Synthesis and Characterization of Tetra- and Trisiloxane-Containing Oligo(ethylene glycol)s— Highly Conducting Electrolytes for Lithium Batteries

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Tetrasiloxane and trisiloxane compounds were attached to oligo(ethylene oxide) chains, -(CH_2CH_2O)-$_n$ ($n = 2-7$), via hydrosilation and dehydrocoupling reactions. The compounds were purified by solvent extraction and distillation before being characterized by ^{1}H, ^{13}C, and ^{29}Si NMR. Upon being doped with lithium bis(oxalato)borate (LiBOB) or lithium bis(trifluorosulfonyl) imide (LiTFSI), the electrolytes showed ambient temperature conductivities ranging from 2×10^{-4} to 6×10^{-4} S cm^{-1}. These low viscosity compounds have conductivities that are among the highest observed to date for liquid "polymer" electrolytes. Temperature-dependent conductivity studies suggest that the ethylene oxide chains contribute to ion transport as a polymer would. The amorphous behavior of the electrolytes was observed by differential scanning calorimetry, which revealed very low glass-transition temperatures before and after doping.

1. Introduction

In 1973, Wright and co-workers discovered that poly(ethylene oxide) (PEO) could be used as an ion conductor upon doping with a salt.[1,2] Since then, a wide range of polymers have been investigated for use as possible electrolytes in high-density lithium batteries.[3−31] In particular, research involving ionically conducting PEO has been at the forefront of lithium-battery research because of its nontoxic and nonflammable nature. The biocompatibility of PEO makes it attractive as an electrolyte in batteries designed for many applications, including those associated with biomedical research. However, there are difficulties associated with the development of highly conductive PEO electrolytes for ambient temperature applications because of its crystalline nature. For instance, high-molecular-weight PEO has an ambient conductivity on the order of 10^{-7} S cm^{-1}.[1,2] This is well below the required conductivity of 1×10^{-3} S cm^{-1} needed for an electrolyte to be considered commercially useful. Recent efforts have therefore focused on the com-

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binations of PEO with stable, more flexible polymers, such as polyphosphazenes[4−9] and polysiloxanes.[10−31]

Polysiloxanes have relatively low glass transition temperatures because of the low bond-rotation energies associated with the SiOSi units. The concept of combining stable, flexible polymers with PEO has led to the development of a variety of polymeric structures with the expressed aim of increasing conductivity. During the past few years, a number of copolymers with comb,[10−12,16] double-comb,[17−19] cyclic,[20−22] and cross-linked structures[23,24,30,31] have been synthesized and investigated as possible candidates for both liquid and solid polymer electrolytes. Recently, our investigations into liquid polymer electrolytes have been influenced by the concept that conductivity will generally increase as the glass-transition temperature (T_g) and viscosity of the electrolyte decreases.[18,25] We have found that when shorter PEO and polysiloxane segments are employed, the conductivity increases. Herein, we report the synthesis of several "oligomeric" compounds synthesized from a tetra- or trisiloxane starting material, with each compound containing only one or two oligoether chains, and their conductivities. Physical and thermal properties are also investigated.

2. Experimental Section

2.1. Materials. 1,3-Bis(trimethylsiloxy)-1,3-dimethyldisiloxane (95%), 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (95%), bis(trimethylsiloxy)methylsilane, 1,1,3,3,5,5-hexamethyltrisiloxane, pentamethyldisiloxane, and 1,1,3,3-tetramethyldisiloxane were purchased from Gelest and distilled prior to use. Diethylene glycol methyl ether, tri(ethylene glycol) methyl ether, and poly(ethylene glycol) methyl ether (M_n 350) were purchased from Aldrich and distilled prior to use. Allyl-terminated oligo(ethylene glycol) methyl ethers ($AlPEO_n$) were synthesized according to the procedures outlined in the literature.[18] 3-Allyloxy-propane-1,2-diol, chlorotrimethylsilane, 4-(hydroxymethyl)-1,3-dioxolan-2-one, and diethyl carbonate were purchased from Aldrich.

Lithium bis(oxalato)borate (LiBOB) was supplied by Chemetall and purified by recrystallization in dried, distilled acetonitrile (Aldrich). Lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) was donated by 3M.

Karlstedt's catalyst solution (divinyltetramethyldisiloxane-Pt(0), 2−3% w/w in xylene) was purchased from Gelest. Tris(pentafluorophenyl)borane (95%; $B(C_6F_5)_3$) was purchased from Aldrich.

Toluene and tetrahydrofuran (THF) were purchased from J. T. Baker and Burdick & Jackson, respectively, and distilled over sodium and benzophenone prior to use. Hexane was predried and distilled over CaH_2 prior to use. Diethyl ether was distilled over sodium and benzophenone. Triethylamine and pyridine were purchased from Aldrich and distilled over CaH_2 prior to use. Sulfuric acid (certified ACS grade) was purchased from Fisher. Acetonitrile was refluxed over CaH_2 for 24 h and distilled before use.

2.2. Apparatus. ^1H and ^{13}C NMR were carried out on a Bruker AC300 spectrophotometer; ^{29}Si NMR was performed on a Varian Unity 500 spectrophotometer. Deuterated chloroform ($CDCl_3$, 99.8%, Aldrich) was used as the solvent. Viscosity measurements were performed on a Brookfield LVDV-I+ viscometer. Differential scanning calorimetry was obtained using a Perkin-Elmer Pyrus Diamond instrument, calibrated with heptane, indium, and dimethylsiloxane. All samples were loaded under dry argon. Undoped samples were cooled very quickly to −160 °C, followed by an increase in temperature from −160 to 200 °C at a rate of 10 °C/min. The Pyris DSC software allowed mathematical computation of the onset of the glass transition. Each sample was duplicated once, with the second heat run quoted.

