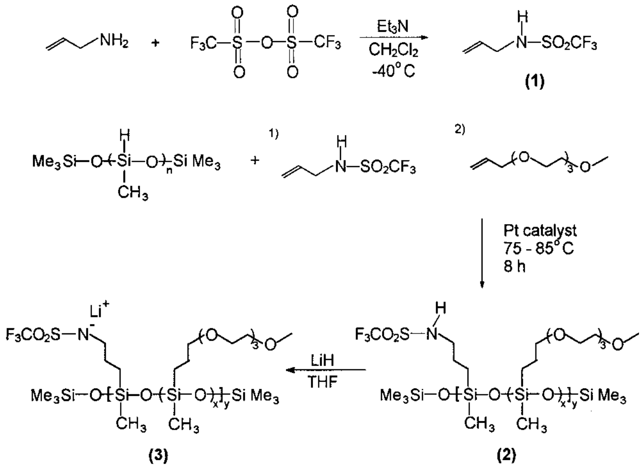
Lithium ion conducting polymers containing trifluoromethylsulfonamide anions and oligoether side chains bound to a polysiloxane backbone exhibit a room-temperature Li^+ conductivity of 1.2×10^{-6} S cm^{-1} and a T_g of −67 °C. Apparently, the flexible comb polymer architecture results in a high concentration of charge carriers and good ionic conductivity.

Introduction

Interest in polymer electrolytes from the standpoints of applications and fundamentals has led to the search for alkali metal salts having weakly coordinating anions, which are an improvement upon the perchlorate and triflate (trifluoromethanesulfonate) anions that are presently used in test cells. For the most part, commercial cells utilize $LiPF_6$ as the electrolyte. The bis(trifluoromethane-sulfonyl)imide (TFSI) $(CF_3SO_2)_2N^-$) anion has emerged as one of the most weakly coordinating anions,[1] and unlike the perchlorate anion, it is not potentially explosive in organic media. Several trifluoromethylsulfonamide salts have been shown to be almost as weakly paired as LiTFSI, including lithium methoxypropyltrifluoromethylsulfonamide (LiMPSA).[2] Salts of this type, (M^+) $(R-N-SO_2CF_3^-)$, can be synthesized readily from most alkylamines, and this synthetic route provides a rich variety of structures.[3]

Though they were originally explored as polymer−salt electrolytes in poly(ethylene oxide), PEO, the perfluoromethylsulfonamides are also attractive anions for the synthesis of new polyelectrolytes. For example, sulfonamides have been tethered to PEO chain ends to produce polyelectrolytes with room-temperature Li^+ conductivity of 5×10^{-6} S cm^{-1} and T_g of −44 °C.[4,5] Due to the electron-withdrawing effects of CF_3, the covalent attachment of trifluoromethylsulfonamides to PEO termini results in even weaker ion pairing and higher ionic conductivity than that of the PEO−sulfonamide polyelectrolytes.[6] Since T_g is relatively high for these systems, the conductivity of the polymer electrolyte should be enhanced by employing a highly flexible polysiloxane or polyphosphazene backbone. A polymer backbone consisting of perfluorosulfonimide units connected by carbonyl groups has been described, and it exhibits Li^+ conductivity of less than 10^{-7} S cm^{-1} at 25 °C, but it conducts extremely well when plasticized with a PEO network.[7] Our group and others have shown that short side chain ethers attached to polysiloxanes exhibit high segmental mobility, and they do not display a significant increase in T_g as salt content is increased.[8,9] These considerations prompted us to explore polyelectrolytes containing trifluoromethylsulfonamide anions and short oligoether side chains attached to a polysiloxane backbone.

Scheme 1. Synthesis of Allyltrifluoromethylsulfonamide and the Synthesis of Polysiloxane/Trifluoromethylsulfonamide Li^+ Polyelectrolytes



Experimental Section

A series of polysiloxanes, bearing trifluoromethylsulfonamide side chains, were synthesized according to Scheme 1. Trifluoromethanesulfonic (triflic) anhydride (in sealed am-

---

* To whom correspondence should be addressed.

