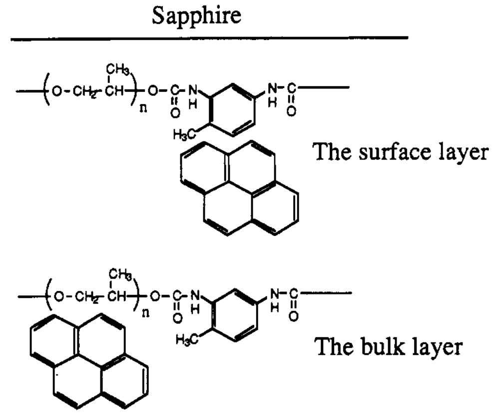

Figure 8. Schematic representation of the location of a pyrene molecule in the surface and the bulk layers of a SPUU film.

place more efficiently in the surface layer of PMMA films and that the concentration of the ground-state dimer is higher in the surface layer than in the bulk layer. The present results agree with this. We have obtained preliminary data that indicate the inhomogeneity in poly(hydroxystyrene) and Itaya's group showed it in polystyrene. Phenomenologically, we consider that this type of inhomogeneity in polymer films is quite general.

Conclusions

TIR fluorescence spectroscopy can provide useful information on the inhomogeneous structure and aggregation of pyrene in the surface layer of SPUU films. It is shown that the environmental polarity and the aggregation of pyrene in the surface layer differ from those in the bulk layer and that the concentration of pyrene in the surface layer is higher than in the bulk layer. However, the concentration of pyrene forming excimers is lower in the surface than in the bulk. These results are ascribed to the microscopic location of pyrene molecules in the polymer chain matrices; pyrene molecules are located in the vicinity of TDI segments in the surface, and they are near PPO segments in the bulk as shown in Figure 8.

The present results indicate that the concentration gradient of pyrene is important in a SPUU film, although the concentration gradient has not been determined quantitatively. The depth profile of pyrene fluorescence in the surface layer can be measured by varying the incident and/or the observation angles. A study on the excitation energy migration and transfer as a function of the depth as well as on the concentration distribution of pyrene in the surface layer is in progress.

Registry No. (TDI)(PPO) (block copolymer), 37273-56-6; pyrene, 129-00-0.

Synthesis and Electrical Response of Single-Ion Conducting Network Polymers Based on Sodium Poly(tetraalkoxyaluminates)

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Sodium ion conducting polyelectrolytes containing a network of tetraalkoxyaluminates linked by polyethers have been prepared by the reaction of $NaAlH_2(OCH_2CH_2OCH_3)_2$ with low molecular weight poly(ethylene glycols) (PEG(300), -(400), -(600), -(1000)). The conductivities of these electrolytes are comparable to those observed for complexes of sodium tetraalkoxyaluminate salts with poly(ethylene oxide)-based host polymers (ca. 10^{-6} S cm^{-1} at 60 °C) indicating strong Na^+–alkoxyaluminate ion pairing. A conductivity enhancement of 110-fold at 40 °C is observed when the cation complexing agent cryptand [2.2.2] is added to the polyelectrolyte prepared from PEG(400). A similar conductivity enhancement was observed (140-fold at 40 °C) when cryptand is added to salt complexes; the conductivity enhancement is likely due to a decrease in ion pairing in the electrolytes.

Introduction

There is considerble interest in the mechanism of ion conduction in polymer electrolytes.[1-3] As part of a program to clarify the factors governing ion conduction in these materials we have synthesized a variety of new polymer electrolytes. The present research involves the synthesis of new host materials for polymer–salt complexes and the design of new polyelectrolytes with characteristics that maximize ionic conductivity in the solid polymer.

The desirable properties for good polymer electrolytes have been delineated through studies of salt complexes of the semicrystalline host poly(ethylene oxide), PEO.[2,3,4] Good hosts have a high concentration of polar groups and are amorphous materials with low glass transition temperatures (T_g's). Host polymers that meet these criteria include comb polymers with flexible inorganic backbones and oligoether side chains[5,6] and linear chain materials such

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Table I. Quantities of Reagents Used in the Synthesis of Polyelectrolytes

polym[a]	Red-Al	mmol	PEG mw	[PEG], mmol
NaAl(300)	5	17	300	18.7
NaAl(400)	5	17	400	18.7
NaAl(600)	5	17	600	18.7
NaAl(1000)	2.5	8.5	1000	9.35

[a] All reactions were carried out in toluene.

as oxymethylene-linked oligoethylene oxide polymers, where the oxymethylene groups break up the regularity of the polymer and thus decrease crystallinity relative to PEO.[7]