LiBOB-doped samples: conductivity was measured by loading the samples into button cells and using a frequency range from 20 to 5×10^5 Hz, and the impedance was recorded over a temperature range from room temperature to 70 °C. In some cases, the conductivity was studied by varying the concentration of LiBOB.

LiTFSI-doped samples: conductivity was measured in cells described previously[29] using a Princeton Applied Research (PAR) potentiostat galvanostat model 273A and a PAR frequency response detector model 1025, which applied an AC current and measured impedance (Z) and phase shift (θ) over frequencies from 100 to 100 000 Hz. The four lowest θ values were used to calculate an average conductivity (σ) for both conductivity experiments and cell calibrations.

2.3. Synthesis of Tetrasiloxane-Based Compounds. *Synthesis of **4.1***. 1,1,3,3,5,5,7,7-Octamethyltetrasiloxane (10 g, 0.0354 mol), $HOPEO_3$ (13.9 g, 0.085 mol), tris(pentafluorophenyl)borane (0.010 g, 1.98×10^{-5} mol), and toluene (75 mL) were added to a 250 mL round-bottom flask and heated to 70 °C. After 24 h, the solvent was removed by Kugelrohr distillation. The product itself was then distilled via Kugelrohr distillation. The product was dissolved in toluene (150 mL) and washed six times with water (10 mL × 6). Toluene was then removed, and the remaining product was dried by heating to 100 °C under vacuum for 24 h. The final product was obtained as a clear colorless liquid. ^1H NMR ($CDCl_3$): δ 3.77 ($SiOCH_2C$), 3.43−3.61 (OCH_2CH_2O), 0.05 ($SiCH_3$). ^{13}C NMR ($CDCl_3$): δ 70.3−72.4 (OCH_2CH_2O), 61.5 ($SiOCH_2C$), 58.8 (OCH_3), 1.0 ($OSi(CH_3)_2O$), −0.9 ($C-OSi(CH_3)_2O$). ^{29}Si NMR ($CDCl_3$): δ −12.8 ($C-O-Si(CH_3)_2O$), −22.5 ($OSi(CH_3)_2O$).

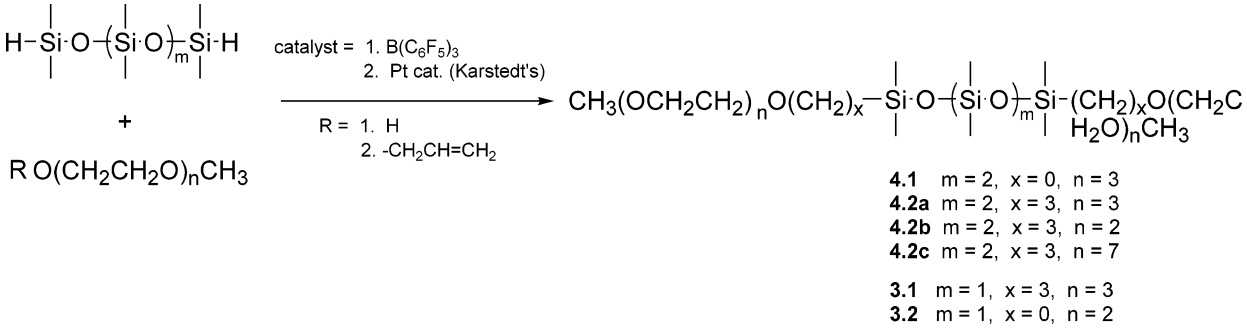
Similar reactions were carried out using oligoether chains of varying lengths, such as $HOPEO_2$ and $HOPEO_7$. For compounds containing longer PEO chains (i.e., PEO_7), the product was not distillable and was therefore dissolved in toluene, refluxed over charcoal for 12 h, and then allowed to cool. The solution was filtered prior to the removal of toluene under reduced pressure to yield a slightly yellow oil.

*Synthesis of **4.2a***. 1,1,3,3,5,5,7,7-Octamethyltetrasiloxane (10 g, 0.0354 mol), $AlPEO_3$ (17.3 g, 0.0850 mol), and Karstedt's catalyst solution (0.13 g, 7.8×10^{-6} mol) were added to a 50 mL round-bottom flask and heated to 75 °C. After 24 h, the product was Kugelrohr distilled to remove catalyst and low-boiling starting material to yield a clear colorless liquid. ^1H NMR ($CDCl_3$): δ 3.45−3.63 (OCH_2CH_2O), 3.25−3.35 (OCH_3, CCH_2O), 1.53 (CCH_2C), 0.46 ($SiCH_2C$), −0.05 to 0.05 ($SiCH_3$). ^{13}C NMR ($CDCl_3$): δ 73.9 (CCH_2O), 69.7−71.8 (OCH_2CH_2O), 58.7 (OCH_3), 23.0 (CCH_2C), 13.9 ($SiCH_2$), −0.5 and 1.0 ($SiCH_3$). ^{29}Si NMR ($CDCl_3$): δ 6.0 ($CH_2SiO(CH_3)_2$), −23.3 ($OSi(CH_2)_2O$).

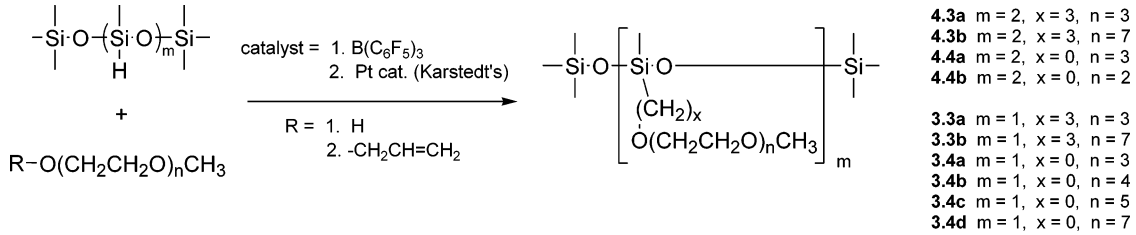
Similar reactions were carried out with oligoether chains of varying lengths, including $AlPEO_2$, which was used to synthesize **4.2b**.

