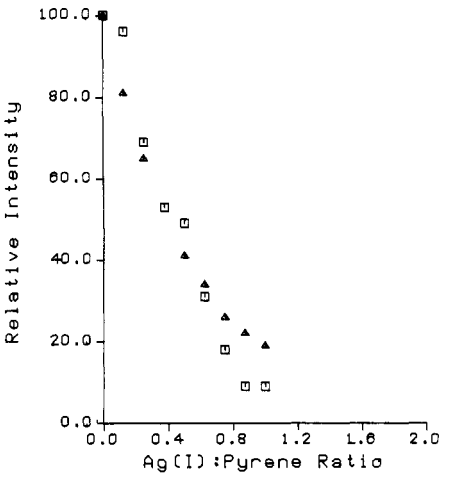

Figure 7. Intensity of emission from PySA (△) and PySA4 (□) in the presence of PEI as a function of the ratio of Ag(I) to pyrene derivative. Wavelengths are the same as indicated in the caption of Figure 5.

polymer indicate that in these systems the electrostatic component of binding is far more important. The fact that Ag(I) quenches PySA4 emission so readily indicates that there is a direct electrostatic interaction. The weak tendency of PySA to form dimers on Ag(I)–PEI indicates that the PySA tends to be in a specific site, which limits its freedom to interact with other PySA ions. In particular, the sulfonate group bearing the negative charge must position itself very close to the positive charge on the Ag(I). This effect is even greater for the protonated polymer.

Conclusions

Lipophilic interactions are much more important in the binding of PySA and PySA4 to Zn(II)- and Cu(II)–PEI than to Ag(I)–PEI and protonated PEI. Both Zn(II) and Cu(II) form strong complexes with nitrogen ligands. The coordination numbers of the complexes with the polymer are probably 6 and 4 for Zn(II) and Cu(II). As a consequence the metal ion site is surrounded by the polymer and the charge is not directly accessible to counterions. For this reason the electrostatic interaction is weak on these polyelectrolytes, leading to binding which is territorial rather than site specific.

Electrostatic interactions are more important when PySA and PySA4 associate with Ag(I)–PEI. Because the coordination number of Ag(I) is lower than for Cu(II) and Zn(II), the charge may be less effectively shielded from counterions and thus more accessible. Alternatively, because Ag(I) forms a weaker complex with PEI, the electrostatic interaction between Ag(I) and counterion may be strong enough to displace one of the bound nitrogens.

The limited degree of excimer formation when PEI is protonated indicates that in this case electrostatic interactions are dominant and the binding is site specific.

A significant result of this work is to show how one can prepare polyelectrolytes that bind territorially due to lipophilic interactions and that bind in a site-specific manner both using PEI as the base polymer. This system can thus provide a means of studying how the type of binding influences the reactivity of bound counterions.

Acknowledgment. We thank Tim Sarette for taking the ANS data. Partial support for this research was provided by NSF Grant CHE-80-25568. The spectrofluorometer used in this study was loaned to us by the U.S. Geological Survey.

Registry No. PySA, 59323-54-5; PySA4, 59572-10-0; ANS·$^1/_2$Mg, 18108-68-4.

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Physical and Spectroscopic Properties of Ternary Polymer Electrolytes Composed of Poly(vinylpyrrolidone), Poly(ethylene glycol), and Lithium Trifluoromethanesulfonate

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ABSTRACT: Poly(vinylpyrrolidone) (PVP) complexes with lithium trifluoromethanesulfonate were plasticized by poly(ethylene glycol) to give solvent-free polymer electrolytes with low glass transition temperatures (from −46 to +3 °C) and good ionic conductivities (5×10^{-5} Ω^{-1} cm^{-1} at 100 °C). The complexes were all determined to be amorphous, and they contained no excess salt over a wide range of polymer salt stoichiometries. The PVP-based electrolytes proved to be thermally stable, and separate phases did not form at 100 °C. Infrared spectroscopy of the plasticized polymer electrolytes demonstrated strong interaction between the lithium cation and the carbonyl of PVP.

