Aluminosilicate/Poly(ethylene glycol) Copolymers: A New Class of Polyelectrolytes

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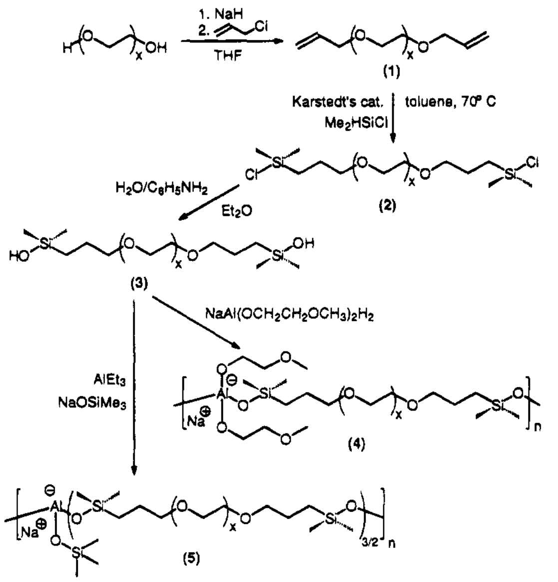
Solvent-free polymer electrolytes are currently under intense scrutiny for use in high-energy density batteries and other electrochemical devices.[1,2] In the most common polymer electrolytes, i.e., polymer–salt complexes, high anion transport numbers and low conductivity result in cell polarization and low power density. In addition, the mobility of both ions complicates the investigation of transport mechanisms. For these reasons, our group and others[3–13] have investigated polyelectrolytes such as modified poly(phosphazene) with covalently bound anions[14,15] and poly(tetraalkoxyaluminate).[16] These polyelectrolytes ensure unity transport number for the cation. However, results from these investigations and others indicate that ion pairing limits the performance of these materials.[17] To address this issue, our group has explored the use of sequestering agents (cryptands)[15,18] and the use of very weakly basic anions attached to the polymer to reduce contact ion pairing. Aluminosilicates are attractive as low-basicity anions that can be incorporated into a polymer by siloxy linkages. In the present research, we prepared several alkoxy aluminosilicate polyelectrolytes to examine the effects of anion basicity on conductivity and explored the influence of added cryptand.

Scheme 1



Polymers were prepared by the following procedure (Scheme 1): Poly(ethylene glycol) ($MW_{av} \approx 300$ leading to **4**, and ≈ 600 leading to **5**) was reacted with excess sodium hydride, followed by allyl chloride, yielding α,ω-bis(allyloxy)poly(ethylene glycol) (**1**). Compound **1** was then catalytically hydrosilylated with dimethylchlorosilane in the presence of Karstedt's catalyst (platinum(0) divinyltetramethyldisiloxane) to form α,ω-bis(chlorodimethylsilyl)poly(ethylene glycol) (**2**), which was quantitatively hydrolyzed, producing α,ω-bis(hydroxydimethylsilyl)poly(ethylene glycol) (**3**). Linear polyelectrolytes were then prepared by the reaction of Red-Al (sodium bis(2-methoxyethoxy)aluminum hydride) with a 5% excess of compound **3**, to yield $[NaAl(OEOMe)_2(OSiMe_2(CH_2)_3(OE)_xO(CH_2)_3SiMe_2O)_{2/2}]_n$ ($x \approx 7.53$; Me = CH_3, OE = OCH_2CH_2) (**4**). The network polyelectrolyte $[NaAl(OSiMe_3)(OSiMe_2(CH_2)_3(OE)_xO(CH_2)_3SiMe_2O)_{3/2}]_n$ ($x \approx 14.9$) (**5**) was synthesized by addition of compound **3** (5% excess) to a stirred solution of triethylaluminum and sodium trimethylsilanolate. The complex of cryptand [2.2.2] (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane), with linear polyelectrolyte **4** was prepared by stirring a stoichiometric quantity of cryptand [2.2.2] with **4** in acetonitrile, followed by solvent removal under high vacuum (compound **6**). The reactions were carried out in a dry nitrogen atmosphere using standard Schlenk and glovebox techniques, and the products were stored under nitrogen.

Mass spectrometry and $^{13}C/^{1}H$ NMR confirmed the identity of the intermediates **1**–**3**. The formation of a covalent bond between the aluminum centers and siloxy oxygens was confirmed by a progressive upfield shift of the ^{29}Si resonance, from $\delta = 31$ ppm (**2**)[19,20] to $\delta = 15.5$ (**3**)[20] to $\delta \approx 0$ in the final polymer products **4** and **5**. Additionally, ^{27}Al NMR spectra of **4** and **5** exhibit broad signals centered around $\delta \approx 60–64$ ppm, a value

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[19] *n*-Propyldimethylchlorosilane (Hüls America) $^{29}Si\{^{1}H\}$ NMR: δ 31.2 ppm (strong, $R_3\mathbf{Si}Cl$), δ 6.97 ppm (weak, $(R_3\mathbf{Si})_2O$).

