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# Siloxyaluminate Polymers with High $Li^+$ Ion Conductivity

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A series of highly conducting lithium siloxyaluminate polymers containing ethylene oxide side chains were prepared. Conductivities of the order of $10^{-5}$ S $cm^{-1}$ at 25 °C were obtained. The materials were shown to be predominantly $Li^+$ ion conductors.

## Introduction

Solid polymer electrolytes have attracted attention because of their potential for application in a variety of all-solid-state electrochemical devices, particularly lithium secondary batteries, sensors, and electrochromic displays.[1−3] It has been reported[4] that improved battery performance is observed for systems containing polymer electrolytes with a $Li^+$ transference number close to unity, and thus, recently, emphasis has been put on the development of single ion conducting electrolytes for use in rechargeable batteries.[5−7] Previous studies[8−10] have successfully shown that significant single ion conductivity may be achieved in poly(alkoxyaluminate) and poly(aluminosilicate) systems. In this vein, we report the preparation and characterization of a series of siloxyaluminate polymers of the type shown in Figure 1. These polymers were specifically designed to reduce anion charge by delocalization over the Si−O (p−d)$\pi$ system and to inhibit close approach of the cation by incorporation of stereochemically bulky groups around the anion. In this way we hoped to reduce ion pairing, one of the factors that reduces cation mobility and therefore conductivity in polyelectrolytes such as these where the anion is bonded to the polymer backbone. Pendent oligoether side chains were introduced onto the inorganic polymer backbone to incorporate an ion conducting region into the polymer.

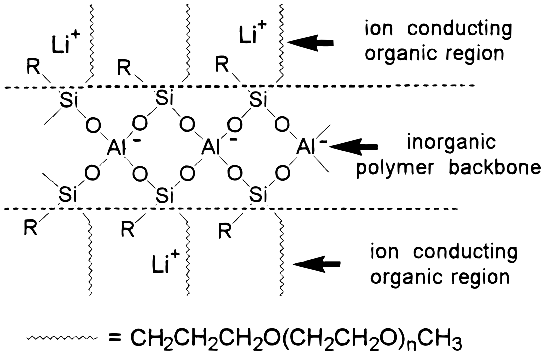

**Figure 1.** Schematic diagram of the siloxyaluminate polymers prepared.

## Experimental Section

**Materials.** Tetrethylene glycol, di- and triethylene glycol monomethyl ether, and poly(ethylene glycol)s with molecular weights 400, 600, 1000, and 2000 (Tokyo Kasei) were dried before use by benzene azeotrope distillation followed by heating under reduced pressure to remove benzene. Diphenyl silanediol, ($Ph_2Si(OH)_2$, Shinetsu Chemical Co.) was recrystallized before use from THF/diethyl ether (mp 139−140 °C). Dimethoxymethylsilane ($HSiMe(OMe)_2$), diethoxysilane ($H_2Si(OEt)_2$, Shinetsu Chemical Co.), lithium aluminum hydride ($LiAlH_4$, 1 M solution in THF, Aldrich Chemical Co.), $PtCl_6\cdot 6H_2O$ (Furuya Chemical Co.), and allyl bromide (Tokyo Kasei) were used as supplied. THF was dried by refluxing over sodium.

**Polymer Preparation.** Polymers were prepared as illustrated in Scheme 1. Since many of the reagents and intermediates were extremely hydrolyzable, all manipulations were carried out on a dry nitrogen/vacuum line in order to rigorously exclude moisture. Allyl ethers (**1**) were prepared by Williams synthesis. Reaction of a THF solution of di- or triethylene glycol monomethyl ether with sodium hydride was followed by the addition of allyl bromide. THF was removed and a diethyl ether solution of the allyl ether product was washed several times with saturated sodium chloride solution. After drying over anhydrous $MgSO_4$, the product was obtained by vacuum distillation.

Hydrosilation of allyl ethers (typically 13 mmol) was performed by refluxing a slight excess of $HSiMe(OMe)_2$ or $H_2Si(OEt)_2$ in THF in the presence of a $PtCl_6\cdot 6H_2O$ catalyst. $HSiMe(OMe)_2$ yielded products with one ether chain (**2**), whereas reaction with $H_2Si(OEt)_2$ gave products with two ether chains attached to the silicon atom (**3**). Products were obtained after vacuum distillation.