*Synthesis of **4.3b***. 1,3-Bis(trimethylsiloxy)-1,3-dimethyldisiloxane (10.0 g, 0.0354 mol), poly(ethylene glycol) allyl methyl ether $AlPEO_7$ (33.0 g, 0.085 mol), and Karlstedt's catalyst solution (0.13 g, 7.8×10^{-6} mol) were added to a round-bottom flask and heated to 70 °C. After 24 h, the product was purified via Kugelrohr distillation. Excess $AlPEO_7$ and related isomers were removed by Kugelrohr distillation. The product was a yellowish to brown liquid and was subsequently decolorized using activated charcoal in refluxing toluene for 12 h. The solution was filtered, and solvent was removed under reduced pressure at 100 °C for 2 h. The purified product (yield 92%) was isolated as a colorless liquid. Structure and purity were confirmed by ^1H, ^{13}C, and ^{29}Si NMR. ^1H NMR

Scheme 1. Synthesis of Linear Siloxane/Oligoether Copolymers via (1) Dehydrocoupling and (2) Hydrosilation of Difunctional Tri- and Tetrasiloxanes



Scheme 2. Comblike and Monosubstituted Tetra- and Trisiloxane Compounds



($CDCl_3$): δ 3.44−3.60 (OCH_2CH_2O), 3.27−3.37 (OCH_3, CCH_2O), 1.52 (CCH_2C), 0.37 ($SiCH_2C$), −0.01 ($Si(CH_3)_3$), −0.07 ($SiCH_3$). ^{13}C NMR ($CDCl_3$): δ 73.8 (CCH_2O), 69.8−71.8 (OCH_2CH_2O), 58.7 (OCH_3), 23.0 (CCH_2C), 13.3 ($SiCH_2$), 1.6 ($Si(CH_3)_3$), −0.7 ($SiCH_3$). ^{29}Si NMR ($CDCl_3$): δ 6.1 ($Si(CH_3)_3O$), −23.4 ($OSi(CH_2)(CH_3)O$).

The reaction was repeated using $AlPEO_3$ to synthesize **4.3a**.

*Synthesis of **4.4a**.* 1,3-Bis(trimethylsiloxy)-1,3-dimethyldisiloxane (10 g, 0.0354 mol), tri(ethylene glycol) methyl ether $HOPEO_3$ (13.9 g, 0.085 mol), tris(pentafluorophenyl)borane (0.010 g, 1.98×10^{-5} mol), and toluene (75 mL) were added to a 250 mL round-bottom flask and heated to 70 °C. After 24 h, the solvent was removed via Kugelrohr distillation. The product itself was then distilled via Kugelrohr distillation. The product was dissolved in toluene (150 mL) and washed six times with water (10 mL × 6). Toluene was then removed, and the remaining product was dried by heating to 100 °C under vacuum for 24 h. The final product was retained as a clear colorless liquid. ^1H NMR ($CDCl_3$): δ 3.77 ($SiOCH_2C$), 3.43−3.61 (OCH_2CH_2O), −0.05 to 0.05 ($SiCH_3$). ^{13}C NMR ($CDCl_3$): δ 70.3−72.4 (OCH_2CH_2O), 61.5 ($SiOCH_2C$), 58.8 (OCH_3), 1.6 ($Si(CH_3)_3$), −1.0 (O_3SiCH_3). ^{29}Si NMR ($CDCl_3$): δ 7.7 ($Si(CH_3)_3O$), −58.9 (O_3SiCH_3).

Similar reactions were carried out with oligoether chains of varying lengths, including $HOPEO_2$, which was used to synthesize **4.4b**. For compounds containing longer PEO chains (i.e., PEO_7), the product was not distillable.

2.4 Synthesis of Trisiloxane-Based Compounds. *Synthesis of **3.1**.* A method similar to the one described for the synthesis of **4.2a** was employed for reactions involving 1,1,3,3,5,5-hexamethyltrisiloxane and $AlPEO_3$. ^1H NMR ($CDCl_3$): δ 3.42−3.58 (OCH_2CH_2O), 3.31 (CCH_2O), 3.27 (OCH_3), 1.50 (CCH_2C), 0.41 ($SiCH_2C$), −0.10 to −0.02 ($SiCH_3$). ^{13}C NMR ($CDCl_3$): δ 73.9 (CCH_2O), 69.7−71.7 (OCH_2CH_2O), 58.7 (OCH_3), 23.1 (CCH_2C), 13.8 ($SiCH_2$), −0.1 and 1.0 ($SiCH_3$). ^{29}Si NMR ($CDCl_3$): δ 6.3 ($OSi(CH_3)_2CH_2$), −22.2 ($OSi(CH_3)_2O$).

Similar reactions were also carried out using $AlPEO_2$ and $AlPEO_7$.

*Synthesis of **3.2**.* A method similar to that described for the synthesis of **4.1** was employed for reactions involving 1,1,3,3,5,5-hexamethyltrisiloxane and $HOPEO_3$. ^1H NMR ($CDCl_3$): δ 3.69 ($SiOCH_2C$), 3.39−3.51 (OCH_2CH_2O), 3.25 (OCH_3), −0.01 ($SiCH_3$). ^{13}C NMR ($CDCl_3$): δ 70.0−72.2 (OCH_2CH_2O), 61.2 ($SiOCH_2C$), 58.6 (OCH_3), 0.6 ($OSi(CH_3)_2O$), −1.3 ($C-OSi(CH_3)_2O$). ^{29}Si NMR ($CDCl_3$): δ −13.0 ($OSi(CH_3)_2OC$), −22.4 ($SiOSi(CH_3)_2OSi$).

