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Communications

A Highly Conductive Solid-State Polymer Electrolyte Based on a Double-Comb Polysiloxane Polymer with Oligo(ethylene oxide) Side Chains

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*Summary: A double-comb polysiloxane with ethylene oxide side chains, poly[bis(2-(2-(2-methoxyethoxy)ethoxy)-ethoxy)propylsiloxane] (**1**), has been prepared. The conductivity and thermal properties of this polymer are compared to those of a single-comb polysiloxane, $-[CH_3RSiO]_n-$ (**2**), which contains an equal number of oxygen donor atoms. Maximum conductivities of 3.9×10^{-4} S cm^{-1} for **1** and 1.0×10^{-4} S cm^{-1} for **2** were found at room temperature with oxygen to Li^+ ratios of about 40:1.*

Carbon-based polymers containing repeat units of poly(ethylene oxide) (PEO) have for the past 30 years been examined as materials for hosting ionically conducting electrolytes.[1] Unfortunately, these systems suffer drawbacks from low flexibility and high glass transition temperatures (T_g) which increase the polymer crystallinity, ultimately lowering the conductance, at ambient temperatures.

The introduction of MEEP (poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene]) in 1984 by Allcock et al.[2] provided a solid-state electrolyte with a flexible inorganic backbone containing ethylene oxide side chains. The resulting polymer has a very low T_g value (−84 °C) and is amorphous over a wide temperature range, resulting in conductivities approximately 3 orders of magnitude greater than that of PEO. Since that time studies on polysiloxane,[3] polysilane,[4] and recently polycarbosilane[5] comb polymers have also shown these species to have potential as effective hosts for solid-state polymer electrolytes. Typically, these silicon-based polymers have one oligo(ethylene oxide) (EO) side chain and an alkyl group (usually methyl) as the other.

We now report the synthesis of the bis-substituted polysiloxane polymer $-[R_2SiO]_n-$ (**1**), analogous to MEEP, where both pendant groups contain oxyethylene chains, *i.e.* a double-comb polymer. This polymer, when doped with lithium bis((trifluoromethyl)sulfonyl)imide (LiTFSI), shows the highest room-temperature conductivity yet observed for such materials, approaching values necessary for commercial solid-state electrolytes.[1] We have also tested a monosubstituted polymer, containing an identical number of ethylene oxide repeat units in the side chain, as a direct comparison to previous work on comb polysiloxanes.[3a]

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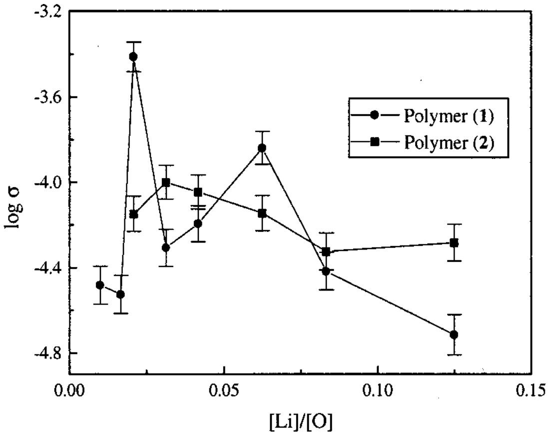
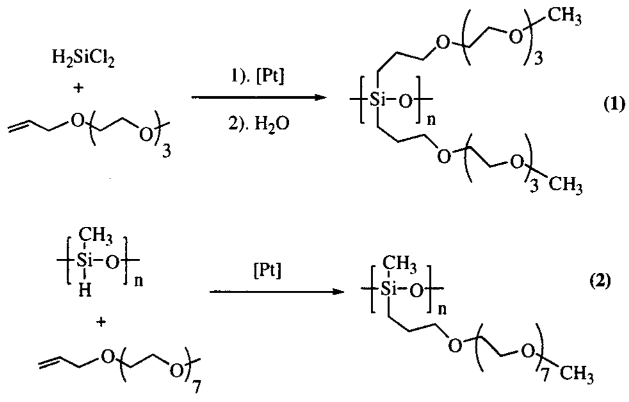


Figure 1. Ambient-temperature composition plots for polymer complexes.

