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Lithium salts of SF_5 alkylsulfonic acids: synthesis, characterization and conductivity

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Abstract

The lithium sulfonates, SF_5CFHSO_3Li (**1**) and $SF_5CF_2SO_3Li$ (**2**), were prepared by reaction of the corresponding sulfonyl fluorides SF_5CFXSO_2F ($X=H$ or F) with lithium hydroxide. The product identities were confirmed by IR and NMR spectroscopies, MS and elemental analysis, and the thermal stabilities were determined via DSC and TGA. The poly(ethylene oxide) (PEO)–salt complexes, $PEO_xLiSO_3CFHSF_5$ (**3**), were prepared for $x=2$ to 16 (where $x=O/Li$ mole ratio) and the bulk conductivities measured between 40 °C and 120 °C. Unlike the $PEO_xLiSO_3CF_2SF_5$ (**4**) complexes, thermal and conductivity measurements do not indicate a plasticizing effect for these complexes; these observations are discussed in terms of hydrogen bonding between $SF_5CFHSO_3^-$ anions.

Keywords: Lithium salts; Sulfur pentafluoride alkylsulfonic acids; Synthesis; Conductivity; NMR spectroscopy; IR spectroscopy

1. Introduction

A number of poly(ethylene oxide) (PEO)–salt complexes that exhibit electrochemical stability and high ionic conductivity have been investigated for use as solid polymer electrolyte (SPEs) in solid-state electrochemical cells. Ionic conductivity through SPEs is known to occur by means of an amorphous component of the polymer–salt complex [1]. Enhanced conductivity at ambient temperatures in polymer–salt complexes can be achieved by the inclusion of plasticizers that suppress crystallinity at or above the operating temperature. Several compounds, $LiN(SO_2CF_3)$, $LiC(SO_2CF_3)_3$ and $SF_5CF_2SO_3Li$, have been found to suppress crystallinity in PEO–salt complexes and exhibit ionic conductivities exceeding 10^{-4} S cm^{-1} at or below 80 °C [2–6]. New plasticizing compounds such as the lithium salt of the dianion $[(CF_3SO_2)_2CR]C_6H_4^{2-}$, where $R=CO$ or SO_2, have also shown suppressed crystallinity and high ionic conductivity when complexed with PEO to form SPEs [7].

This paper reports the synthesis and characterization of two new lithium salts that potentially, when complexed with PEO, would be excellent candidates as solid-state ion conductors; previously the conductivity of complexes containing $SF_5CF_2SO_3Li$ was published [6]. The pentafluorosulfur-containing lithium sulfonates, SF_5CFHSO_3Li (**1**) and $SF_5CF_2SO_3Li$ (**2**), were synthesized by the reaction of the corresponding sulfonyl fluorides, SF_5CFXSO_2F ($X=H$ and F), with lithium hydroxide. In this work the conductivity of PEO–salt complexes of **1** were determined and these results are compared to those for the PEO–salt complexes of **2** [6].

2. Results and discussion

The SF_5-fluoroalkyl sulfonate salts, SF_5CFXSO_3Li ($X=H$ or F), were prepared via the following steps:

(i) Reacting perfluorovinyl sulfur pentafluoride, $SF_5CF{=}CF_2$, with distilled sulfur trioxide. The reaction was carried out in a modified Carius tube under pressure and with mild heating (up to 110 °C) to produce $SF_5\overline{CFCF_2OS}O_2$ [8,9].

$$SF_5CF{=}CF_2 + SO_3 \longrightarrow SF_5\overline{CFCF_2OS}O_2$$

(ii) Reacting the β-sultone with water at temperatures between 45–60 °C to produce SF_5CFHSO_2F [9].

$$SF_5\overline{CFCF_2OS}O_2 + H_2O \longrightarrow SF_5CFHSO_2F + CO_2 + HF$$

(iii) Fluorinating SF_5CFHSO_2F to produce $SF_5CF_2SO_2F$.