Similar reactions were also carried out using $HOPEO_2$ and $HOPEO_7$.

*Synthesis of **3.3a**.* $AlPEO_3$ (110 g, 0.540 mol), bis(trimethylsiloxy)methylsilane (100 g, 0.450 mol), and Karlstedt's catalyst solution (0.40 g, 1.68×10^{-5} mol) were added to a 250 mL round-bottom flask and heated to 70 °C. After 24 h, the product was purified via fractional distillation and recovered as a clear colorless liquid. ^1H NMR ($CDCl_3$): δ 3.45−3.58 (OCH_2CH_2O), 3.27−3.37 (OCH_3, CCH_2O), 1.58 (CCH_2C), 0.39 ($SiCH_2C$), 0.04 ($Si(CH_3)_3$), −0.05 ($SiCH_3$). ^{13}C NMR ($CDCl_3$): δ 73.8 (CCH_2O), 69.7−71.5 (OCH_2CH_2O), 58.7 (OCH_3), 22.6 (CCH_2C), 13.3 ($SiCH_2$), 1.6 ($Si(CH_3)_3$), −0.7 ($SiCH_3$). ^{29}Si NMR ($CDCl_3$): δ 6.3 ($SiO(CH_3)_3$), −23.0 ($OSi(CH_3)(CH_2)O$).

The procedure was repeated with $AlPEO_7$ to synthesize **3.3b**.

*Synthesis of **3.4a**.* $HOPEO_3$ (17.8 g, 0.109 mol), bis(trimethylsiloxy)methylsilane (22.0 g, 0.0990 mol), tris(pentafluorophenyl)borane (0.010 g, 1.98×10^{-5} mol), and toluene (75 mL) were added to a 250 mL round-bottom flask and heated to 70 °C. After 24 h, the solvent was removed under reduced pressure prior to the product ($3NM_23$) being purified via Kugelrohr distillation. Solvent extraction was used to further purify the product, which was dissolved in toluene (150 mL) and washed six times with water (10 mL × 6). Toluene was then removed under vacuum by heating to 100 °C. The product was fractionally distilled and retained as a clear colorless liquid. ^1H NMR ($CDCl_3$): δ 3.77 ($SiOCH_2C$), 3.47−3.62 (OCH_2CH_2O), 0.06 ($Si(CH_3)_3$), 0.00 ($SiCH_3$). ^{13}C NMR ($CDCl_3$) δ 70.4−72.3 (OCH_2CH_2O), 61.3 ($SiOCH_2C$), 58.8 (OCH_3), 1.5 ($Si(CH_3)_3$), −3.9 ($SiCH_3$). ^{29}Si NMR ($CDCl_3$): δ 6.9 ($OSi(CH_3)_3$), −57.8 (O_3SiCH_3).

The reaction was repeated using $HOPEO_4$, $HOPEO_5$, and $HOPEO_7$ to synthesize **3.4b**, **3.4c**, and **3.4d**, respectively.

2.5 Conductivity Measurements. Procedures involving the building of cells were carried out in an argon-filled drybox. The polymer electrolytes were prepared by doping the polymers with lithium bis(oxalato)borate (LiBOB) or lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) in a THF solution under dry, inert

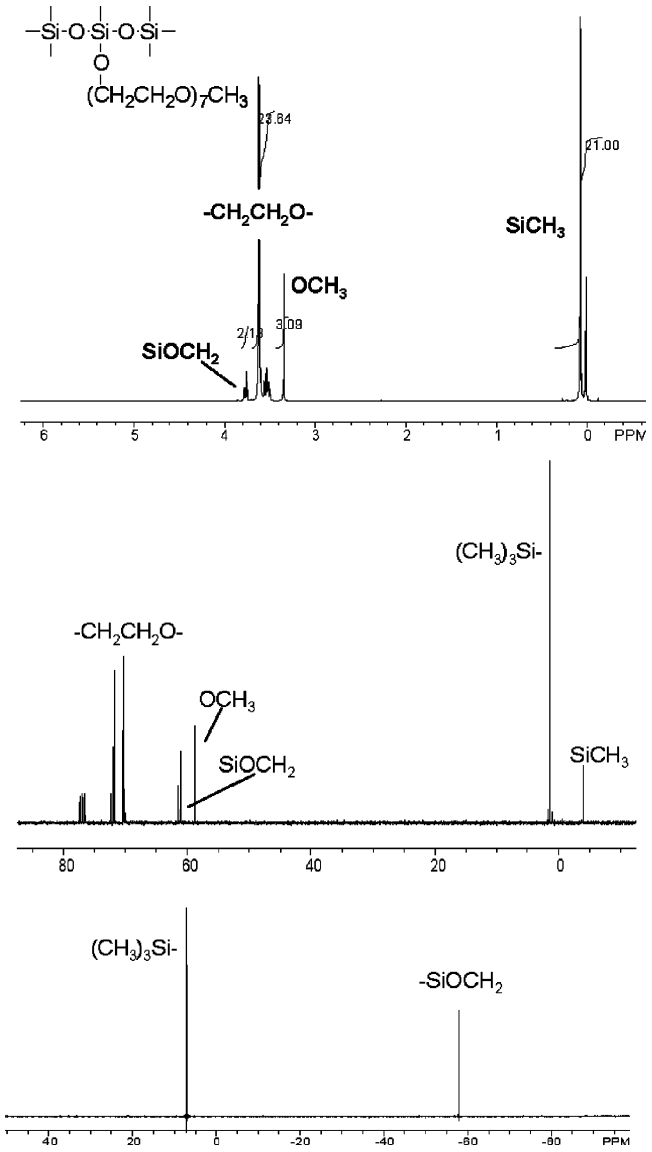


Figure 1. ^{1}H (top), ^{13}C (middle), and ^{29}Si (bottom) NMR of **3.3b**.