(1) Armand, M.; Gorecki, W.; Andreani, R. In *Second International Symposium on Polymer Electrolytes*; Scrosati, B., Ed.; Elsevier Applied Science: New York, 1990.

(2) Lascaud, S.; Perrier, M.; Vallee, A.; Besner, S.; Prud'homme, J.; Armand, M. *Macromolecules* **1994**, *27*, 7469−7477.

(3) Dillon, R. E. A. Ph.D. Thesis, Northwestern University, 1999.

(4) Ito, K.; Nishina, N.; Tominaga, Y.; Ohno, H. *Solid State Ionics* **1996**, *86−88*, 325−328.

(5) Tominaga, Y.; Ohno, H. *Solid State Ionics* **1999**, *124*, 323−329.

(6) Tominaga, Y.; Ito, K.; Ohno, H. *Polymer* **1997**, *38*, 1949−1951.

(7) Watanabe, M.; Suzuki, Y.; Nishimoto, A. *Electrochim. Acta* **2000**, *45*, 1187−1192.

(8) Khan, I. M.; Yuan, Y.; Fish, D.; Wu, E.; Smid, J. *Macromolecules* **1988**, *21*, 2684−2689.

(9) Siska, D. P.; Shriver, D. F. In *New Materials for Batteries and Fuel Cells*; Doughty, D. H., Nazar, L. F., Arakawa, M., Brack, H. P., Naoi, K., Eds.; Materials Research Society: Warrendale, PA, 2000; Vol. 575.

10.1021/cm000420n CCC: $20.00

pules) and lithium hydride were purchased from Aldrich and handled under an inert atmosphere. Allylamine and triethylamine (Aldrich) were dried over CaH_2 and distilled under N_2 atmosphere before use. Polymethylhydrosiloxane (PMHS, M_w = 1900) and Karstedt's catalyst (Pt(0) tetramethyldivinyldisiloxane complex in xylenes) were obtained from Gelest. Allyltri(oxyethylene)methyl ether was prepared as described elsewhere[9] and dried over 4 Å molecular sieves. Dichloromethane was dried over P_2O_5, toluene over CaH_2, and THF over Na/benzophenone, and these rigorously dried materials were distilled and handled under a dry nitrogen atmosphere.

Synthesis of Allyltrifluoromethylsulfonamide (1). To a mixture of allylamine (1.0 g, 17.5 mmol) and triethylamine (2.0 g, 20 mmol) in 40 mL of CH_2Cl_2 at −40 °C, 5.0 g of triflic anhydride (18 mmol) was added dropwise under a nitrogen atmosphere. The solution was stirred for 4 h at room temperature, and volatiles were removed under reduced pressure. The remaining viscous liquid was dissolved in 30 mL of 4 M NaOH and washed with CH_2Cl_2 (3 × 25 mL). The aqueous portion was then neutralized with HCl, and the mixture was extracted with CH_2Cl_2 (3 × 30 mL). The organic extracts were then dried over $MgSO_4$ and filtered. The liquid product was isolated by the removal of CH_2Cl_2 under vacuum. ^1H NMR of (**1**) ($CDCl_3$): δ 5.9 ppm (m, 1H, $CH_2{=}C\mathit{H}CH_2{-}$), 5.35 ppm (m, 2H, $C\mathit{H_2}{=}CHCH_2{-}$), 4.9 ppm (s-broad, 1H, $N{-}\mathit{H}$), 3.9 ppm (m, 2H, $CH_2{=}CHC\mathit{H_2}{-}$). ^{19}F NMR ($CDCl_3$): δ −77.9 ppm (s). IR: (neat, KBr plates) υ_{N-H} 3315 cm^{-1}.