Single-ion conductors should also have these properties. Polar groups are no longer required to complex salt, but they are needed to increase the dielectric constant, thus reducing ion-pair formation. Hardy[8] demonstrated that the polyelectrolytes sodium poly(styrenesulfonate) and poly(diallyldimethylammonium chloride) have negligible ionic conductivities at room temperature, but their conductivities approach those observed in polymer–salt complexes when they are plasticized with low molecular weight poly(ethylene glycol). Since Hardy's observations many new single-ion conductors have been reported that do not require plasticizers to induce ionic conductivity. These materials include lithium cross-linked phosphate networks,[9] poly(oligo(oxyethylene methacrylate)-*co*-lithium methacrylate),[10] and comb polymers with phosphazene, siloxane, or nylon backbones with charged anionic (alkylsulfonate and 1,3-*tert*-butylphenoxide) or cationic (quaternary ammonium) groups on the side chains.[11-13] In this paper we describe the synthesis, characterization, and electrical response of a new class of sodium ion conductors based upon sodium tetraalkoxyaluminate polyether networks.

Experimental Section

Materials. Poly(ethylene glycol) (PEG, Aldrich, mw_{av} = 300, 400, 600, 1000) were dried under vacuum at 60 °C for 2 days. Red-Al (Aldrich, sodium bis(2-methoxyethoxy)aluminum hydride, 3.4 M solution in toluene) was used as received. Toluene (MCB) was refluxed over sodium under an inert atmosphere and distilled before use. Methoxyethanol (Aldrich) was dried by refluxing over $CaSO_4$ for several hours and then distilling under an inert atmosphere. Acetonitrile (MCB) was reluxed over calcium hydride and distilled under an inert atmosphere. Cryptand [2.2.2] was used as received. The polymers PEO (Polysciences) and oxymethylene-linked poly(ethylene oxide), here called aPEO, were purified or prepared as previously described; both polymers were rigorously dried under high vacuum for 48 h before being transferred to an inert atmosphere glove box.[6,14] The salt $NaAl(OC_2H_4OCH_3)_4$ was prepared by the reaction of Red-Al with excess methoxyethanol under a dry N_2 atmosphere and was recrystallized from hexane.

Synthesis of Polyelectrolytes. A general procedure for the synthesis of the sodium tetraalkoxyaluminate polymers is given below, and the experimental details are summarized in Table I. The polymers synthesized from the liquid poly(ethylene glycols) (PEG(300), -(400), and -(600)) were prepared by the slow addition of excess polymer to a stirred solution of Red-Al at room temperature under a flowing N_2 atmosphere. In the preparation of the polymer containing PEG(1000), the PEG was dissolved first in 30 mL of toluene and Red-Al was added slowly under a flowing N_2 atmosphere. To ensure complete reaction of the hydrides, all reaction mixtures were stirred for 1 h before addition of 1 mL of methoxyethanol. These solutions were then stirred at room temperature for 12 h. The solvent was removed in vacuo, and then the polymer was heated to 70 °C under vacuum for 2 days. The resulting light brown solid polymer was washed with toluene for 2–3 days in a Soxhlet extractor to remove any unreacted polyethers. The Soxhlet extraction was done under an inert atmosphere with the toluene distilled from sodium in situ. (The infrared spectrum of the material recovered from extraction in the absence of sodium confirmed the presence of hydroxyl groups.) The cellulose thimbles were dried in a 120 °C oven for 3 days to reduce hydrolysis of the polymers. After Soxhlet extraction was complete, the material remaining in the thimble was dried under vacuum (ca. 2×10^{-5} Torr) for more than 48 h and then stored in a dry, inert atmosphere. Elemental analysis of the polymers NaAl(400), NaAl(600), and NaAl(1000), (C, H, and Al) agrees with the formulation of $Al(OCH_2CH_2OCH_3)_2$ linked by $O(CH_2CH_2O)_x$ to form polyanions with Na^+ as the counterion. (NaAl(400), $NaAlO_{13.7}C_{23.4}H_{48.7}$: calcd C 46.87, H 8.20, Al 4.51; obsd C 46.38, H 8.10, Al 4.67. NaAl(600), $NaAlO_{17.2}C_{32.4}H_{66.8}$: calcd C 48.79, H 8.44, Al 3.58; obsd C 48.51, H 8.50, Al 3.55. NaAl(1000), $NaAlO_{27.3}C_{50.6}H_{103.2}$: calcd C 50.73, H 8.68, Al 2.25; obsd C 49.40, H 8.49, Al 2.92.

Cryptand complexes of NaAl(400) were prepared with stoichiometric quantities of cryptand [2.2.2] and polyelectrolyte placed in a closed vessel. Typically, 0.5 g (1.3 mmol) of cryptand and 0.78 g (1.3 mmol) of NaAl(400) were used. The reactants were stirred overnight in 30 mL of CH_3CN and dried under vacuum after removal of the solvent. All transfers of the cryptand, polyelectrolyte, and solvent were carried out under an inert atmosphere.