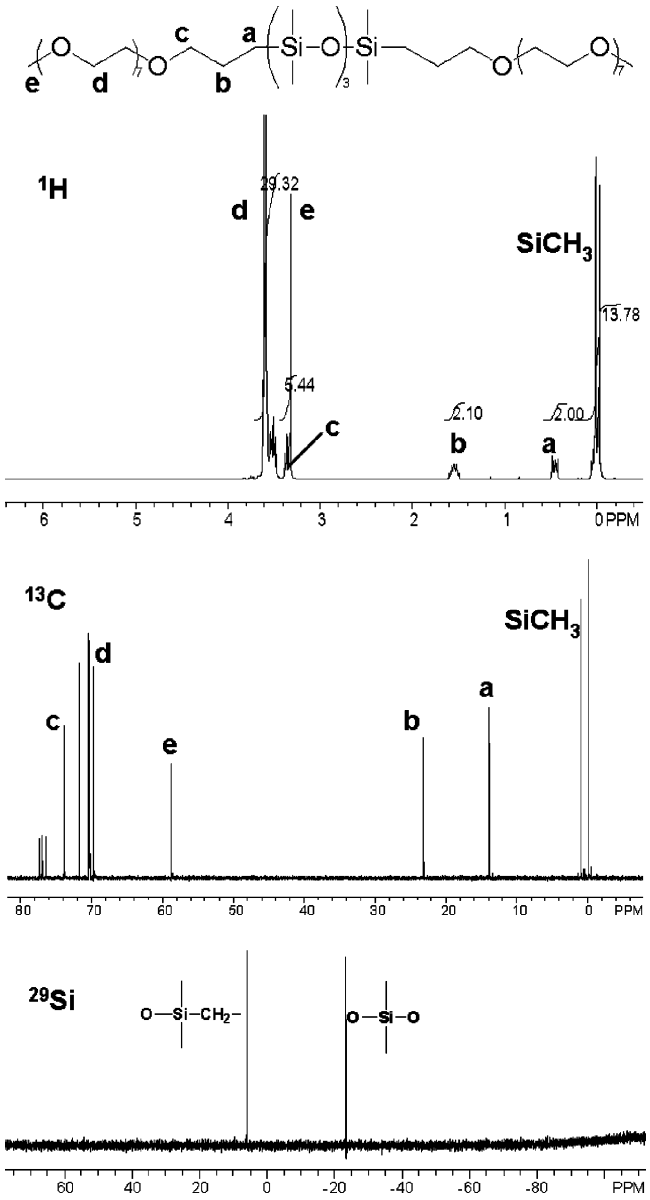


Figure 2. ^{1}H, ^{13}C, and ^{29}Si NMR of **4.2c**.

conditions. The solvent was removed under vacuum on a Schlenk line once a homogeneous mixture was achieved. The sample was then placed under vacuum, $<10^{-5}$ Torr, for 48 h. Doping levels are reported as the ratio of ethyl oxide groups (EO) per lithium cation (Li^{+}). The oxygens associated with the siloxane "backbone" are not included in this ratio.

3.1. Synthesis and Characterization. As it seemed possible that only a few siloxane bonds (−SiOSi−) were needed to give a copolymer flexibility, a variety of tetra- and trisiloxane compounds were synthesized. Short-chain siloxane compounds containing functional SiH groups were purchased, purified, and then substituted with oligoether chains. A variety of linear-type disubstituted siloxanes were prepared via dehydrocoupling and hydrosilation reactions (Scheme 1). In these cases, the terminal silicons were substituted with oligoether chains. In addition, short-chain compounds analogous to the comb polysiloxane electrolytes synthesized previously were also prepared (Scheme 2). These compounds have terminal silicons, which remain unsubstituted, whereas the central silicon(s) are substituted with oligoether chains. Hydrosilation of the Si−H-containing siloxane starting material was carried out with allyl-terminated oligoether compounds (ranging from 2 to approximately 7 repeat units) in the presence of Karlstedt's catalyst. The oligomers synthesized via this method are termed spacers, because the oligoether chain is connected to the Si atoms via a propyl group. Correspondingly, dehydrocoupling reactions involving hydroxy-terminated oligoether chains ($n = 2-7$) were carried out in the presence of a tris(pentafluorophenyl)borane catalyst. The compounds synthesized via this route are termed nonspacers, because the oligoether chain is attached directly to the siloxane units via a Si−O−C bond.

A very high level of purity could be achieved because most of the products had relatively low boiling points. Under reduced pressure, the compounds are distillable and therefore can be efficiently separated from any impurities (e.g., starting material and catalysts). Distillation of the compounds yielded clear, colorless liquids that were analyzed by ^{1}H, ^{13}C, and ^{29}Si NMR. Typical NMR spectra for the purified nonspacer and spacer compounds are shown in Figures 1 and 2, respectively. In the few cases in which the final product had a relatively high boiling point and could not be distilled (such as the disubstituted tetrasiloxane compounds containing oligoether chains with seven repeat units, e.g., **4.2c** and **4.3b**), refluxing over activated charcoal was carried out in order to decolorize the product and remove remaining residual catalyst. The nonspacer compounds were also purified by removing any unreacted starting material by solvent extraction.