The polymers presented were synthesized *via* hydrosilylation reactions of the corresponding allyl ethers having the desired ethylene oxide side chain, as outlined in Scheme 1.[6] The resulting polymers were then fractionated from low-weight oligomers and unwanted hydrogenated side products by washing with hexane. Gel permeation chromatograms of these polymers, eluted with THF containing 0.5 wt % of tetra-*n*-butylammonium nitrate, showed monodisperse profiles.[6] Silicon-29 NMR spectroscopy indicated that the polymer was linear polysiloxane (δ −21.0 ppm), with no cyclic material present.[6]

Scheme 1



Complex impedance measurements were carried out as described previously.[4] As shown in Figure 1, the ambient-temperature conductivity for polymers **1** and**2** is greatest at O:Li ratios of 48:1 (3.9×10^{-4} S cm^{-1}) and 32:1 (1.0×10^{-4} S cm^{-1}), respectively. The ambient-temperature conductivity (σ) of the disubstituted polymer is 1 order of magnitude higher than for MEEP−LiTFSI[7a] (8×10^{-5} S cm^{-1}) and MEEP−lithium triflate (2.7×10^{-5}) systems.[7b] It is interesting to note that the monosubstituted polysiloxane complex **2** is comparable to other comb polysiloxanes examined, since it exhibits one maximum doping level (32:1).[3] In contrast, the disubstituted system **1** displays two maxima at both low and high doping levels, 48:1 and 16:1. To understand this behavior, we examined the thermal properties of these polymers and their complexes.

Differential scanning calorimetry thermograms of these polymer complexes are substantially different. The thermogram for monosubstituted polymer **2** at a doping level of 48:1 is similar to those of other methyl-substituted polysiloxanes,[3] showing a low T_g value (−80 °C) followed by a crystallization exotherm at −57 °C and finally a melt endotherm (T_m) at −7 °C. These temperatures steadily increase as the doping level is raised to an O:Li level of 24:1; with higher lithium content only T_g is seen.[3] In contrast, the disubstituted polysiloxane complexes only show a glass transition endotherm (T_g) irrespective of the lithium ion content, varying from −80 to −32 °C for complexes with O:Li ratios between 100:1 and 8:1. We attribute this latter behavior to the greater substitution at silicon with ethylene oxide units, causing thermal motions to occur within both the side chains. Such behavior could disrupt side-chain crystallinity and chain entanglement[1b] and cause the polymer complex to be amorphous at all temperatures.[2]

Variable-temperature analyses of these polymer electrolytes show behavior similar to that for other known examples;[3−5] Vogel−Tamman−Fulcher[8] (VTF) plots are shown for the two highly conductive systems **1** and **2** in Figure 2. These plots obey the VTF equation, $\sigma = \sigma_0 \exp[-B/T - T_0]$, at all doping levels. This indicates that the free-volume model is applicable for all polymer complexes.[1a] As anticipated from this model, when the conductivity is at a maximum both polymers **1** and **2** show their lowest ideal glass transition temperatures (T_0), 149.2 and 185.4 K, respectively.

The observation of two conductivity maxima for the lithium-doped disubstituted polymer is unusual but is not without precedent. Two conductivity maxima as a function of salt concentration have also been observed in polymer electrolytes composed of divalent salts and