Hydrosilylation of Allyltrifluoromethylsulfonamide. PMHS (0.5 g, 7.56 mmol SiH) and the Pt(0) catalyst (10 μL) were mixed in toluene (10 mL) at 50 °C. Allyltrifluoromethylsulfonamide (0.3 g, 1.6 mmol) was added, the reaction mixture was stirred for 8 h at 65 °C, and the product was characterized. ^1H NMR ($CDCl_3$): δ 5.4 ppm (broad, 1H, $N{-}\mathit{H}$), 4.7 ppm (s, SiH), 3.3 ppm (m, 2H, $-CH_2CH_2C\mathit{H_2}NH-$), 1.7 ppm (m, 2H, $-CH_2C\mathit{H_2}CH_2NH-$), 0.6 ppm (m, 2H, $-C\mathit{H_2}CH_2CH_2NH-$), 0.1 ppm (m, backbone $Si{-}CH_3$). ^{19}F NMR ($CDCl_3$): δ −77.9 ppm (s). IR: (neat sample between KBr plates) υ_{N-H} 3315 cm^{-1}.

Attachment of Oligoether Side Chains. To the hydrosilylated product described above, sufficient allyl(trioxyethylene)methyl ether was added to substitute 95% of the available SiH sites. The temperature of this mixture was raised to 75 °C, and the reactants were stirred for 8 h to form the comb polymer. ^1H NMR of (**2**) ($CDCl_3$): δ 3.7 ppm (m, CH_2CH_2O), 3.4 ppm (s, $-OCH_3$ and $-Si{-}CH_2CH_2C\mathit{H_2}O-$), 3.2 ppm (m, 2H, $-CH_2CH_2C\mathit{H_2}NH-$), 1.8 ppm (m, 2H, $-CH_2C\mathit{H_2}CH_2NH-$), 1.6 ppm (m, 2H $-Si{-}CH_2C\mathit{H_2}CH_2O-$), 0.6 ppm (m, 2H, $-C\mathit{H_2}CH_2CH_2NH-$ and $-Si{-}C\mathit{H_2}CH_2CH_2O-$), 0.1 ppm (m, backbone $Si{-}CH_3$). ^{19}F NMR ($CDCl_3$): δ −77.9 ppm (s). IR: (neat, KBr plates) υ_{N-H} 3137 cm^{-1}.

Solvent was removed from the comb polymer under high vacuum. The polymer was then redissolved in 5−10 mL of dry THF, and this solution was added to a slurry containing a 2-fold molar excess of LiH in 5−10 mL of THF. After 24 h, excess LiH was filtered off, and the product was isolated under vacuum. ^{19}F NMR ($CDCl_3$): δ −77.2 ppm (s). The composition of the polymer was determined by the feed ratios of the reactants, and the composition was verified by the integrated NMR spectra of the product, which indicated the lack of unreacted allyl groups.

Solvent was removed from the newly synthesized polymers under high vacuum (6 × 10^{-6} Torr) at >85 °C for 3 days, and IR data indicated that H_2O is absent. Conductivity of the polyelectrolyte was determined by complex impedance analysis, and the material was characterized by differential scanning calorimetry.

Results and Discussion

Synthesis. The synthesis of allyltrifluoromethylsulfonamide followed the procedure which Lascaud et al. described for lithium methoxypropyltrifluoromethylsulfonamide (LiMPSA),[2] where we used allylamine in place of methoxypropylamine. A similar procedure was attempted for the synthesis of a vinyloxypropylamine analogue, without success.