Table 1. Conductivity and Viscosity Data for Some Tetra and Trisiloxane Compounds[a]

compd	O:Li (EO/Li^+)	conductivity at 25 °C (S cm^{-1})	conductivity at 37 °C (S cm^{-1})	viscosity at 25°C
4.1	15	3.93×10^{-4}	5.51×10^{-4}	7.2
4.2a	15*	2.4×10^{-4}	3.6×10^{-4}	5.0
4.2b	15	2.39×10^{-4}	3.51×10^{-4}	3.9
4.3b	15	1.87×10^{-4}	3.22×10^{-4}	57.8
4.4a	15	4.15×10^{-4}	5.77×10^{-4}	6.7
4.4b	15	5.75×10^{-4}	7.56×10^{-4}	3.9
3.1	15	3.08×10^{-4}		12.7
3.2	15		6.35×10^{-4}	
3.3a	15	2.39×10^{-4}	3.53×10^{-4}	4.95
3.3a	15*	2.8×10^{-4}	3.7×10^{-4}	4.95
3.3b	15	3.16×10^{-4}		16.3
3.4a	15*	3.9×10^{-4}	4.8×10^{-4}	3.3
3.4b	15	3.09×10^{-4}	4.31×10^{-4}	
3.4c	15	3.12×10^{-4}	4.03×10^{-4}	
3.4d	15	3.65×10^{-4}	5.75×10^{-4}	7.0

[a] Conductivity measurements performed upon doping with LiBOB salt, except where indicated by (*). Compounds were doped with LiTFSI. Viscosities are quoted for undoped samples.

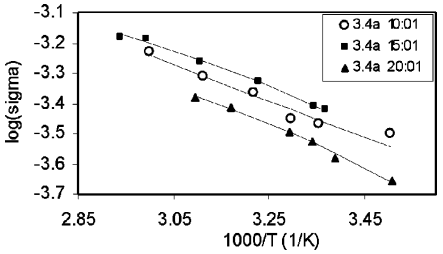


Figure 3. Variable temperature conductivity of **3.4a**, at $EO:Li^+$ dopings of 10:1, 15:1, and 20:1.

Table 2. Thermal Properties of Doped Electrolytes

	4.2a $O:Li^+$ 15:1	**3.3a** $O:Li^+$ 15:1	**3.4a** $O:Li^+$ 10:1	**3.4a** $O:Li^+$ 15:1	**3.4a** $O:Li^+$ 20:1	**3.4a** $O:Li^+$ 32:1
MW	691	427	385	385	385	385
log(σ) (25 °C)	−3.62	−3.56	−3.47	−3.41	−3.55	−3.94
T_g (°C)	−101.7	−107.4	−103.9	−114.0	−108.1	−113.1
T_0 (°C)	−92.3	−141.8	−207.6	−83.0	−73.8	−26.3
E_a (kJ mol^{-1})	4.21	6.24	17.0	1.8	1.5	0.4

3.2. Conductivity. The samples were doped with lithium bis(oxalato)borate (LiBOB), a relatively new lithium salt developed by Lischka et al.[32] The salt was chosen because it fulfills a set of stringent requirements that are essential for lithium ion cell applications. AC impedance measurements for some of the siloxane/LiBOB complexes are summarized in Table 1. Because LiBOB is soluble in the oligoether−siloxane compounds, the resulting complexes were found to be completely homogeneous liquids. The compounds show higher conductivities than their polymeric analogues and are among the most highly conducting polymer electrolytes ever reported. Only oligoether chains containing single silicon end groups are more conductive.[27] The most conductive tetrasiloxane, and also one of the least viscous, was **4.4b**. It contains diethyleneoxide chains connected to the internal silicons and has a conductivity of 5.75×10^{-4} S cm^{-1} at room temperature. The relatively low viscosity of the electrolyte could account for its high conductivity. **3.4d** shows the highest conductivity for a trisiloxane-based electrolyte: $\sigma = 3.65 \times 10^{-4}$ S cm^{-1} (25 °C). The influence of regioselectivity on the conductivities of the compounds is not yet fully understood. However, in the cases of **4.1** and **4.4a**, in which either the terminal (**4.1**) or central (**4.4a**) silicons are substituted with ethylene oxide chains, the compounds show similar conductivities and viscosities.

(32) Lischka, U.; Wietelmann, U.; Wegner, M. DE 19829030 C1, 1999.

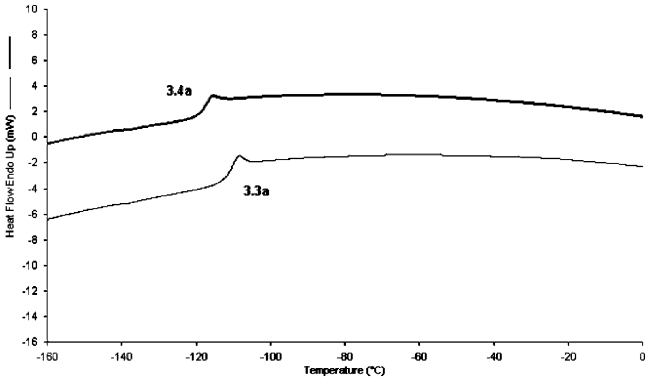


Figure 4. DSC plot for **3.3a** and **3.4a**.

A number of compounds were also doped with lithium bis(trifluoromethanesulfonyl) imide (LiTFSI). The conductivities of these complexes were measured over a temperature range of 25 to 70 °C. Figure 3 shows the plots of conductivity against temperature (log(s) vs 1000/*T*) for **3.4a**. For a single molecule, or nonpolymeric electrolyte, a straight line that could be fitted into the Arrhenius equation would be expected. Instead, the plots show slight curvatures normally associated with polymeric electrolytes. The curvatures in the plots suggest that the oligoether chains contribute to ion transport much like a polymer would. Hence, the curves were fitted against the Vogel−Tamman−Fulcher (VTF) equation:

$$\sigma = AT^{-1/2}\exp[-B/(T - C)]$$

By employing the VTF equation, we were able to determine the activation energy E_a and the ideal glass-transition temperature T_0 from the parameters *B* and *C*. *C* is associated with T_0, whereas $B = E_a/R$ (R = ideal gas constant, 8.31 J mol^{-1} K^{-1}). E_a values determined using the VTF equation were similar in magnitude to the shorter polysiloxane electrolytes studied by Jin et al.[33] However, no apparent trend, such as E_a decreasing with molecular weight, was observed (Table 2). This is probably because E_a is so small that bond rotation at the investigated temperatures readily occurs, and therefore the parameter is no longer an obstacle to conductivity. Glass-transition data is discussed later.