Synthesis of Polymer–Salt Complexes. Polymer-salt complexes of the polymers aPEO and PEO with the salt $NaAl(OC_2H_4OCH_3)_4$ and $NaCF_3SO_3$ were prepared with stoichiometric quantities of polymer and salt (1.2 g (28.6 mmol) of aPEO, or 1.26 g (28.6 mmol) of PEO, 1.16 g (3.3 mmol) of $NaAl(OC_2H_4OCH_3)_4$) placed in a closed vessel. The reactants were stirred at room temperature in 30 mL of CH_3CN until a homogeneous mixture was obtained. The solvent was then removed, and the complex dried under vacuum for more than 48 h. The aPEO cryptand–salt complex was obtained from stoichiometric quantities of cryptand [2.2.2] (0.62 g, 1.65 mmol), polymer aPEO (1.2 g, 28.6 mmol), and the salt $NaAl(OC_2H_4OCH_3)_4$ (1.16 g, 3.3 mmol). These solids were also stirred in CH_3CN overnight and then rigorously dried after removal of the solvent.

Characterization of Electrolytes. Carbon (^{13}C proton decoupled) and proton NMR spectra were obtained on a Varian XL-400 MHz spectrometer. Spectra of the solid polymers were determined on toluene-swollen samples; a solvent peak was used as an internal reference.

Differential scanning calorimetry (DSC) traces were obtained on a Perkin-Elmer DSC-2 with liquid N_2 cooling. Samples were placed in hermetically sealed aluminum pans. The instrument was calibrated by using four standards (Ga, cyclohexane, decane, and heptane). Transitions were measured at three heating rates (80, 40, and 20 °C/min). Glass transitions were taken as the midpoint of the inflection; melting points were taken as the peak of the transition. The reported values of T_g were obtained by linear extrapolation of the data to 0 °C/min heating rate.

Samples for ac impedance were pressed into pellets inside airtight conductivity cells. A Teflon spacer ring surrounded the sample to avoid any sample flow at elevated temperatures. The manipulation of the samples was performed under a dry inert atmosphere. Stainless steel or Na/Hg electrodes were used in

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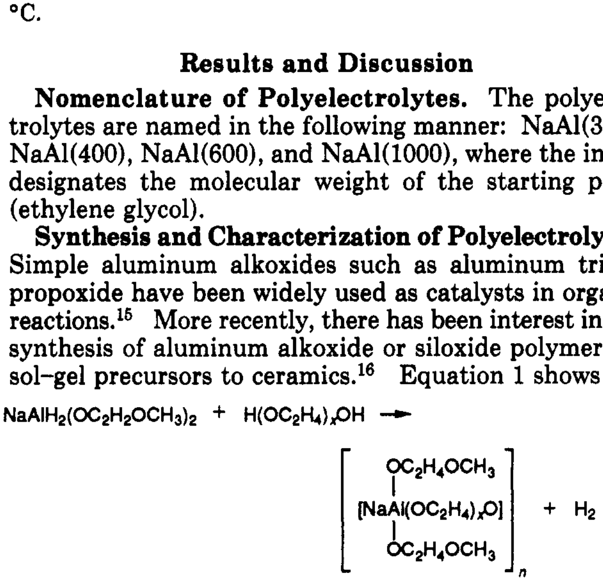
these measurements. Na/Hg electrodes were prepared by coating Cu disks with saturated sodium amalgam. The surface area of the sample was generally 0.96 cm^2, and the sample thickness was generally 0.1 cm. The frequency-dependent impedance of the samples was measured on an HP 4192A impedance analyzer (5 Hz to 5 MHz) or a Solartron 1250 frequency response analyzer/1286 potentiostat (10^{-2} Hz to 60 kHz). The sample cell was placed in a regulated air bath (±0.1 °C) for conductivity measurements, and the conductivity measured between 40 and 110 °C.

Results and Discussion

Nomenclature of Polyelectrolytes. The polyelectrolytes are named in the following manner: NaAl(300), NaAl(400), NaAl(600), and NaAl(1000), where the index designates the molecular weight of the starting poly(ethylene glycol).

Synthesis and Characterization of Polyelectrolytes. Simple aluminum alkoxides such as aluminum triisopropoxide have been widely used as catalysts in organic reactions.[15] More recently, there has been interest in the synthesis of aluminum alkoxide or siloxide polymers as sol–gel precursors to ceramics.[16] Equation 1 shows the



$$\mathrm{NaAlH_2(OC_2H_2OCH_3)_2 + H(OC_2H_4)_xOH \longrightarrow \left[\overset{OC_2H_4OCH_3}{\underset{OC_2H_4OCH_3}{[NaAl(OC_2H_4)_xO]}}\right]_n + H_2} \qquad (1)$$

idealized reaction for the synthesis of the aluminate polymer. Double alkoxides of the general formula $\mathrm{NaAl(OR)_4}$ have been known since 1929[17] and can be readily synthesized by the reaction of $\mathrm{AlCl_3}$ and excess NaOR at room temperature. This simple route cannot be employed in the synthesis of these polyelectrolytes as it is difficult to remove the NaCl by-product from the resulting polymer. On the other hand, when a complex metal hydride reacts with poly(ethylene glycol) the only by-product of the reaction is $\mathrm{H_2}$.