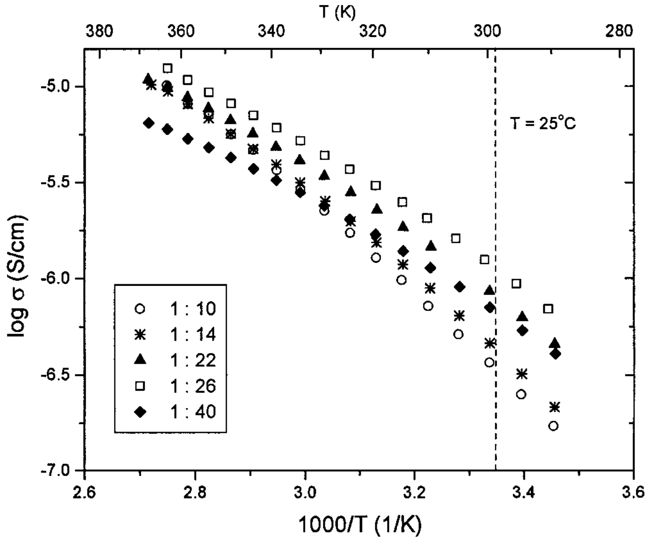


Figure 1. Variation of conductivity with temperature for Li$^+$ trifluoromethylsulfonamide/polysiloxane polyelectrolytes. The legend indicates the ratio of Li$^+$ to etheric oxygen units.

Table 1. Conductivity and T_g Values for the Series of Polysiloxane/Trifluoromethylsulfonamide Polyelectrolytes

polymer concn (EO units/Li$^+$)	σ (25 °C) (S cm^{-1})	σ (80 °C) (S cm^{-1})	T_g (°C)
10	3.7 × 10^{-7}	7.1 × 10^{-6}	−36.5
14	4.6 × 10^{-7}	6.9 × 10^{-6}	−45.4
22	8.6 × 10^{-7}	7.7 × 10^{-6}	−62.1
26	1.3 × 10^{-6}	9.3 × 10^{-6}	−67.1
40	7.1 × 10^{-7}	4.8 × 10^{-6}	−69.7

Allyltrifluoromethylsulfonamide readily underwent hydrosilylation with PMHS at fairly low temperatures (60−70 °C). Alkyl signals at 3.3, 1.7, and 0.6 ppm in the ^1H NMR were used to follow the progress of the reaction. A singlet at −77.9 ppm in the ^{19}F NMR spectrum remained unchanged from that of allyltrifluoromethylsulfonamide. The N−H stretch in the IR spectrum also remained at 3316 cm^{-1}. Upon hydrosilylation of allyl(trioxyethylene)methyl ether, the N−H stretch shifted to 3137 cm^{-1}, and the intensity of the SiH peak decreased in the ^1H NMR. Upon completion of the reaction with LiH, the N−H absorption was absent in the IR spectrum, and the ^{19}F NMR signal shifted to −77.2 ppm. The polyelectrolytes with high ion concentrations are extremely tacky semisolids, while polymers having lower concentrations of bound ions are viscous liquids at room temperature.

Conductivity. Conductivity data were obtained on rigorously dried samples by complex impedance analysis of samples sandwiched between stainless steel electrodes in cells having O-ring seals. T_g data were obtained with a differential scanning calorimeter on sealed samples, and the data are summarized in Table 1 for the polysiloxane/trifluoromethylsulfonamide polyelectrolytes. The temperature dependence of the conductivity (Figure 1) was fit by the Vogel−Tamman−Fulcher (VTF) equation, indicating that the mechanism for ion conduction is dependent upon the high-amplitude segmental motion of the polymer host.[10] Table 2 displays the results of a two-parameter fit to the VTF equation in which T_o was fixed at $T_g - 50$.

Table 2. VTF Parameters[a] for Polysiloxane/Trifluoromethylsulfonamides

polymer	A_2[b]	B_2 (K)	T_o (K)	T_g (K)
1:10	0.009 52	1097	186	236
1:14	0.005 44	1055	178	228
1:22	0.003 42	1046	161	211
1:26	0.004 37	1077	156	206
1:40	0.001 36	997	153	203

[a] Two-parameter fit, keeping T_o constant at 50 K below T_g. [b] A_2 is in units of S $K^{1/2}$ cm^{-1}.

