SYNTHESIS AND CHARACTERIZATION OF COMB SHAPE SINGLE ION CONDUCTORS BASED ON POLYEPOXIDE ETHERS AND PERFLUORINATAED LITHIUM SALTS

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Introduction

Most single ion conductors for lithium batteries are synthesized by fixing either alkyl sulfonate or carboxylate to the polymer backbones. However, due to their limited solubility and dissociation in polyether media, their ambient conductivities are usually in the range of 10^{-7}-10^{-8} $S.cm^{-1}$ [1, 2]. There are several approaches to improve the ambient conductivities of single ion conductors. One is to modify the structure of the host polymer to lower its glass transition temperature and thus improve ionic conductivity through increased ion mobility. Another is to modify the structure of the anion by putting strong electron-withdrawing atoms, most preferably being fluorine, adjacent to it to decrease the electron density on the anions and thus increase the ionic conductivity through increased number of free conducting lithium cations. The best approach, of course, is to combine the above two favorable changes in one structure.

It was shown in our group[3] that the comb-shaped polyepoxides with trimethylene oxide (TMO) as side chains have lower glass transition temperatures with increasing lithium salt concentration than those with EO as side chains, which is more effective in providing higher chain mobility especially at lower temperatures. In this paper we synthesized two polyepoxide ether prepolymers, one with four TMO units at the side chain and the other with five EO units at the side chain, and different allyl group containing lithium salts, either perfluorinated or non fluorinated **(Scheme 1)**. They were connected together by 1,1,4,4-tetramethyldisilethylene through hydrosilylation chemistry. The focus of this paper is to compare the effect of the structure of polymer and lithium salts on the ionic conductivities of the resulted single ion conductors.

Experimental

Materials. Tetrahydrafuran (B&J, distilled in glass) was obtained from VWR and was refluxed over CaH_2 for several days before use. 1,1,4,4-tetramethylsilethylene, platinum-divinyltetramethyl disiloxane complex in vinylsilicon was obtaineded from Gelest, Inc. All the other starting materials were obtained from Sigma-Aldrich and were used directly without further purification.

Synthesis. The step wise synthesis of 2-(2-{2-[2-(2-Methoxyethoxy) ethoxy]ethoxy}ethoxy)ethanol and 3-{3-[3-(3-Methoxypropoxy)propoxy] propoxy}propan-1-ol was following the literature procedure [3, 4, 5]. The synthesis of corresponding epoxide ether and the prepolymers, $PE(TMO)_4$ and $PE(EO)_5$ were following the reference [3, 5, 6, 7, 8]. The obtained prepolymers were viscous liquids, $PE(TMO)_4$, $M_w = 5.5 \times 10^3$, PDI = 2.48; $PE(EO)_5$, $M_w = 4.4 \times 10^4$, PDI = 3.13.

The synthesis of **Salt I** and **Salt II** was accomplished in Clemson University.

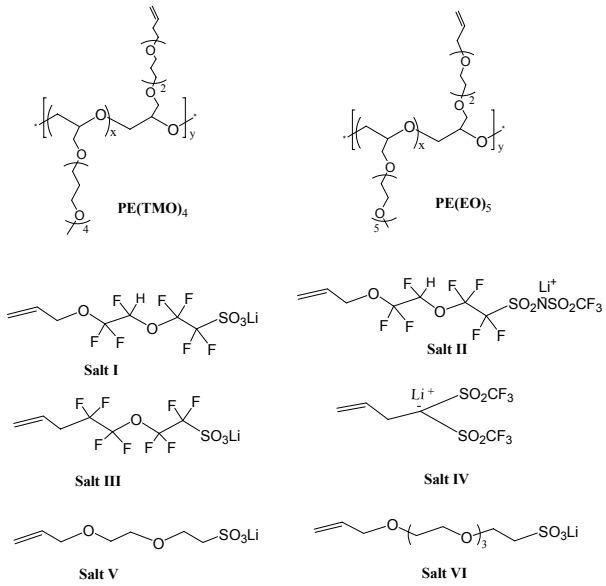
The synthesis of **Salt III** was accomplished by first synthesizing $CH_2{=}CHCH_2(CF_2)_2O(CF_2)_2SO_2F$ following the literature procedure [9, 10], and then neutralized with 3M LiOH in H_2O/ethanol solution. The solution was filtered to remove LiF, concentrated and dried at 85°C under vacuum in the presence of P_2O_5 for two days.