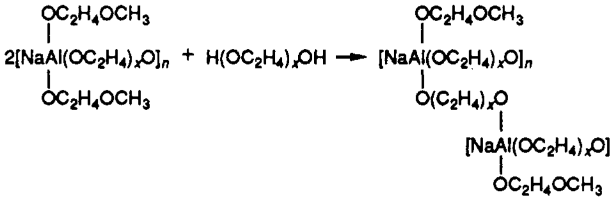
To a first approximation these polymers can be regarded as poly(ethylene oxide) with charged $\mathrm{Al(OR)_2(OR')_2^-}$ groups and charge-compensating $\mathrm{Na^+}$ ions interspersed throughout the backbone. The ^{13}C and ^{1}H spectra of these polymers fit well with this picture. The ^{13}C spectra consist essentially of a single broad peak centered at 75 ppm due to the $\mathrm{CH_2}$ group in the polymers. The ^{1}H spectra exhibit resonances at 3.5 ppm with small shoulders slightly upfield that can be assigned to the $\mathrm{CH_2}$ and $\mathrm{CH_3}$ on the short-side-chain protons, respectively. The introduction of the inorganic group into the backbone results in an amorphous polyelectrolyte if the length of the poly(ethylene oxide) chains bridging the metals is sufficiently small. Other workers have employed similar strategies, incorporating either organic or inorganic groups in the chain yielding amorphous host materials for polymer–salt complexes.[6,18] For example, Armand has formed cross-linked amorphous networks by the reaction of poly(ethylene glycol) with trioctylaluminum.[19] In the polymers described here, however, ratios of the reactants are chosen to yield a polyelectrolyte rather than a neutral network.

Table II. Thermal Transitions of Aluminate Polymers

polym	$\mathrm{Na^+}$/EO	T_g,[a] K	T_g, J (10 °C/min)
NaAl(300)	0.16	247	251
NaAl(400)	0.12	242	246
NaAl(600)	0.08	230	231
NaAl(1000)	0.05		334 (T_m)

[a] Extrapolated to zero heating rate.

Solubility data indicate that the linear-chain representation for our polymers is an over simplification. For example the polymer is insoluble in both toluene and acetone, indicating that it probably exists as a cross-linked network. The cross-linking apparently arises from a redistribution reaction of excess poly(ethylene glycol) such as the extreme example illustrated in eq 2. In agreement



$$\mathrm{2\overset{OC_2H_4OCH_3}{\underset{OC_2H_4OCH_3}{[NaAl(OC_2H_4)_xO]_n}} + H(OC_2H_4)_xOH \longrightarrow \overset{OC_2H_4OCH_3}{\underset{\underset{\underset{OC_2H_4OCH_3}{[NaAl(OC_2H_4)_xO]_n}}{O(C_2H_4)_xO}}{[NaAl(OC_2H_4)_xO]_n}}} \qquad (2)$$

with this interpretation the polymer dissolves very slowly in alcohols, which bring about redistribution to low molecular weight alkoxyaluminates. Similarly the polymer is attacked by water to yield insoluble aluminates.

Our alkoxyaluminate polymer electrolytes resemble most closely the lithium phosphate liked poly(ethylene oxide) networks reported by LeNest et al.[9] In both these polymers the anionic group is an intimate part of the polymr chain rather than a substituent of a group attached to the polymer backbone.[8] The concentration of $\mathrm{Na^+}$ in these aluminate networks is significantly higher than in other single-ion conductors, such as the poly(phosphazenesulfonates),[10] and is approximately equal to salt concentrations in typical polymer–salt complexes.

The thermal behavior of the polymers was investigated by differential scanning calorimetry, DSC, and the observed transitions are listed in Table II. The polymers with short polyether chains, poly(ethylene glycol) mw ≤ 600, are amorphous. The T_g rises slightly with increasing $\mathrm{Na^+}$ concentration. The polymer NaAl(1000) is semicrystalline with a melting endotherm at 60 °C. This transition is quite close to the observed transition of pure PEO, 65 °C.[13] The similarity of these two transitions implies that the distance between the Al ions in this polymer is too large to prevent crystallization of the ethylene oxide chains. No glass transition was observed for this polymer. The trend of increasing T_g with increasing salt concentration is commonly seen in the polymer–salt complexes. The salt is thought to act effectively as a weak cross-linking agent in polymer–salt complexes. In polymer–salt complexes, however, the rise in T_g is usually much larger than is observed for these polyelectrolytes. The apparently very strong ion-pairing effects between the tetraalkoxyaluminate anion and the $\mathrm{Na^+}$ may be correlated with the small increase in T_g with increasing ion concentration. The tight $\mathrm{AlO_4^-}$–$\mathrm{Na^+}$ ion pair or possibly the coordination of $\mathrm{Na^+}$ by the ether oxygen of the anion may lead to a smaller effective field seen by basic oxygen atoms on another chain segment, resulting in weak interchain links by ion–dipole interactions. Another series of polyelectrolytes, the poly(phosphazenesulfonates), shows no significant rise in T_g over the concentration range studied, and here again the fairly strong cation–sulfonate ion pairing may reduce the electrostatic interchain interaction.[10]