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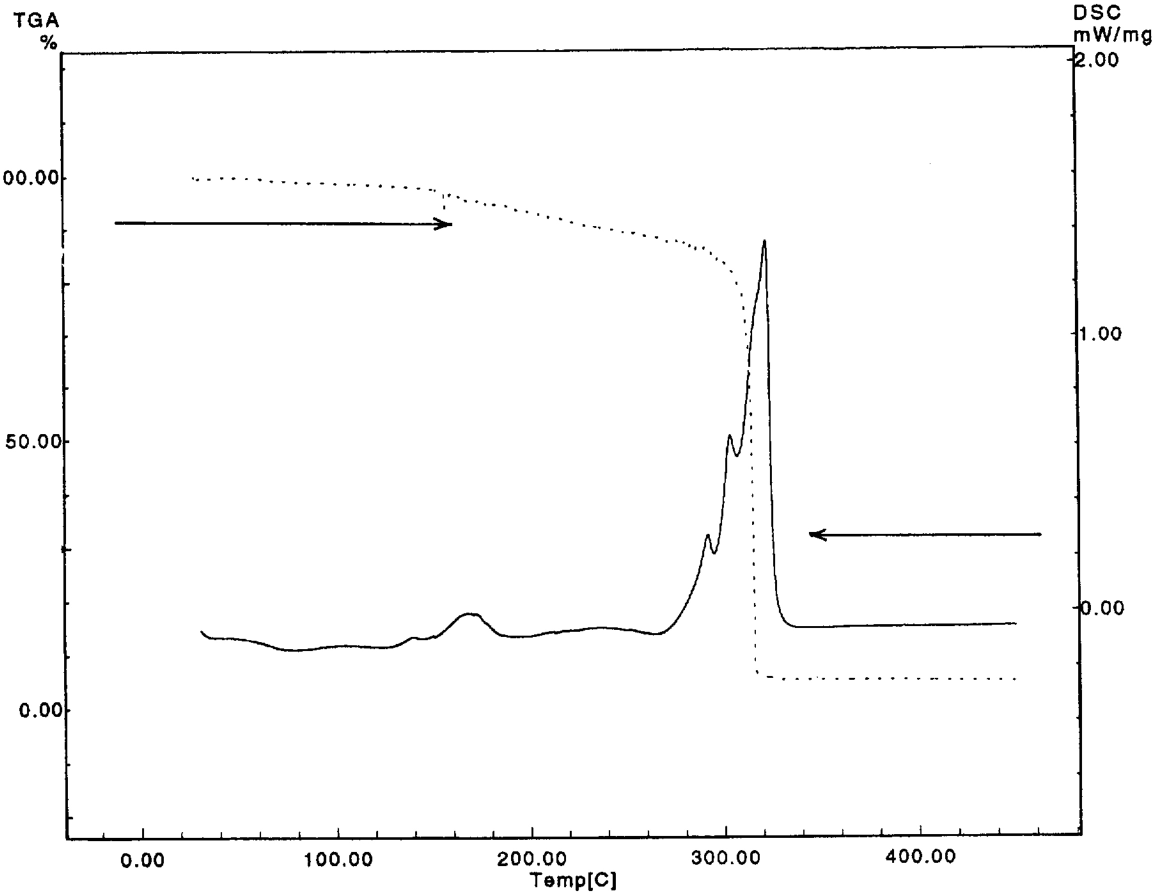

Fig. 1. DSC and TGA traces for $LiSO_3CHFSF_5$.

$$SF_5CFHSO_2F + F_2 + NaF \longrightarrow SF_5CF_2SO_2F + NaHF_2$$

The subsequent reaction of the two sulfonyl fluorides, SF_5CFHSO_2F and $SF_5CF_2SO_2F$, with lithium hydroxide resulted in the corresponding lithium sulfonates **1** and **2**.

$$SF_5CFXSO_2F + 2LiOH \longrightarrow SF_5CFXSO_3Li + LiF + H_2O$$

(1) X=H
(2) X=F

The resulting lithium salts were white powdery compounds, thermally stable well above 100 °C. DSC/TGA data (Figs. 1 and 2) indicate main decomposition events at ~310 °C and 270 °C for salts **1** and **2**, respectively, and confirm the absence of water (which is evident as a mass loss below 100 °C in the TGA data for samples exposed briefly to air).