The synthesis of **Salt IV** was accomplished by first synthesizing 4,4-Bis(trifluoromethylsulfonyl)butene-1 following the literature procesure [11] and then neutralized with 3M LiOH solution and dried at 85°C under vacuum in the presence of P_2O_5 for two days.

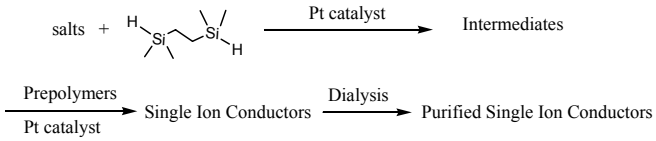
The synthesis of **Salt V and Salt VI** were accomplished by first stepwise synthesis of the corresponding alcohols [5], which were then halogenated by $SOCl_2$ in the presence of pyridine [12], sulfonated with Na_2SO_3 [13], ion exchanged with DOWEX^R HCR-W_2 ion exchange resin and finally neutralized with 3M LiOH solution. The salts were dried at 85°C under vacuum in the presence of P_2O_5 for two days.

The synthesis of the single ion conductors proceeded through two steps; first the allyl group containing salts were reacted with a five fold excess of 1,1,4,4-tetramethyldisilethylene in either dry THF (perfluorinated salts) or DMSO/THF (for non-fluorinated salts) in the presence of Pt complex catalyst at 70°C for four days. The calculated amount of isolated intermediates were then reacted with the allyl group containing prepolymers (**Scheme 2**) in suitable solvents under the catalysis of Pt complex at 70°C for one week. The obtained single ion conductors were then subjected to dialysis using a membrane with a molecular weight cut-off of 3,500 for one week. Finally the single ion conductors were dried in vacuum oven at 85°C with P_2O_5 for two days and in the antechamber of dry box with P_2O_5 for another day.

Measurements. ^{1}H-and ^{13}C-NMR (TMS as internal reference) spectra were collected on Bruker 300. Glass transition temperature T_g was measured using a Perkin Elmer-7 DSC instrument. The heating rate was kept at 10K/min and the T_g is defined as the heat capacity jump temperature. The molecular weights of the prepolymers were determined by using Agilent 1100 series gel permeation chromatography equipped with a refractive index detector. A PLgel 10μm miniMIX-B 250 x 4.6 mm column was employed and calibrated by using polystyrene standard samples with molecular weight ranging from 500 to 3,000,000. A solartron^{TM} SI 1254 four-channel frequency response analyzer and a 1286 electrochemical interface were used to measure the impedance of electrolyte films of known thickness in constant volume cells with blocking electrodes [14].



Scheme 1. Prepolymers and lithium salts



Scheme 2. Synthesis of single ion conductors

Results and Discussions

$PE(TMO)_4$ Based Single Ion Conductors. Figure 1 shows the ionic conductivities of $PETMO_4$ based single ion conductors. The ionic conductivities of perfluorinated salts (III and IV) based single ion conductors were more than one order of magnitude higher than those of non-fluorinated salts (V and VI) based ones. This ionic conductivity order falls in expectation and can be well explained by the difference in the number of free conducting lithium cation, since the lithium mobility in all those single ion conductors are same (see T_gs in **Table 1**). The fluorine substituents reduce the electron density of the anion, which allows more lithium cation to dissociate and thus provides higher ionic conductivity. Comparing the conductivity of salt III and salt IV based single ion

conductors, it indicates that more electron withdrawing group around the anion can effectively free more lithium cations to carry charge and thus provide higher ionic conductivity. Among non-fluorinated salts based single ion conductors (Salt V *versus* Salt VI), they showed essentially the same ionic conductivity, since the environment around the anion doesn't change.