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Table III. Conductivity Values and Arrhenius Parameters for Aluminate Polymers and Salt Complexes

polym	σ(50 °C), S cm^{-1}	σ(80 °C), S cm^{-1}	E_a, eV	A, S cm^{-1} K
NaAl(300)	5.0×10^{-7}	3.4×10^{-6}	0.61	6.4×10^{5}
NaAl(400)	6.1×10^{-7}	3.6×10^{-6}	0.60	4.1×10^{5}
NaAl(600)	4.0×10^{-7}	1.7×10^{-6}	0.54	1.4×10^{5}
NaAl(1000)	2.8×10^{-7}	8.8×10^{-7}	0.39	1.0×10^{2}
$PEO_9NaAl(OR)_4$[a,b]	6.6×10^{-8}	2.2×10^{-6}	0.91	2.7×10^{9}
$aPEO_9NaAl(OR)_4$	1.8×10^{-7}	6.9×10^{-7}	0.64	4.7×10^{5}
NaAl(400):[2.2.2]	4.2×10^{-5}	1.7×10^{-4}	0.43	8.1×10^{4}
$aPEO_9NaAl(OR)_4$: 0.5[2.2.2]	4.5×10^{-5}	1.3×10^{-4}	0.34	3.2×10^{3}
$aPEO_8Na$:2.9 × $10^{-5}(SO_3CF_3)$[c]	2.9×10^{-5}	1.6×10^{-4}	0.66	1×10^{7}

[a] R = $CH_2CH_2OCH_3$. [b] Data fit $T > 65$ °C. [c] VTF parameters for $aPEO_8NaTF$: $T_0 = 202$ K, $B = 0.092$ eV, $A = 3.61$ S K$^{1/2}$ cm^{-1}, $T_g - T_0 = 42$ K.

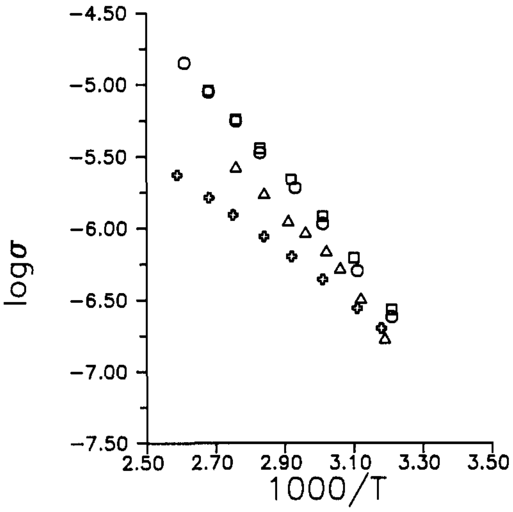

Figure 1. Temperature dependent conductivity for aluminate polymers: ✣, NaAl(1000); △, NaAl(600); □, NaAl(400); ○, NaAl(300).

The conductivities of the aluminate polymers at 50 and 80 °C are listed in Table III. The semicrystalline NaAl(1000) has a lower conductivity than the amorphous polymers NaAl(600), NaAl(400), and NaAl(300), Figure 1. This suggests that the ionic conductivity in these polyelectrolytes occurs mainly in the amorphous phase, as with polymer–salt complexes. The data in Table II show that these aluminate polymers, unlike the poly(phosphazenesulfonates) and the poly(siloxanesulfonates) and many polymer–salt complexes, exhibit no conductivity maximum with increasing salt concentration.[10,12] The conductivity of the amorphous polymers at 50 °C is approximately the same; at elevated temperatures conductivity rises with increasing Na^+ concentration. The conductivities of the two polymers with the highest Na^+ concentration, NaAl(300) and NaAl(400), are almost identical. One explanation for the observed concentration-dependent conductivity is that the increase in T_g of these polymers with increasing salt concentration is not large enough to affect the ionic conductivity significantly.