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Table 1. VTF Parameters and Glass Transitions

polymer	$\sigma_0{}^a$/S/K$^{1/2}$ cm^{-1}	$(B/k_B)^a$/K	$T_0{}^a$/K	$T_g{}^b$/K
4 $[NaAl(OEOMe)_2(OSiMe_2(CH_2)_3(OE)_xO(CH_2)_3SiMe_2O)_{2/2}]_n$ ($x \approx 7.53$)[c]	0.626	1048	196.1	224.2
5 $[NaAl(OSiMe_3)(OSiMe_2(CH_2)_3(OE)_xO(CH_2)_3SiMe_2O)_{3/2}]_n$ ($x \approx 14.9$)[c]	0.0347	620	206.9	214.9
6 $[(\mathbf{4}):[2.2.2]]_n$	2.49	1028	188.8	222.8
7 $[NaAl(OEOMe)_2((OE)_xO)_{2/2}]_n$ ($x \approx 6.8$)[d,e]	31.7	3201	109	247
8 $[NaAl(OEOMe)_2((OE)_xO)_{2/2}]_n$ ($x \approx 9.0$)[d]	0.214	1406	180	242
9 $[(\mathbf{8}):[2.2.2]]_n$	2.36	1107	185	

[a] Parameters obtained from a three-variable fit to the VTF equation: $\sigma = \sigma_0 T^{-1/2} \exp[-B/(k_B(T - T_0))]$. [b] Onset of transitions extrapolated to zero heating rate. [c] $x \approx 7.53$ indicates $MW_{av} \approx 300$ for the poly(ethylene glycol) initially used in the synthesis; $x \approx 14.9$ indicates $MW_{av} \approx 600$. [d] $x \approx 6.8$ indicates $MW_{av} \approx 300$ for the poly(ethylene glycol) used in the synthesis; $x \approx 9.0$ indicates $MW_{av} \approx 400$. [e] Anomalous VTF parameters are attributed to the limited amount of data available for fitting.

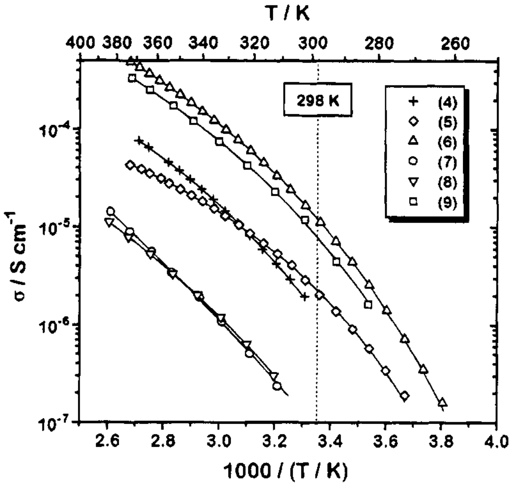

Figure 1. Temperature-dependent conductivity of aluminate (**7**–**9**), aluminosemisilicate (**4**, **6**), and aluminosilicate (**5**) polyelectrolytes, and corresponding three-parameter VTF fits (solid lines). Best-fit VTF parameters are given in Table 1.

indicative of asymmetric, 4-coordinate oxoaluminum.[21,22] Anal. Calcd for **4**: C 47.95, H 8.83, Si 7.29, Al 3.33, Na 2.84. Found: C 46.82, H 8.44, Si 6.99, Al 3.21, Na 3.10. Anal. Calcd for **5**: C 50.43, H 9.07, Si 7.45, Al 1.72, Na 1.47. Found: C 50.60, H 9.01, Si 7.26, Al 1.68, Na 1.42.[23]

Glass transition temperatures and the fits of conductivity data to the Vogel–Tamman–Fulcher equation are given in Table 1 along with values for the related tetraalkoxyaluminate polymers **7**–**9** synthesized in our laboratory by Doan et al.[16] Examination of DSC traces for polymers **4**–**6** shows no evidence of melting transitions, indicating completely amorphous structures. Conductivity data (Figure 1) show a progressive increase of room temperature conductivities in the series **7**–**4**–**5**, which correlates well with decreasing anion basicity, and also with decreasing glass transition temperature, T_g. The number of siloxy segments proximal to the aluminate center (none in the alkoxyaluminates, two in the linear polymer, and four in the network polymer) may influence conductivity through two mechanisms. The decrease of oxygen basicity with increasing silicon content may reduce contact ion pairing.[24] Additionally, the larger Al–O–Si bond angle, longer bonds involving the Si atom, and extremely low rotational barrier about the Si–O bond may increase polymer flexibility in the vicinity of the anion. Thus a decrease in T_g is expected with added SiO groups, as observed in the sequence **7**–**4**–**5**. A decrease in T_g indicates an increased degree of polymer segmental motion which in turn leads to improved ion transport in polymers.[25]

Addition of cryptand to the linear polyelectrolyte **4** in a 1:1 cryptand:sodium ratio effected nearly an order of magnitude increase in the conductivity at all temperatures. This increase is comparable to those observed by Doan[16] and Chen[15,18] (typically 1.5–2 orders of magnitude) and has been attributed to a decrease in ion pairing between the bound anion and the encapsulated mobile cation.[17] The smaller cryptand effect observed here is attributed to the reduced ion pairing between sodium ions and the weakly basic aluminosilicate anions. Interestingly, the addition of cryptand has very little effect on Tg (Table 1).

In conclusion, Na^+ conductivity in polyelectrolytes increases in the series $Al(OR)_4{}^-$ to $Al(OSiR_3)_4{}^-$ because of decreases in basicity. We are aware of only one other sodium-conducting polyelectrolyte with a room-temperature conductivity that is reported to exceed the performance attained by the present systems without the use of plasticizers or other additives.[13] Conductivity is also enhanced significantly by a reduction in ion pairing upon addition of cryptand [2.2.2], although the effect is not as dramatic as has been observed with less conductive systems. The synthesis of analogous lithium ion conductors should be straightforward and is in progress.

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