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[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

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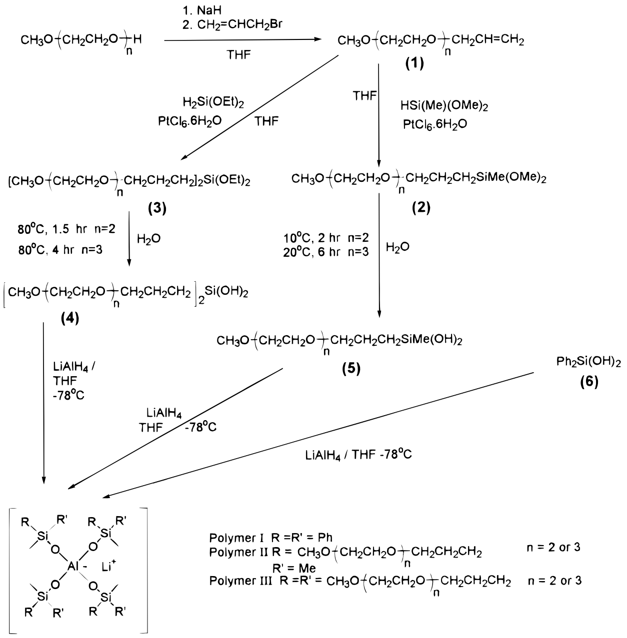
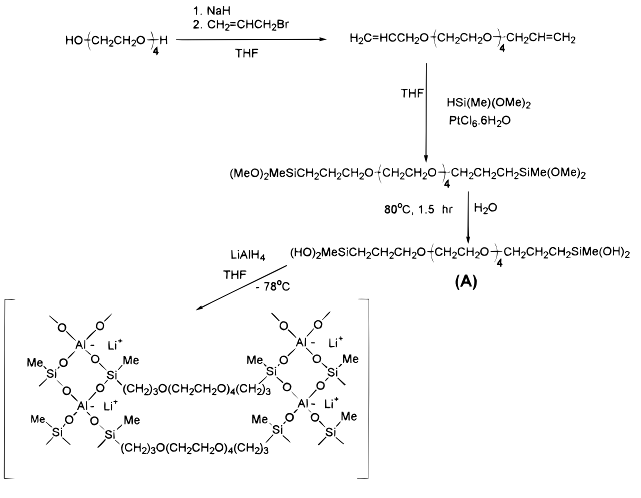
**Scheme 1. Preparation of Lithium Siloxyaluminate Polymers**



**Scheme 2. Preparation of Cross-Linked Lithium Siloxyaluminate Polymers**



Polymer IV

Silanediols **4** and **5** were obtained by hydrolysis of intermediates **2** and **3** (typically 4 mmol in 40 mL of distilled water). The initially oily dimethoxides (**2**) and diethoxides (**3**) gradually dissolved in the aqueous phase upon stirring to give perfectly homogeneous liquids. Products were extracted with diethyl ether, dried overnight over anhydrous $MgSO_4$, and collected after removal of solvents by vacuum distillation.

Polymers **I**−**III** were obtained by the almost quantitative reaction of silandiols **4**−**6** (typically 0.8 mmol), with $LiAlH_4$ at −78 °C in 5 mL of THF. Reaction was confirmed by the absence of $\nu$(OH) in the region 3370−3390 $cm^{-1}$ of the IR spectra of the polymers as well as by hydrogen evolution in excess of 90% of the theoretical volume.

In addition to polymers with pendent ether or phenyl groups attached to the Si atom, a cross-linked lithium siloxyaluminate polymer was prepared as illustrated in Scheme 2. Identities of the final polymer products, obtained after vacuum-drying, as well as all intermediates were confirmed by both $^1$H NMR and IR spectroscopy. Data for polymers I − IV are illustrated in Table 1. Since the polymers were all extremely hydrolyzable, they were transferred to an argon filled drybox prior to cell assembly for electrochemical characterization.

**Electrical Measurements.** The temperature dependence of polymer electrolyte conductivity was determined by ac impedance measurement in the frequency range 100 kHz−100 Hz (signal amplitude 10 mV) using a Hewlett-Packard Model HP 4194A frequency response analyzer. Cells consisted of polymer films (typically 0.1 mm thick) sandwiched between stainless steel electrodes. Bulk electrolyte resistance ($R$) was determined from the width of the high-frequency semicircle in the Cole−Cole plot. The cationic current fraction of samples sandwiched between nonblocking lithium electrodes was determined using the combined ac impedance/dc polarization method of Evans et al.[11] The time dependence of dc conductivity for larger applied potentials was also determined (Kenwood Model PW18-1.8Q power supply and Iwatsu Model VOAC 7413 digital multimeter).