The temperature dependence of the ionic conductivity is shown in Figure 2. In amorphous electrolytes Arrhenius plots of log σ vs $1/T$ are often curved. The temperature-dependent conductivity data is often fit by the Vogel–Tammann–Fulcher equation, eq 3. It was not possible

$$\sigma = AT^{-1/2}e^{-B/(k_B(T-T_0))} \qquad (3)$$

to adequately fit the conductivity data for the aluminate polymers by the VTF equation. This behavior contrasts with our observations for $aPEO_8NaTF$, which yields a curved conductivity plot that is readily fit by the VTF equation.[20] Below 40 °C the conductivity drops precipitously ($\sigma < 10^{-8}$ S cm^{-1}) and cannot be measured on our instruments. Therefore, the broad curvature in a plot of log σ vs $1000/T$ that is commonly seen in polymer electrolytes is not evident. The Arrhenius equation, eq 4, gives

$$\sigma = A'T^{-1}e^{-E_a/(k_BT)} \qquad (4)$$

a much better fit of the data. The fitting parameters for this equation are listed in Table III. The activation energy for ion conduction in these electrolytes is higher than the activation energy calculated for Arrhenius fits of the poly(phosphazenesulfonates) but are close to those observed in salt complexes with comparable T_g's.[4,5,10,20]

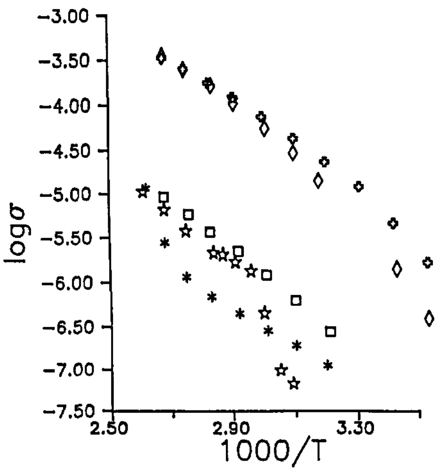

Figure 2. Temperature-dependent conductivity of aluminate polyelectrolytes and related polymer–salt complexes: *, $PEO_9NaAl(OR)_4$; ☆, $aPEO_9NaAl(OR)_4$; ◇, $aPEO_8NaCF_3SO3$; □, NaAl(400); ✣, NaAl(400):[2.2.2].

The conductivity of these polyelectrolytes, approximately 10^{-6} S cm^{-1} at 60 °C, is significantly lower than that of most polymer–salt complexes and is lower than that of the sodium ion conductors reported by Liu et al.[13] The low conductivity may be due to extensive ion pairing. To test this hypothesis, complexes of the salt $NaAl(OC_2H_4OCH_3)_4$ and polymers closely related to the networks studied were synthesized: $PEO_9NaAl(OC_2H_4OCH_3)_4$ and oxymethylene-linked PEO, $aPEO_9NaAl(OC_2H_4OCH_3)_4$. (The polymer aPEO is similar in structure to the polyelectrolyte NaAl(400) but has a CH_2 group rather than the charged inorganic group interspersed throughout the ethylene oxide chain.) Above the melting point of PEO the PEO polymer–salt complex has approximately the same conductivity as NaAl(400). Interestingly, the analogous complex with aPEO has a lower conductivity than both the PEO complex and NaAl(400) at elevated temperatures. As shown in Figure 3 both the salt complexes and the polyelectrolytes have significantly lower conductivity than the complex $aPEO_8NaCF_3SO_3$. At this concentration the $NaCF_3SO_3$ complex also shows considerable ion pairing.[21] However, the ion pairing is apparently much stronger in the sodium tetraalkoxyaluminate salt complexes. The oxygens directly bonded to the aluminum in the polymer and in the salts may be sufficiently basic to interact with the sodium cation and form strong ion pairs. It may be possible to reduce the basicity of aluminate anions by using Si–O–Al linkages rather than C–O–Al linkages employed here. Armand has

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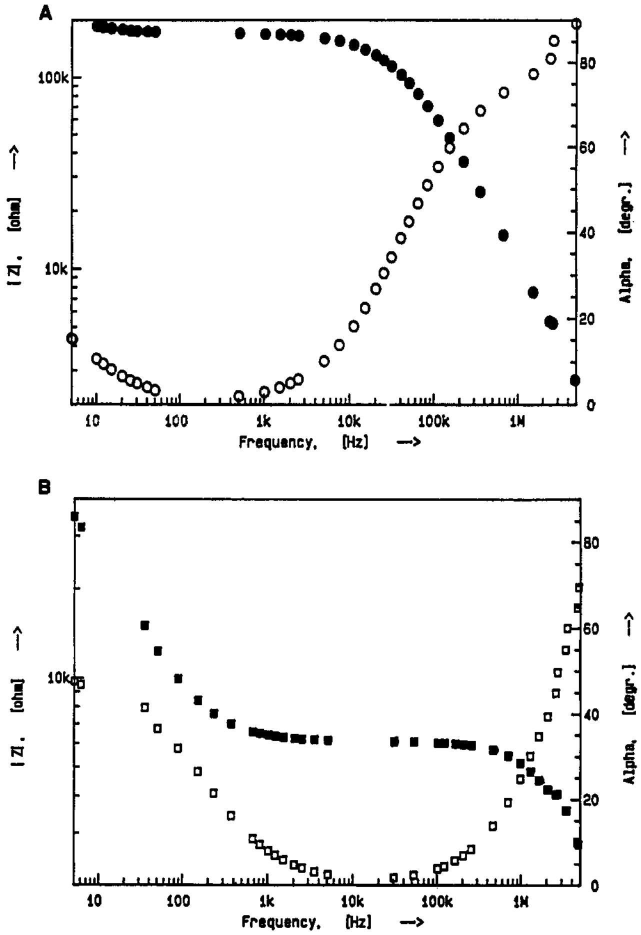