The lithium sulfonates were characterized by infrared spectroscopy as well as ^1H, ^{13}C and ^{19}F NMR spectroscopy. The IR spectrum contained the characteristic S–F stretch of the SF_5 group at 857 and 880 cm^{-1}, respectively, for **1** and **2**. One of the S–F deformation modes occurs at 597 cm^{-1} for **2** and at 602 cm^{-1} for **1**; similar values for SF_5CFH- and SF_5CF_2-containing sulfonyl fluorides, sulfonate salts and sulfonic acids have been reported and range from 832–914 cm^{-1} (S–F stretch) and 586–598 cm^{-1} (S–F deformation) [10,11]. The asymmetric and symmetric S=O stretching modes appear at 1310 and 1088 cm^{-1} for **2** and at 1296 and 1083 cm^{-1} for **1**, respectively, while the CF stretching bands appear as strong bands at 1246 and 1228 cm^{-1} for both compounds. These absorption bands agree well with reported values [10].

The ^1H NMR spectrum of **1** consists of the CH chemical shift at 6.15 ppm ($J_{H\text{–}F(eq)} = 5.6$ Hz), this value being indicative of an acidic-type methine proton. Other systems containing a methine proton with similar chemical shifts include $F_5SCH(SO_2F)C(O)OCH_3$ (6.26 ppm), $F_5SCH(SO_2F)C(O)OCH(CH_3)_2$ (6.4 ppm) and $F_5SCH(SO_2F)C(O)OC(CH_3)_3$ (5.88 ppm) [12–14]. The acidic nature of the methine proton in $F_5SCH(SO_2F)C(O)OR$ [where $R = CH_3$ and $CH(CH_3)_2$] has also been demonstrated by forming the corresponding salts with NH_3 and $N(CH_2CH_3)_3$ [15].

The ^{19}F NMR spectra of both **1** and **2** show an AB_4 pattern for the SF_5 grouping. For the AB_4 patterns of the SF_5 grouping in **1** and **2**, the equatorial fluorine resonances were observed as doublets and the axial fluorine resonances as a nine-line pattern of multiplets. Both compounds exhibit fine structure in the AB_4 pattern due to second-order effects. The ^{19}F NMR chemical shifts for equatorial and axial fluorines in the SF_5 grouping occur at 51.8 and 75.0 ppm, respectively, for compound **1** and at 45.0 and 68.4 ppm, respectively, for compound **2**. Increased shielding of the SF_5 equatorial and axial fluorines upon replacement of hydrogen by fluorine on the