## Results and Discussion

Room-temperature conductivities of the polymers determined by ac impedance are summarized in Table 2. Since films of polymer *I* were very rigid and the conductivity determined at 25 °C was extremely low ($<10^{-12}$ S $cm^{-1}$) it was mixed with poly(ethylene glycol)s of various molecular weight ($PEG_x$) in the ratio polymer repeat unit:($-CH_2CH_2O-$) of 25:1 to obtain measurable conductivity. The temperature dependence of conductivity is illustrated in Figure 2.

Conductivities of systems containing $PEG_{1000}$ and $PEG_{2000}$ were low at room temperature but showed a rapid increase above 40 °C corresponding to the melting point of the oligomer. Increasing conductivity was observed with a reduction in the molecular weight, reflecting the reduction in viscosity of the electrolyte and concomitant increase in ionic mobility. The low conductivity of the pure polymer shows that facile ion motion through the rigid polymer, for example, by hopping from anion site to anion site, is not favorable. The results illustrated in Figure 2 are typical of those obtained for salts dissolved in oligoethers and as such polymer **I** may be considered as a new type of hybrid salt in these systems. It can also be regarded as a model compound for polymers **II** and **III**, which contained oligoether chains attached to the polymer backbone.

The temperature dependence of ac conductivities of films of polymers **II** and **III** is illustrated in Figures 3 and 4. For both polymers, an increase in the number of ethylene oxide units from $n = 2$ to $n = 3$ was accompanied by an increase in the ionic conductivity. Conductivity of polymer **III** systems with two ethylene oxide side chains per silicon atom was less than that for polymer **II** systems for both $n = 2$ and $n = 3$. The curved conductivity plots of Figures 3 and 4 were characteristic of an all-amorphous polymer system.

It is well-known[12] that ion motion in polymer electrolytes formed by the dissolution of a salt in poly(ethylene oxide) is facilitated by segmental motion of the ethylene oxide chains. It therefore seems reasonable to ascribe the enhanced ac conductivities of polymers **II** and **III** over the model compound polymer **I** (without added PEG) to the presence of the pendent oligoether chains in the former. For polymers containing chains with three ether oxide repeat units ($n = 3$), the ether oxide proportion of the polymer (organic region in Figure 1) which acts as an ion conducting pathway is increased, allowing more facile ion motion. However, in the case where there are two pendent ether chains

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[11] Evans, J.; Vincent, C. A.; Bruce, P. G. *Polymer* **1987**, *28*, 2234.

[12] Ratner, M. A. In *Polymer Electrolyte Reviews*; MaCallum, Vincent, Eds.; Elsevier Applied Science: London, 1987; Vol. 1, p 173.

**Table 1. $^1$H NMR and IR Data for the Polymers Prepared[a]**

| polymer | $^1$H NMR/IR data |
|---|---|
| **I** | $^1$H NMR: 6.85−7.89 (m, 10H, aromatic)<br>IR: 1120 cm$^{-1}$ (Si−O−Al) |
| **II** ($n$ = 2) | $^1$H NMR: 0.10 (s, 3H, $CH_3Si$), 0.23−0.63 (m, 2H, $-CH_2Si$), 1.30−1.89 (m, 2H, $-\mathit{CH_2}CH_2Si$), 3.36 (s, 3H, $CH_3O-$), 3.57 (t, 10H, $CH_2O-$)<br>IR: 1065 cm$^{-1}$ (Si−O−Al) |
| **II** ($n$ = 3) | $^1$H NMR: 0.10 (s, 3H, $CH_3Si$), 0.24−0.67 (t, 2H, $-CH_2Si$), 1.29−1.90 (m, 2H, $-\mathit{CH_2}CH_2Si$), 3.37 (s, 3H, $CH_3O-$), 3.59 (t, 14H, $CH_2O-$)<br>IR: 1075 cm$^{-1}$ (Si−O−Al) |
| **III** ($n$ = 2) | $^1$H NMR: 0.30−0.78 (t, 4H, $-CH_2Si$), 1.32−1.86 (m, 4H, $-\mathit{CH_2}CH_2Si$), 3.34 (s, 6H, $CH_3O-$), 3.58 (t, 20H, $CH_2O-$)<br>IR: 1080 cm$^{-1}$ (Si−O−Al) |
| **III** ($n$ = 3) | $^1$H NMR: 0.26−0.71 (t, 4H, $-CH_2Si$), 1.29−1.88 (m, 4H, $-\mathit{CH_2}CH_2Si$), 3.35 (s, 6H, $CH_3O-$), 3.59 (t, 28H, $CH_2O-$)<br>IR: 1070 cm$^{-1}$ (Si−O−Al) |
| **IV** | $^1$H NMR: 0.10 (br, $CH_3Si$), 3.36 (br, $-CH2O$) |
| intermediate A | $^1$H NMR: 0.1 (s, 6H, $CH_3Si$) 0.42−0.88 (m, 4H, $-CH_2Si$), 1.35−1.81 (m, 4H, $-\mathit{CH_2}CH_2Si$), 3.63 (br, 20H, $-CH_2O$) |