Conductivities were measured at various doping levels in order to determine optimum salt concentrations. This is depicted in Figure 3, in which doping levels of 10:1, 15:1, and 20:1 are shown for **3.4a**. Doping levels are reported as the ratio between ethylene oxide oxygens and lithium cations, $O:Li^+$. Compound **3.4a** showed highest conductivities at all temperatures when doped with an $O:Li^+$ ratio of 15:1. Other compounds also had optimum doping levels around 15:1, but it seems that this can differ slightly from compound to compound. For example, polysiloxane-based electrolytes have been found to have higher conductivities when doped with slightly less lithium salt (24:1).[18,19]

3.3. Viscosity. The high-molecular-weight liquid polysiloxane electrolytes synthesized previously are usually very viscous compounds. By synthesizing the smaller oligomeric-type compounds, we achieved significant decreases in viscosity. The conductivities for these compounds have increased substantially. The relationship between viscosity and conductivity is significant, although other factors, including structure, stability, solubility, and thermal properties, also need to be taken into account to fully understand why certain compounds are more conductive than others. For example, upon doping with a lithium salt, we usually observe a 10−20-fold increase in the viscosity of the liquid siloxane electrolyte. Apart

(33) Jin, J. J.; Lyons, L. J.; Wang, Q.; West, R. *Polym. Prepr.* **2003**, *44*, 1148.

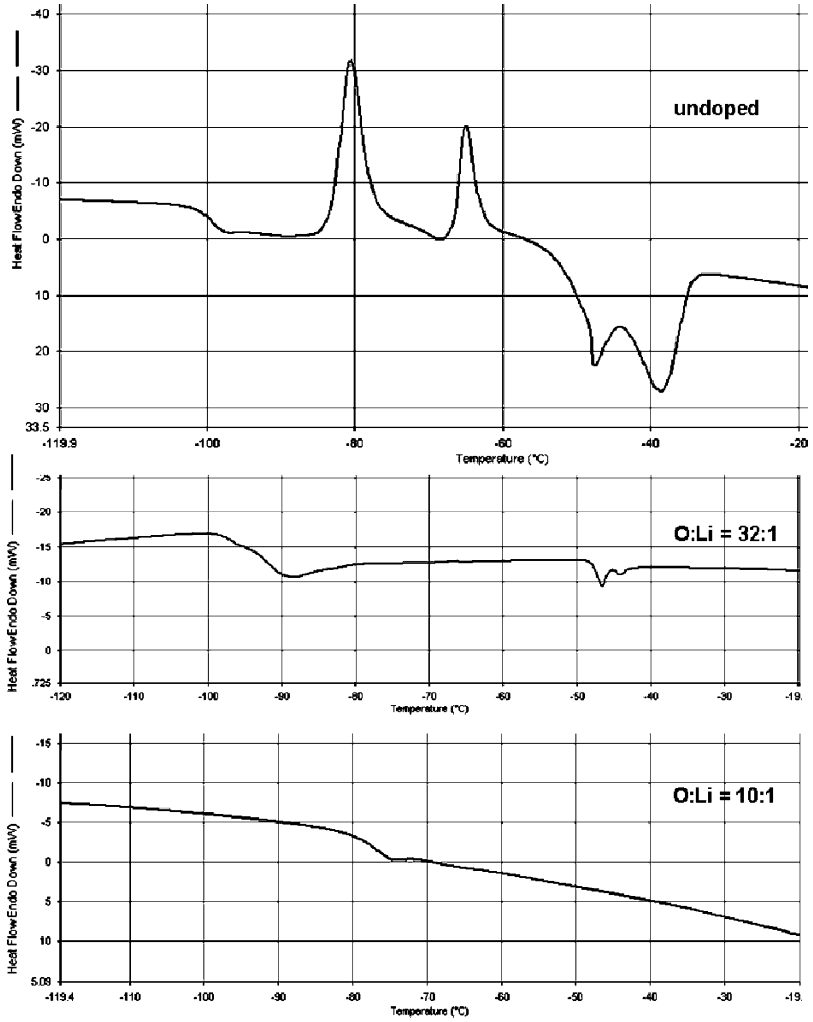


Figure 5. DSC plots for **4.2a**: undoped (top), O:Li = 32:1 (middle), and O:Li = 10:1 (bottom).

from the practical considerations, which concern the loading of the liquid electrolytes into cells, the viscosity can have a great effect on conductivity. Conductivity (σ) is inversely proportional to viscosity (η), because ion mobility decreases as viscosity increases:

$$\sigma \times \eta = \text{constant}$$

We have found that oligoether-substituted oligosiloxanes are more highly conducting than the longer, more viscous polysiloxane electrolytes.

3.4. Thermal Properties. Research has focused on the synthesis of polysiloxane/PEO electrolytes because of the stability and flexibility that the siloxane segments impart. Because the siloxane unit possesses a very low bond-rotation energy, siloxane-containing polymers generally have relatively low glass-transition temperatures. To further understand the electrolytic behavior of the oligomeric compounds synthesized here, we investigated the thermal properties using differential scanning calorimetry (DSC). A typical DSC curve is shown in Figure 4 (compound **3.4a**). The T_g's of some of the electrolytes are also listed in Table 2. The thermal data gave interesting results, as these are the lowest glass transitions observed for siloxane/oligoether copolymers. Although the low values are not necessarily surprising considering the molecular weights of the compounds, it is important to note that amorphicity is maintained. Hence, it can be concluded that the amorphous nature normally associated with a polysiloxane can be induced by having only two or three siloxane repeat units connected to the crystalline oligoether chain.