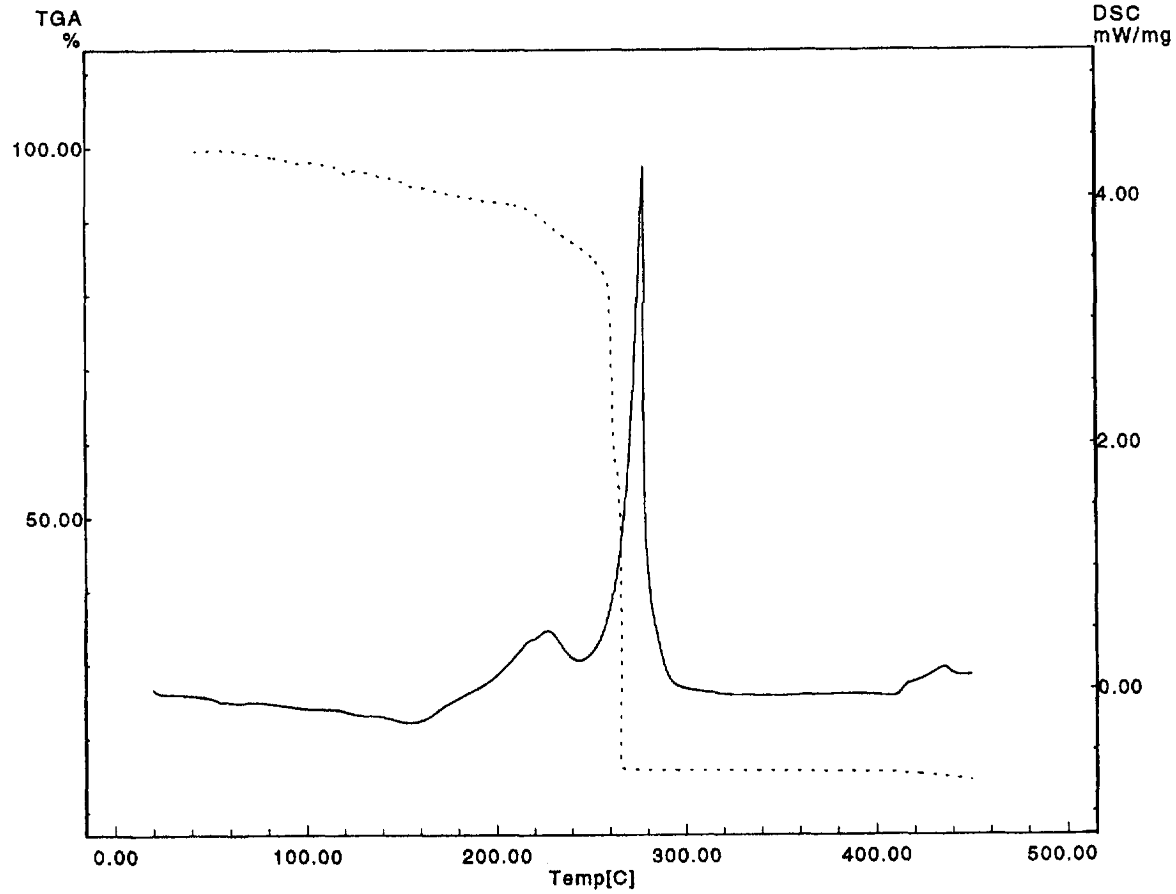

Fig. 2. DSC and TGA traces for $LiSO_3CF_2SF_5$.

adjacent carbon is observed. Compounds of similar structure, $SF_5CX_2SO_2F$ and $(SF_5CX_2SO_3)_2Ca$ where X = H and/or F, show a similar progression of increasing shielding of the fluorines in the SF_5 grouping [10,11]. The CF resonance for **1** occurs as a doublet of multiplets ($J_{F-H} = 44.1$ Hz) at − 155.5 ppm. Compound **2** exhibits CF_2 resonance as a doublet of pentets ($J_{F-F(ax)} = 4.9$ and $J_{F-F(eq)} = 14.1$ Hz) at − 88.7 ppm.

Chemical shifts in the ^{13}C NMR spectra of **1** and **2** occur at 115.1 and 124.2 ppm, respectively; these chemical shifts agree well with reported values for other SF_5-fluoroalkyl sulfonate acids/salts [10,16]. The coupling constants J_{C-F} and $J_{C-F(eq)}$ found for **1** are 267.3 and 17.2 Hz, respectively. The coupling constant J_{C-H} for compound **1** was found to be 178.7 Hz. Compound **2** exhibited coupling constants J_{C-F} and $J_{C-F(eq)}$ of 334.2 and 21.4 Hz, respectively.

Two strong endotherms were observed (Fig. 3) for the complexes of $PEO_xLiSO_3CFHSF_5$ (**3**), at 50–70 °C and ~ 0 °C, with the lower temperature event observed principally with $x = 3$–8. The appearance of a second, lower endotherm at higher salt contents has also been seen in other PEO-based complexes [4]. The Arrhenius plot (Fig. 4) for **3** indicate that the bulk ionic conductivities were similar to those of other PEO-based electrolytes [17] and were less than 10^{-7} S cm^{-1} at ambient temperature for all prepared stoichiometries. Breaks in the Arrhenius curves for the 16:1 and 8:1 complexes at ~ 70 °C and ~ 50 °C, respectively, are consistent with the phase transitions recorded at these temperatures: impedances were too large to obtain conductivity data near 0 °C for these complexes.

The calorimetric and thermal data for **3** stand in marked contrast to those obtained for PEO complexes prepared from salt **2**. In the latter series of complexes, a plasticizing effect was observed based on the following facts: (i) the exotherm at 50–70 °C was greatly diminished, but no significant new endotherms arose with increasing salt content, and (ii) high ionic conductivities (> 10^{-5} S cm^{-1}) could be obtained at ambient temperature. Both of these sets of data were reproducible and the thermal and impedance data are consistent, yet it is surprising that such closely related salts can display very different behavior in the PEO matrix. The change is related to the formation of a crystalline phase at ~ 0 °C at appropriate stoichiometries for complexes of PEO with salt **1** but not with salt **2**.