[a] $^1$H NMR (δ, ppm, $CDCl_3$, TMS); IR (KBr).

**Table 2. Conductivities at 25 °C of the Polymers Prepared**

| polymer | conductivity at 25 °C (S cm$^{-1}$)[a] |
|---|---|
| **I** | $<10^{-12}$ |
| **II** ($n$ = 2) | $1.0 \times 10^{-5}$ |
| **II** ($n$ = 3) | $2.3 \times 10^{-5}$ |
| **III** ($n$ = 2) | $4.1 \times 10^{-6}$ |
| **III** ($n$ = 3) | $8.3 \times 10^{-6}$ |
| **IV** | $1.6 \times 10^{-6}$ |

[a] Conductivity determined by the ac impedance method.

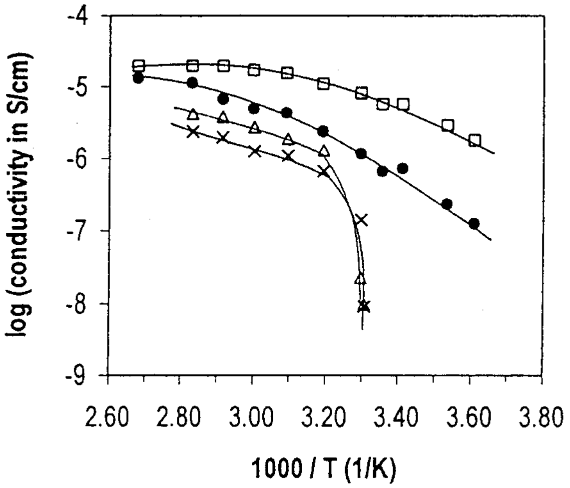

**Figure 2.** Temperature dependence of the conductivity of polymer *I*/poly(ethylene glycol) (PEG) mixtures. Polymer **I**: PEG ratio = 1:25 PEG molecular weight (□) 400; (●) 600; (△) 1000; (×) 2000. Conductivity determined by the ac impedance method.

per silicon atom (polymer **III** systems), the net Li$^+$ concentration per polymer repeat unit is significantly reduced. Conductivity of a polymer electrolyte may be most simply represented by eq 1, where $n$ is the number

$$\sigma = \sum n_i \mu_i q_i \qquad (1)$$

of charge carriers with mobility $\mu$ and charge $q$.[13] It appears that in polymer **III** systems, the decreased Li$^+$ concentration is not sufficiently compensated for by the increased cation mobility, the net result being a reduction in conductivity compared to polymer **II** systems. Of all the ether containing systems prepared, cross-linked polymer **IV** exhibited the lowest conductivity. Not only was the Li$^+$ concentration reduced, but suppression of ethylene oxide chain motion reduced ion mobility.

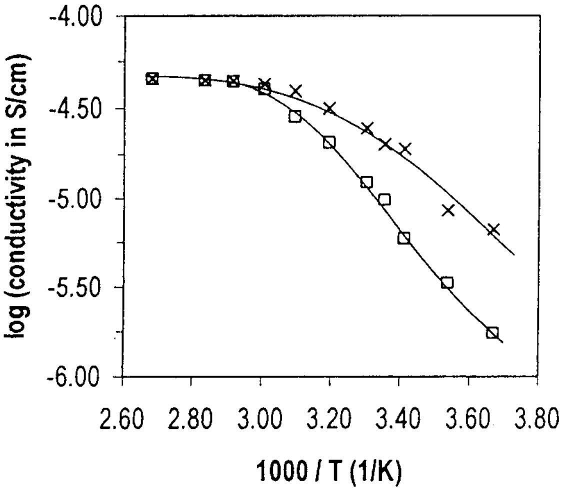

**Figure 3.** Temperature dependence of the conductivity of polymer **II** (×) $n$ = 3, (□) $n$ = 2. Conductivity determined by the ac impedance method.