Figure 3. Bode plots for polyelectrolytes at 50 °C against stainless steel electrodes: (A) NaAl(400); ○ = phase angle, ● = impedance; (B) NaAl(400):[2.2.2], ☐ = phase angle, ■ = impedance.

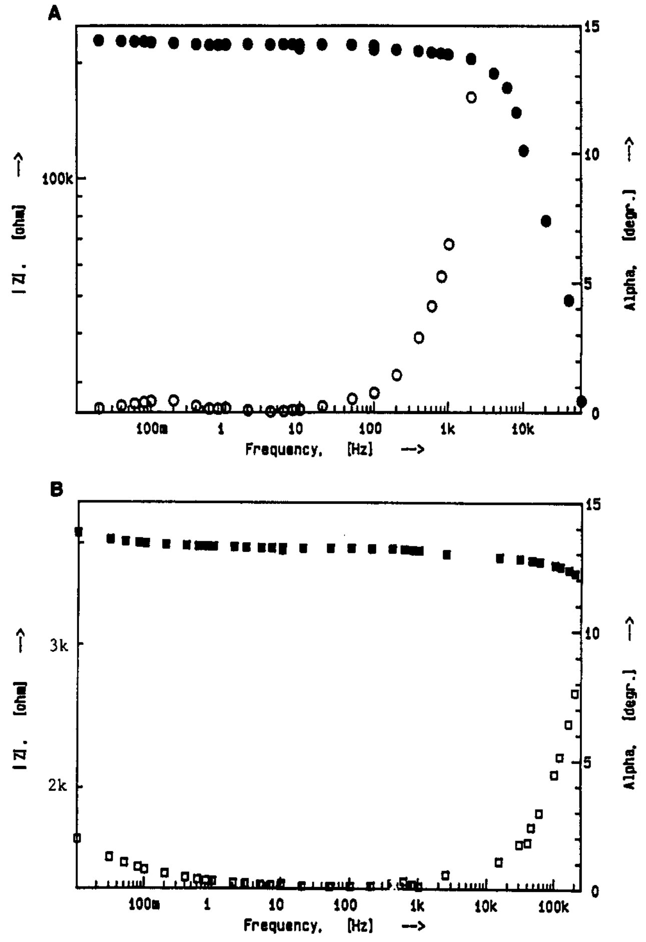

Figure 4. Bode plots for polyelectrolytes at 50 °C against Na/Hg electrodes: (A) NaAl(400), ○ = phase angle, ● = impedance; (B) NaAl(400):[2.2.2]; ☐ = phase angle, ■ = impedance.

observed that the salt $LiAl(OSi(CH_3)_3)_4$ forms complexes with PEO with conductivities greater than those observed for the analogous $LiCF_3SO_3$ complexes at 50 °C.[22] The high degree of ion pairing in the aluminate polyelectrolytes may explain the small rise in T_g as well as the low conductivity. In highly ion paired systems the strong ion–ion interactions would tend to decrease the strength of ion–dipole interactions between the salt and the polymer and thus reduce the weak cross-linking effects.

Further evidence for ion pairing in both the polyelectrolyte NaAl(400) and the salt complex $aPEO_9NaAl(OC_2H_4OCH_3)_4$ was obtained by modifying the system by the addition of a cation complexing agent. When cryptand [2.2.2], $(N\{[CH_2CH_2O]_2CH_2CH_2\}_3N)$ is added to the polymer NaAl(400) such that $[2.2.2]/Na^+ = 1$, the conductivity increases 100-fold at 40 °C. Similar increases in conductivity have been observed when cation complexing agents such as cryptands or crown ethers are added to other polyelectrolytes.[13,23] The increased conductivity is generally attributed to a decrease in ion-pairing interactions. For a different set of aPEO salt complexes we have shown that an increase in ionic conductivity with cryptand addition correlates well with increased solubility and hence decreased ion–ion interactions.[20] The conductivities of NaAl(400):[2.2.2] and $aPEO_9Na[Al(OC_2H_4OCH_3)_4]$:0.5-[2.2.2] are comparable at 50 and 80 °C. The similar conductivities of the salt complex and the polyelectrolyte even though less cryptand is added to the complex can be rationalized by the relation between the conductivity of the ith ion, σ_i, the number of carriers, n_i, their charge q_i and mobility μ_i, eq 5. Anions, cations, and charged ion aggregates contribute to the conductivity, but ion pairs do not.