A model to explain these observations must focus on the different chemistry of the two anions. In particular, it appears that anion **1** is capable of hydrogen bonding. Evidence for this includes the proton chemical shift and the reactivity of similar compounds with bases. In these complexes, it seems

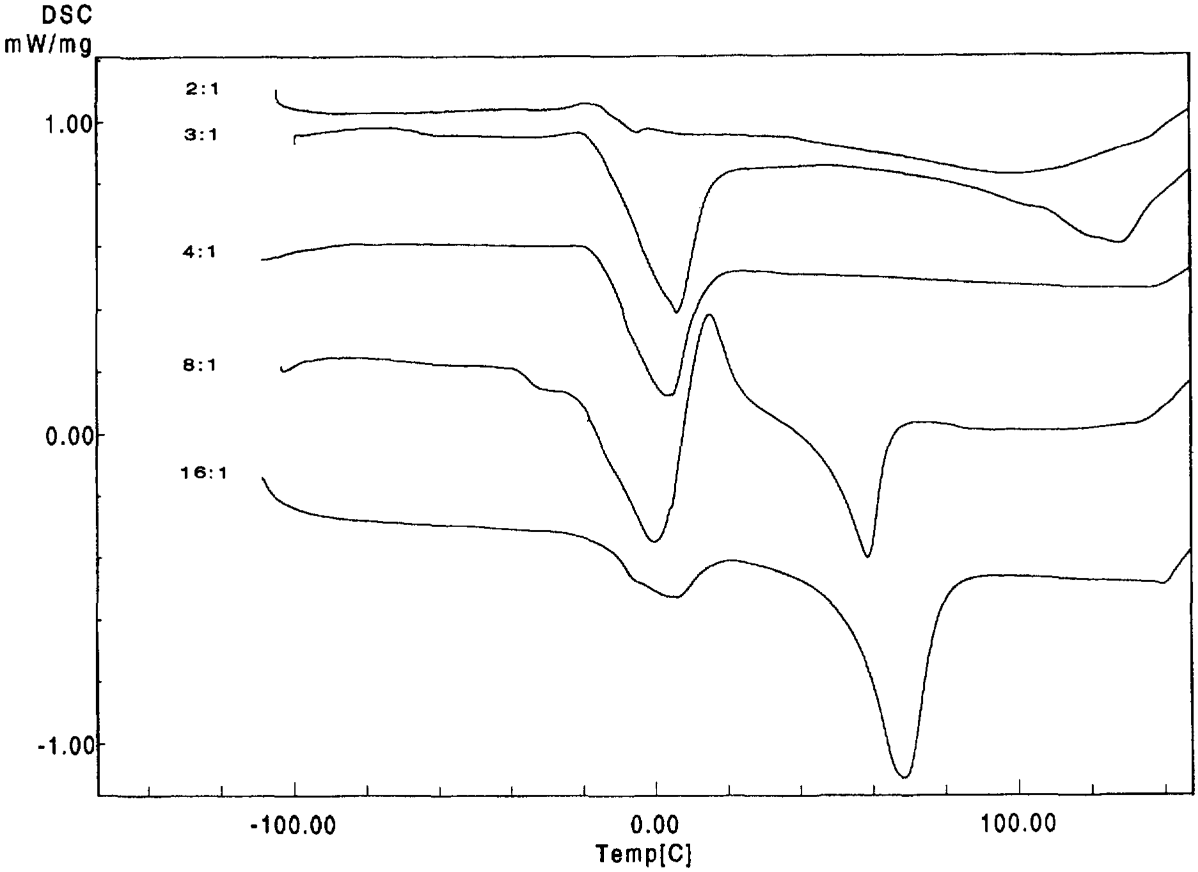

Fig. 3. DSC traces for PEO$_x$LiSO$_3$CFHSF$_5$ complexes.