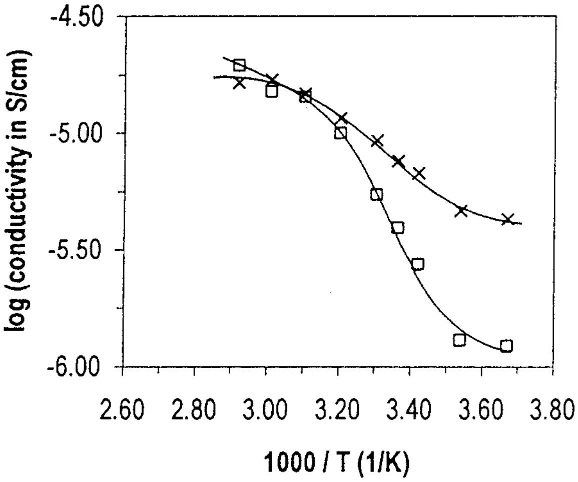

**Figure 4.** Temperature dependence of the conductivity of polymer **III** (×) $n$ = 3, (□) $n$ = 2. Conductivity determined by the ac impedance method.

The response of polymer **II** ($n$ = 3) to a 50 mV dc potential at 25 °C is shown in Figure 5 for the case where both blocking (stainless steel) and nonblocking (lithium) electrodes were used. A 50 mV potential was applied across the cell (sample thickness 0.1 mm) and the current was measured as a function of time. When stainless steel electrodes were used, the current rapidly dropped close to zero in the first 30 s and subsequently remained constant over the next 3 h. The dc steady-

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(13) MacCallum, J. R.; Vincent, C. A. In ref 11, p 23.

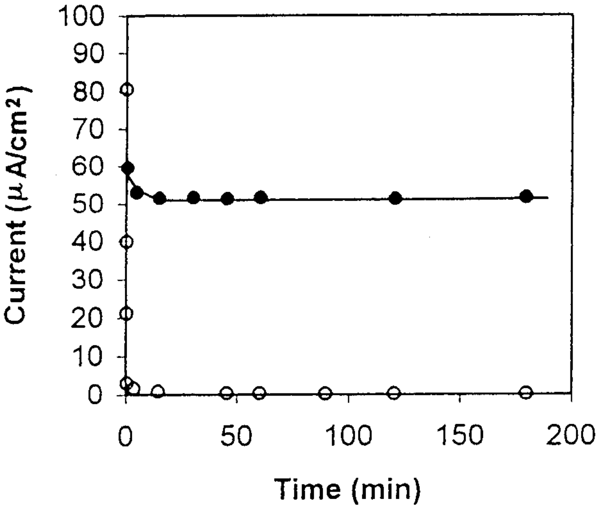

**Figure 5.** Time dependence of current upon application of a 50 mV dc potential for polymer **II** ($n = 3$) sandwiched between (●) nonblocking lithium electrodes, (○) blocking stainless steel electrodes. Temperature = 25 °C, polymer film thickness = 0.1 mm.

state conductivity was determined as $2.1 \times 10^{-8}$ S cm$^{-1}$. This value is of the order of 1/1000 that of the ionic conductivity determined by ac impedance. When nonblocking lithium electrodes were used, even after 3 h a current of 52 $\mu$A cm$^{-2}$ was maintained. The cationic current fraction measured using the method of Evans et al.[11] was determined as 0.71. It has been reported[14] that the transport properties of polymer electrolytes cannot be precisely extracted from cationic current fraction data alone however, the data from these two experiments would seem to suggest that a significant proportion of the charge is carried by the nonblocked Li$^+$ ions. This polymer, containing three ether oxide units in the pendent chain, was quite soft. If some low molecular weight siloxyaluminate units were present, this would account for the fact that 100% single ion conduction was not observed.

## Conclusion

We have shown that siloxyaluminate polymers with high Li$^+$ conductivity may be prepared. The polymer molecular design allows for anion charge delocalization, while the presence of stereochemically bulky groups in the vicinity of the anion inhibits close approach of the cation. These two factors reduce ion pairing while the presence of ethylene oxide side chains enhances cation motion.

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