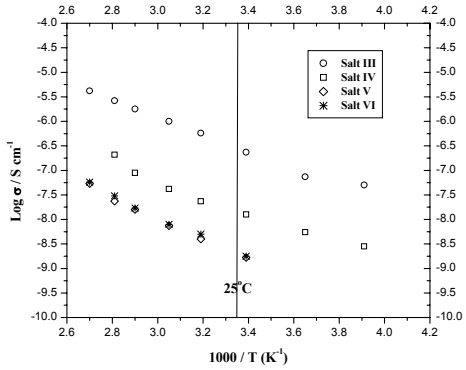


Figure 1. Arrhenius ionic conductivities of $PE(TMO)_4$ based single ion conductors at the salt concentration of EO/Li = 54.

$PE(EO)_5$ Based Single Ion Conductors. Figure 2 shows the ionic conductivities of $PE(EO)_5$ based single ion conductors. It basically shows the same order as observed for $PE(TMO)_4$ based single ion conductors, i.e. the ionic conductivity of perfluorinated salts based single ion conductors are much higher than that of non-fluorinated salt based single ion conductor. It is interesting to see that the ionic conductivity of salt II based single ion conductor is higher than that of salt I based single ion conductor. This is very similar to those commonly observed conductivity difference in binary salt polymer electrolytes when lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) is compared with lithium triflate. This can be attributed to, as mentioned above, the more electron-withdrawing group around the anion allowing the dissociation of more free conducting lithium cations.

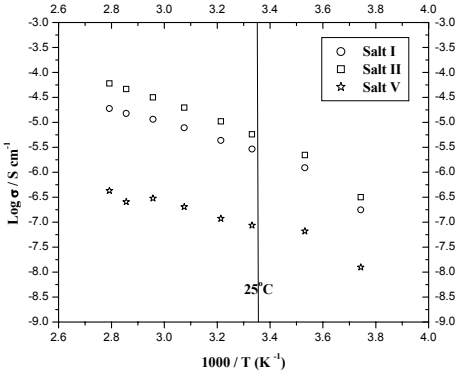


Figure 2. Arrhenius ionic conductivities of $PE(EO)_5$ based single ion conductors at the salt concentration of EO/Li=40.

Comparison. For a specific lithium salt, i.e. salt V, the ionic conductivity of $PE(EO)_5$ based single ion conductor is more than one order of magnitude higher than that of $PE(TMO)_4$ based single ion conductor. It is noticed from Table 1 that the glass transition temperature of $PE(TMO)_4$ based single ion conductor is much lower than that of $PE(EO)_5$ based single ion conductor, indicates higher ion mobility for the former case, so the lower conductivity of $PE(TMO)_4$ system must be due to fewer number of free conducting lithium cation. Previously it is also noticed that for LiBAMB based network single ion conductors, those containing both 50% and 75% TMO in the side chains have lower ionic conductivities than those containing pure EO side chains [15]. These results clearly indicate that TMO containing polymers have relatively lower dielectric constants than EO containing polymers, which results in fewer free conducting lithium cation and thus lower ionic conductivity.

Table 1. Physical properties of single ion conductors

Salt	$PE(TMO)_4$ based SIC			$PE(EO)_5$ based SIC		
	EO/Li	T_g/°C	$\log\sigma_{25}$/S cm^{-1}	EO/Li	T_g/°C	$\log\sigma_{25}$/S cm^{-1}
I	---	---	---	40	-69.4	-5.55
II	---	---	---	40	-69.5	-5.26
III	54	-78.1	-6.59	---	---	---
IV	54	-79.0	-7.81	---	---	---
V	54	-79.1	-8.70	40	-72.4	-7.08
VI	54	-78.7	-8.72	---	---	---

Note: T_g of $PE(TMO)_4$ is –86.8°C; T_g of $PE(EO)_5$ is –76.3°C.

Conclusions

For both $PE(TMO)_4$ and $PE(EO)_5$ systems, the ionic conductivities of perfluorinated salts based single ion conductors are much higher than those of non-fluorinated salts based single ion conductors. More electron-withdrawing group around the anion can render more free conducting lithium and result in higher ionic conductivity of the corresponding single ion conductor. Even though $PE(TMO)_4$ can provide higher mobility for the lithium cation, its lower dielectric constant tends to release less free conducting lithium cation, which results in the final ionic conductivity of $PE(TMO)_4$ based single ion conductor is lower than that of $PE(EO)_5$ based single ion conductor.

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