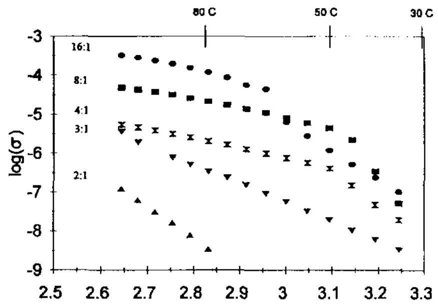

Fig. 4. Arrhenius plots for PEO$_x$LiSO$_3$CFHSF$_5$ complexes.

likely that hydrogen bonding would arise between the methine acidic proton and other sulfonate groups.

The role of hydrogen bonding in directing the crystallization of a polymer–salt complex is not understood – it may be conjectured that the assembly and ordering of [PEO$_x$Li$^+$] helical units, observed in structural studies on similar complexes [18], is facilitated by hydrogen bonding between the anions.

3. Experimental details

3.1. Materials

The sulfonyl fluorides, SF$_5$CFHSO$_2$F and SF$_5$CF$_2$SO$_2$F, were prepared according to literature methods [9]. Methanol (Aldrich) was distilled to use. Lithium hydroxide monohydrate (reagent grade; Matheson, Coleman & Bell) was used as received. PEO ($M_w = 5 \times 10^6$) was obtained from Aldrich Chemical Company. Acetonitrile (reagent grade) was obtained from Mallinckrodt Chemical Company.

3.2. General methods

NMR spectra were recorded with a Varian EM390 spectrometer operating at 90 MHz for ^{1}H analyses and 84.67 MHz for ^{19}F analyses, and with a Bruker AMX-400 spectrometer operating at 100.6 MHz for ^{13}C analyses; $(CH_3)_4Si$ and $CFCl_3$ were used as reference standards. IR spectra were obtained between potassium bromide plates using a Nicolet 20 DX spectrometer. Mass spectra were recorded with a Finnigan MAT 8230 system operating at 30 eV. Elemental analysis were determined by Beller Mikroanalytisches Laboratorium, Gottingen, Germany. A Mel-Temp melting point apparatus was used to determine melting points; these values are reported without correction.

Differential scanning calorimetry (DSC) was performed with 20–25 mg samples loaded in hermetically-sealed Al pans in a Shimadzu DSC-50Q apparatus. Samples were heated to 150 °C, quenched below −100 °C, then heated at 10 °C min^{-1} from −100 °C to 150 °C. Thermogravimetric analyses (TGA) utilized a Shimadzu TGA-50 apparatus. Samples

(15–20 mg) were loaded into a Pt pan and heated from 30–450 °C at 10 °C min^{-1} under N_2 flow (50 ml min^{-1}).

3.3. Synthesis of SF_5CFHSO_3Li (1)

To a 100 ml three-necked flask containing a Teflon stirring bar and fitted with an addition funnel, a reflux condenser and a thermometer, 40 ml of anhydrous methanol and 1.84 g (43.9 mmol) of $LiOH \cdot H_2O$ were added. The flask was cooled in an ice bath and 4.58 g (18.9 mmol) of SF_5CFHSO_2F was added with stirring at such a rate that the temperature was maintained below 20 °C. The turbid mixture was stirred at room temperature for 16 h, then heated to reflux for 4 h. The mixture was cooled in an ice bath and filtered to remove the precipitate. The solvent was removed under vacuum from the filtrate to give 4.48 g of crude product. The crude product was dissolved in THF and filtered, followed by removal of residual THF under vacuum. The resulting paste was triturated with hexane and dried under vacuum for 2 d to give 4.12 g (16.7 mmol) of product for a yield of 88%; m.p. 295 °C sintering, 315 °C darkening.

The infrared spectrum of **1** exhibited the following bands (cm^{-1}): 3001 (vw); 1321 (s); 1296 (vs); 1228 (vs); 1135 (m); 1083 (m); 917 (sh); 881 (sh); 857 (vs); 828 (m); 732 (m); 678 (w); 646 (m); 603 (m); 567 (w). ^{1}H NMR [CD_3CN, $(CH_3)_4Si$ ext.] δ: 6.15 (d, p, $J_{H-F(eq)} = 5.6$ Hz) ppm. ^{19}F NMR (CD_3CN, $CFCl_3$ ext.): (AB_4), $\phi_A = 75.0$ (9 lines, rel. int. = 1.0) ppm; $\phi_B = 51.8$ (d, m, rel. int. = 4.0) ppm; $J_{AB} = 153.8$ Hz; $CFH = -155.5$ (d, m, rel. int. = 1.1) ppm; $J_{F-H} = 44.1$ Hz. ^{13}C NMR [CD_3CN, $(CH_3)_4Si$ int.] δ: 115.1 (d, d, p) ppm; $J_{C-F} = 267.3$ Hz, $J_{C-H} = 178.7$ Hz, $J_{C-F(eq)} = 17.2$ Hz. Analysis: Calc. for $CHF_6S_2O_3Li$: C, 4.48; H, 0.41; F, 46.3; S, 26.06%. Found: C, 5.03; H, 0.53; F, 45.5; S, 26.74%.