$$\sigma = \sum n_i q_i \mu_2 \qquad (5)$$

(As the ionic conductivities of both the parent polyelectrolyte and the parent salt complex are very low, we can assume that the number of carriers in these materials is also small when compared to the complexes with cryptand added.) The ionic mobility should depend on the degree of polymer segmental motion and the size of the ion (larger ions move more slowly). Addition of [2.2.2] to both the polyelectrolyte and the salt complex increases the concentration of charge carriers, but for the polyelectrolyte only one charge carrier is released, the $[Na(2.2.2)]^+$ complex cation. Cryptand addition to the polymer–salt complex releases both a relatively large anion and a large cation. If we assume the number of free ions in the parent electrolytes is small compared to the number in the electrolytes with crypt added, we would expect similar conductivities for materials with the same concentration of carriers, when all the carriers are large.

The addition of cryptand does not greatly change the overall appearance of the impedance spectra of the polyelectrolytes against two different interfaces. The Bode plots (impedance and phase angle plotted as a function of frequency) for these polymers give the expected rapid rise of the phase angle at low frequency when the electrodes are blocking the cations (Figure 3). When the electrolytes

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are sandwiched between Na^+-reversible Na/Hg electrodes, the observed impedance response of the cryptand-modified electrolyte is similar to that of the parent electrolyte but shifted to higher frequency as illustrated by the Bode plots (Figure 4). The interfacial behavior of the polyelectrolyte–cryptand complex studied here against Na/Hg electrodes is in sharp contrast to the observations of Chen in our laboratory.[23] When [2.2.2] is added to a poly(phosphazenesulfonates), a small low-frequency second arc was found in the impedance spectrum. This arc was ascribed to a slow charge-transfer process between electrolyte and electrode involving the release of Na^+ from the cryptand. (No arc was observed for the cryptand-modified aluminate polyelectrolyte in the same frequency range.) Apparently the release of the cation from the cryptand is faster relative to ion migration in the aluminate networks than in the polyphosphazene sulfonates. NMR studies of Na^+ release from [2.2.2] in several solvents have shown that the rate of cation release is highly solvent dependent but does not correlate with the dielectric properties of the solvent.[24] The difference in the observed interfacial behavior for the aluminate networks and the poly(phosphazenesulfonates) may be due to the different nature of the solvent properties of the polymers or perhaps to the different concentrations of cation within the polymers. Further studies with these and related polyelectrolytes should yield insight into how the nature of the polymer affects the degree of conductivity enhancement and the interfacial kinetics when cryptands are added to polymer electrolytes.

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Interfacial Interactions of Titanium-Coated Polyester Films

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The chemical composition of the interfacial region between sputter-coated titanium metal and both plasma-pretreated and nonpretreated poly(ethylene terephthalate) (PET) film is presented. Upon application of a gaseous (nitrous oxide/argon) plasma, titanium/polyester adhesion increased dramatically following metallization compared to the nonpretreated analogue. To relate this phenomenon to a physical and/or chemical change, X-ray photoelectron spectroscopy, Auger electron spectroscopy, and transmission electron microscopy have been used to characterize both the surface and interfacial regions of these films.

Introduction

Although a number of techniques have been discovered to improve metal adhesion to plastics, two distinct methodologies have progressed and been commercially applied. The first method concerns the application of a thin polymeric coating to the polymer that acts as a binding agent between the film and subsequently vacuum sputtered metal.[1,2] The second method used to increase sputtered metal-to-polymer adhesion is to chemically modify or clean the surface of the polymer substrate prior to metal deposition.[3-5]

In the case of polyesters, a limited number of authors have described the effects of plasma processing on poly(ethylene terephthalate).[3,6] Yasuda et al. exposed PET to both argon and nitrogen plasmas.[7] Following treatment with either plasma, plasma-induced surface oxygen species were detected; however, no functional assignments were made. Dunn et al. have studied the effects of oxygen and argon plasma on the surface properties of poly(ethylene terephthalate) by both photoelectron[8] and infrared[9] spectroscopic techniques. Oxygen plasma treatment incorporated additional carbonyl functionality into the polyester; however, argon plasma treatment resulted in a decrease of both C=O and C—O. These results suggested that the surface of the PET film was oxidized by O_2 plasma treatment but carbonized by the Ar plasma.

One of the most important aftereffects of PET plasma treatment with a nitrous oxide/argon gas mixture is a substantial increase in adhesion to sputter-deposited titanium. In a previous study,[10] the chemical alterations in PET that were induced by N_2O/Ar plasma treatment prior to metallization were determined by application of a variety of analytical methods. Surface functionalization was achieved via photochemical dissociation of the ester moiety arising from short-term plasma exposure. The purpose of

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