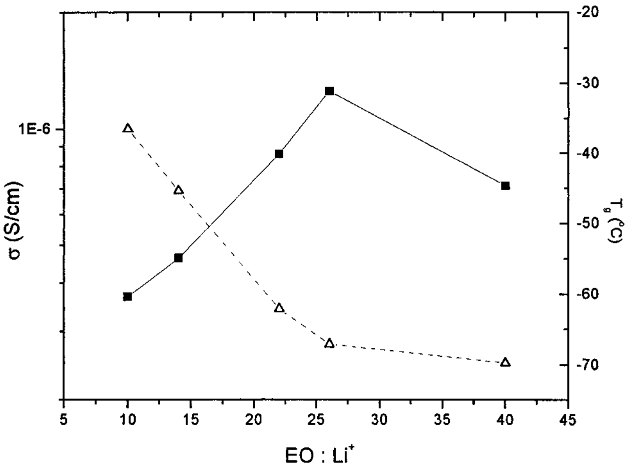


Figure 2. Variation of conductivity and T_g with ion concentration in the Li^+ trifluoromethylsulfonamide/polysiloxane polyelectrolytes; △, T_g; ■, σ at 25 °C.

The room-temperature conductivity and T_g of the new polyelectrolytes are displayed as a function of ion concentration in Figure 2, which shows that the maximum room-temperature Li^+ conductivity is 1.2×10^{-6} S cm^{-1} at an ion concentration of 1 Li^+ to 26 etheric oxygen (EO) units. Above this ion concentration, T_g increases significantly, indicating reduced segmental mobility, which is associated with decreased ion transport. This increase in T_g is attributed in part to electrostatic interactions between the cations and the anions in the polymer and cation interaction with the solvating ether chains. The minimum T_g, −69 °C, is slightly higher than that of the cross-linked polysiloxane/aluminosilicate networks.[9]

Because the trifluoromethylsulfonamide anion is bound by only one tether to the polymer backbone, the number of solvating side chains does not decrease with increased ion concentration as rapidly as that for polyelectrolytes where each anion is bound in two or three sites along the polymer backbone.[9] Thus, the conductivity of the present system reaches a maximum at a higher ion loading for the simple comb polyelectrolytes than for the networks. A large concentration of charge carriers is present at the conductivity-optimized ion concentration, and this factor combined with the weakly coordinating nature of the trifluoromethylsulfonamide anion leads to a Li^+ conductivity which exceeds that of the Na^+ conductivity of the best polysiloxane/aluminosilicate networks synthesized to date.

The conductivity of our polysiloxane/trifluoromethylsulfonamide polyelectrolytes is somewhat lower than that of sulfonamide-terminated PEO compounds synthesized by Tominaga et al.[5] Their PEO material contains a high concentration of solvating sites, while the polysiloxane backbone and its methyl groups in the present study have low polarity, so they occupy volume which is not conducive to ion transport. However, there are prospects for optimizing the lengths of both the oligother side chain and the anion-bearing side chains to bring the conductivity of the polysiloxane-based system close to that of the trifluoromethylsulfonamide-terminated PEO materials.

In summary, comb polysiloxane polyelectrolyte containing trifluoromethylsulfonamide anions and oligoether side chains was synthesized, and it exhibits a maximum room-temperature Li^+ conductivity of 1.2×10^{-6} and a T_g of −67 °C. Because this polymer contains anions attached to the polymer backbone by only one tether, the conductivity maximum occurs at a higher ion loading than that of similar network architectures where the anion is bound through two or more linkages to the polymer network.

Acknowledgment. This research was supported by the ARO AASERT Grant No. DAAH-04-95-1-0524 and the MRSEC program of the National Science Foundation, No. DMR-9120521, at the Materials Research Center of Northwestern University.

CM000420N

---

(10) Ratner, M. A.; Shriver, D. F. *Chem. Rev.* **1988**, *88*, 109.