3.4. Preparation of $PEO_xLiSO_3CFHSF_5$ (3)

$LiSO_3CFHSF_5$ was thoroughly dried under vacuum at 120 °C for 48 h to remove residual water or solvent. PEO–salt complexes were prepared by co-dissolution of the desired stoichiometry of salt and PEO in acetonitrile. Complexes were dried in vacuo for 48 h and maintained under an inert atmosphere. Stoichiometries are described by PEO_x-$LiSO_3CFHSF_5$, where x reflects the mole ratio of C_2H_4O to Li.

3.4.1. Characterization of $PEO_xLiSO_3CFHSF_5$ (3)

Bulk ionic conductivities were measured on 1/2 in pressed pellets of the complexes in a hermetically-sealed cell using a Solartron 1260 impedance analyzer. Samples were heated to 100 °C and then quenched below −30 °C prior to data collection. Responses were measured from 10 MHz to 0.1 Hz between −30 °C and 100 °C. Bulk conductivities were derived from the high-frequency touchdown on Nyquist plots and the known cell geometry.

3.5. Synthesis of $SF_5CF_2SO_3Li$ (2)

To a 100 ml three-necked flask containing a Teflon stirring bar and fitted with an addition funnel, and a reflux condenser, 40 ml of water and 1.13 g (26.9 mmol) of $LiOH \cdot H_2O$ were added. Over a 20 min period, 3.49 g (13.4 mmol) of $SF_5CF_2SO_2F$ was added with stirring. The mixture was heated at reflux for 2 d until the lower phase was no longer present. The cloudy solution was then heated to reflux at 100 °C for 4 h, cooled and filtered. The solvent was removed by rotary evaporation; drying in vacuo for 10 d gave 1.72 g (6.5 mmol) of product for a yield of 49%; m.p. 270 °C sintering, stable to greater than 350 °C.

The infrared spectrum of **2** exhibited the following bands (cm^{-1}): 1310 (vs); 1246 (vs); 1194 (s); 1140 (s); 1088 (s); 967 (w); 905 (sh); 880 (vs); 840 (vs); 676 (m); 628 (w); 597 (m); 574 (w); 542 (w). ^{19}F NMR (CD_3CN, $CFCl_3$ ext.): (AB_4), $\phi_A = 68.4$ (9 lines, rel. int. = 1.0) ppm; $\phi_B = 45.0$ (d, m, rel. int. = 4.1) ppm; $J_{AB} = 149.6$ Hz; $CF_2 = -88.7$ (d, p, rel. int. = 1.9) ppm; $J_{F-F(ax)} = 4.9$ Hz, $J_{F-F(eq)} = 14.1$ Hz. ^{13}C NMR [CD_3CN, $(CH_3)_4Si$ int.] δ: 124.2 (t, p) ppm; $J_{C-F} = 334.2$ Hz, $J_{C-F(eq)} = 21.4$ Hz. MS (m/z) FAB^-: 785 ($2M \cdot SF_5CF_2SO_3$); 547 ($2M \cdot F$); 521 $(SF_5CF_2SO_3)_2Li$; 283 ($M \cdot F$); 264 (M); 257 ($SF_5CF_2SO_3$); 149 (CF_3SO_3); 130 (CF_2SO_3); 127 (SF_5); 80 (SO_3). Analysis: Calc. for $CF_7S_2O_3Li \cdot H_2O$: C, 4.26; H, 0.71, F, 47.1; S, 22.73%. Found: C, 4.31; H, 0.55; F, 46.3; S, 23.6%.

Acknowledgments

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