In addition to the second-order glass transitions, some of the undoped siloxanes showed first-order melt and crystallization peaks. For example, undoped **4.2a** showed two crystallization peaks and two melt peaks, which are due to the ordering of the oligoether chains (Figure 5).[10] However, upon addition of only a relatively small amount of lithium salt, the melt and crystallization peaks disappeared. This suggests that upon complexation with the lithium salt, the crystallinity of the oligoether chains is reduced, leading to significant decreases in the first-order transitions. It is also important to note that all transitions occurred at relatively low temperatures and no other transitions were observed above −40 °C. The complexes were therefore found to be completely amorphous at all temperatures of practical interest. The addition of a plasticizing agent normally results in a decrease in the T_g of polymer complexes. However, the T_g's observed here actually increase as more salt is added, in agreement with previous studies of salt-doped polymers.[34]

Another trend regarding the thermal properties of the compounds was also observed. In general, spacer compounds have T_g's that are about 10 °C higher than those of their nonspacer analogues. This would suggest that the nonspacer compounds are slightly more flexible than the spacer ones. Indeed, previous research has shown nonspacer copolymers to be more conductive than their corresponding spacer analogues; this is also the case with the electrolytes discussed here. For example, the nonspacer electrolyte **3.4d** has a conductivity of 3.65×10^{-4} S cm^{-1} whereas the analogous spacer type, **3.3b**, has a conductivity of 3.16×10^{-4} S cm^{-1}. Another

(34) Choi, S.; Kim, J. H.; Kang, Y. S. *Macromolecules* **2001**, *34*, 9087.

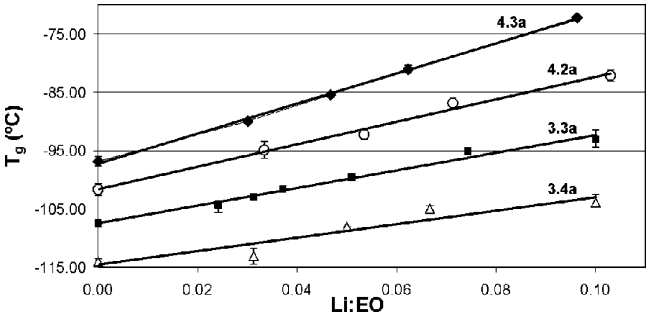


Figure 6. Glass-transition temperature vs Li^+:O.

trend, which has also been observed previously,[34−36] is the relationship between the salt concentration of the electrolyte and the corresponding T_g's. As the concentration of salt increases, the T_g of the complex increases linearly (Figure 6). For example, in the case of the tetrasiloxane-based compounds, an increase in salt concentration leads to a 20 °C increase in T_g. As stated earlier, the viscosity also increases significantly upon doping with lithium salts. Increasing the viscosity and T_g of the electrolyte leads to a decrease in conductivity because the mobility of the ions through the liquid medium is hampered. Conversely, increasing the number of available ions, i.e., [Li^+], leads to higher conductivities, as shown in the following equation:[37]

$$\sigma(T) = \sum n_i q_i \mu_i$$

Ionic conductivity (σ) at a given temperature (T) is proportional to the sum of the number of free ions (n_i), ion mobility (μ_i), and the charge of the carrier ions (q_i). On the basis of these parameters and the effects on T_g and viscosity, there is an optimum Li^+ ion concentration for each of the samples.

From the data extracted from the VTF equation, we found that compounds such as **3.4a** have a higher T_0 than T_g. This is contrary to the expected tendency that T_0 is usually 20−50 °C lower than T_g. The new trend in T_0 and an extremely low E_a, coupled with the fact that the compounds fit the VTF equation and show low glass transition temperatures, suggests that these compounds conform wholly neither to models of small molecules nor to models of polymers. In addition, the relationship between low T_g's and high conductivity was not uniformly observed for the electrolytes described here. Previously, Hooper et al. found that conductivity increased with decreasing glass-transition temperatures, although this was not necessarily the case with our compounds. For example, **3.4a** had the lowest T_g (−114 °C) but was not the most conducting electrolyte.

4. Conclusion

Tetra- and trisiloxanes containing oligoether chains of various lengths were synthesized, purified, and characterized as possible electrolytes for lithium batteries. Conductivity data showed that these low-viscosity materials have some of the highest conductivities ever reported for polymeric electrolytes approaching 1×10^{-3} S cm^{-1} at 37 °C, with very low viscosities of less than 10 cP. These pure compounds are more conductive than the polysiloxane-based electrolytes studied previously. The siloxanes studied here were also found to exhibit characteristics of both polymers and small molecules and therefore cannot be fully classified as either. Conductivity vs temperature plots of the doped compounds fit the VTF equation, and in this respect, these complexes can be classed as polymeric electrolytes. Glass-transition temperature studies also confirmed the amorphous nature of the compounds before and after doping. Indeed, the thermal properties of the electrolytes are very similar in nature to the polysiloxane/oligoether electrolytes reported by our group previously.[17−20]

Acknowledgment. We acknowledge The Department of Commerce (National Institute of Standards and Technology) and Argonne National Laboratory (Advanced Technology Program) for funding and support.

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(35) Kim, H. K.; Byoung, R. M.; Won, J.; Kang, Y. S. *J. Phys. Chem.* **2003**, *107*, 5901.
(36) Liang, W.; Kuo, P. *Macromolecules* **2004**, *37*, 840.
(37) Lin, C.; Kao, H.; Wu, R.; Kuo, P. *Macromolecules* **2002**, *35*, 3083.