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(6) Synthesis of polymer **1**: dichlorosilane (40 g, 0.1 mol, 25% solution in xylene) was added to a solution of triethylene glycol allyl methyl ether (41.12 g, 0.2 mol) and chloroplatinic acid (20 μmol) in THF (50 mL) at 0 °C. The mixture was heated at 60 °C for 12 h, after which time the solvents were removed by heating to 150 °C under reduced pressure to yield a brown oil: yield 40.1 g (80%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.70−3.50 (m, 28 H, OCH_2), 3.35 (s, 6 H, OCH_3), 1.85 (m, 4 H, CH$_2$CH_2CH$_2$), 1.15 (m, 4 H, SiCH_2). ^{29}Si NMR (99 MHz, CDCl$_3$): δ 32.6. No residual Si−H functionality could be detected by either ^{1}H and ^{29}Si NMR or IR spectroscopy. Anal. Calcd for $C_{20}H_{42}SiO_8Cl_2$: Cl, 13.92. Found: Cl, 14.04. To 10 g of this product was rapidly added a water/pyridine solution (1:4) to yield a brown oil. This oil was dissolved in 30 mL of diethyl ether, to precipitate pyridinium hydrochloride, and filtered. Removal of solvent under reduced pressure yielded a yellow oil. The polymer was purified by repeatedly washing with hexane; yield 8.5 g (95%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.70−3.50 (m, 28 H, OCH_2), 3.35 (s, 6 H, OCH_3), 1.75 (m, 4 H, CH$_2$CH_2CH$_2$), 0.60 (m, 4 H, SiCH_2). ^{29}Si NMR (99.3 MHz, CDCl$_3$): δ −21.0 (CH$_2$−*Si*−O). Anal. Calcd for $C_{20}H_{42}SiO_9$: C, 52.84; H, 9.31. Found: C, 52.35; H, 9.47. GPC: one peak was observed by refractive index, $M_w = 4.0 \times 10^3$ compared to polystyrene standards ($M_w/M_n = 1.35$). Synthesis of polymer **2**: poly(methylhydrosiloxane) (1.2 g, 0.02 mmol of Si−H, Aldrich) was added to a solution of heptaethylene glycol allyl methyl ether (7.20 g, 0.02 mmol) and chloroplatinic acid (20 μmol) in THF (100 mL). This mixture was heated at reflux for 12 h, after which time the solvent was removed in vacuo. The resulting polymer was further purified by repeatedly rinsing with hexane; yield 8.0 g (95%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.70−3.50 (m, 32 H, OCH_2), 3.35 (s, 3 H, OCH_3), 1.75 (m, 2 H, CH$_2$CH_2CH$_2$), 0.60 (m, 2 H, SiCH_2), 0.13 (s, 3 H, Si−CH_3). ^{29}Si NMR (99.3 MHz, CDCl$_3$): δ −22.4 (CH$_3$−*Si*−O), 7.3 (*Si*−(OCH$_3$)$_3$). Anal. Calcd for $C_{19}H_{40}SiO_9$: C, 51.79; H, 9.15. Found: C, 51.34; H, 9.16. GPC: one peak was observed by refractive index, $M_w = 1.2 \times 10^4$ compared to polystyrene standards ($M_w/M_n = 1.25$).

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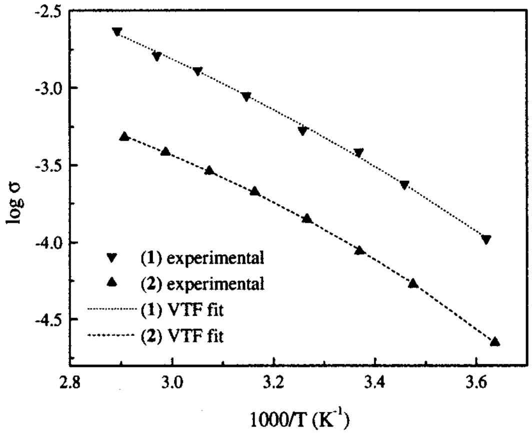

Figure 2. Variable-temperature conductivities for polymer complexes.

PEO[9a] as well as divalent salts in an amorphous analogue, POMOE.[9b] The observation of the second maximum was attributed to either the formation of ion aggregates or the formation of crystalline phases. The presence of only glass transitions in the DSC data for lithium-doped disubstituted polymers suggests that the formation of crystalline phases does not occur in these systems. The high conductivities observed for the disubstituted polymer are more likely due to the degree of ion association between the lithium cation and the sulfanimide anion. As observed previously by EXAFS spectroscopy, the degree of ion association can change as a function of salt content;[10] however, we do not have any spectroscopic measure of ion association in these systems.

These preliminary results indicate that double-comb polysiloxane polymers with pendant oligo(ethylene oxide) side chains are approximately a factor of 4 higher in conductivity than their analogous monosubstituted counterparts. We are currently investigating what effect varying the EO chain length has on the thermal behavior and conductance of these polymers. Likewise, we are studying the conductivity of polysiloxanes that contain branched side chain EO units[11] and the effect that these bulkier pendant groups have on the polymer's ability to aid in ionic conductance.

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