Introduction

Polar polymers with low glass transition temperatures (T_g) form polymer–salt complexes that are good solvent-free polymer electrolytes.[1] The necessity of a low T_g excludes many potential polymer hosts.[2,3] For example, poly(vinylpyrrolidone) (PVP, 1) is known to complex many

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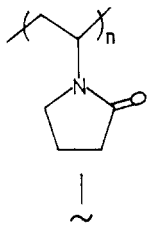
inorganic salts,[4] but the materials have high values of T_g and are poor ionic conductors. Recent work has shown that it is possible to lower T_g and hence induce high ionic conductivity in polyelectrolytes by the addition of a plasticizer.[5,6] In the present study we explored the use of poly(ethylene glycol) (PEG, **2**) to improve the conductivity of the salt complexes of a rigid polar polymer poly(vinylpyrrolidone).



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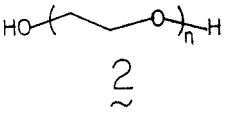

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Experimental Section

Poly(vinylpyrrolidone) (Polysciences, MW = 360 000) was dried under vacuum (ca. 10^{-2} torr) for >72 h at room temperature. The PVP contained 0.02% inorganic impurities by weight, as judged by ashing a sample of the polymer. The ac complex impedance of PVP(1.0)/PEG(2.0) indicated no conduction due to ionic impurities at the limit of our detection (ca. 10^{-9} Ω^{-1} cm^{-1}) at 100 °C. Lithium trifluoromethanesulfonate (LiTf) was prepared by neutralizing HSO_3CF_3 (Aldrich) with a LiOH (Baker) solution until a pH of ca. 7 was reached. The salt was recrystallized from a CH_3CN/C_6H_6 solution and then dried under vacuum (ca. 10^{-2} torr) for 62 h at 130 °C. The salt was determined to be anhydrous by IR. Poly(ethylene glycol) (Aldrich, average MW = 300) was used as received. Methanol (MGB, reagent grade) was dried over I_2-activated Mg and distilled under a N_2 atmosphere.

All complexes were prepared in a dry argon atmosphere to prevent contamination with H_2O. A mixture of PVP, PEG, and salt in methanol was stirred for 2–3 h until a homogeneous solution was formed. The solvent was removed under vacuum, and the complex was further dried under vacuum (ca. 10^{-2} torr) at 40–50 °C. When higher drying temperatures were employed, the complexes lost PEG. All of the complexes were stored under dry argon.

An upper limit on the water contamination was determined by an indirect IR method because the OH stretching and H_2O deformation modes are masked in the infrared spectra of these polymer electrolyte systems by the OH stretch of PEG and the carbonyl stretch of PVP, respectively. To circumvent this problem, two polymer films (0.1 mm thick, 12.7-mm diameter) were exposed to an argon atmosphere saturated with D_2O. One of the films was checked to verify the presence of D_2O by the IR absorption at ca. 2550 cm^{-1}, and the other was dried under conditions similar to those used in the preparation of the polymer complexes. The dried polymer film contained no discernable OD bands in the IR. An upper limit of 500 ppm water in the dried sample was deduced from an IR calibration on D_2O in 2-propanol.

Films of the polymer complexes for IR spectroscopy were cast from methanol solution onto Teflon plates or directly onto NaCl or Irtran I plates. The solvent was slowly removed under vacuum, and the films were further dried under conditions similar to those used in the bulk preparations. All infrared spectra were run on a Perkin-Elmer 283 dispersive infrared spectrometer.

The frequency-dependent impedance properties of the polymer complexes were measured with a Hewlett-Packard 4800A vector impedance meter (500 kHz to 5 Hz). The samples were pressed into disks for conductivity measurements at 10 000 PSI (0.5-in. die diameter), with the thickness of the pellets varying from 0.50 to 1.50 mm. The disks were loaded into a sealed conductivity cell between Pt electrodes, and the impedance response was measured from 30 to 100 °C.

All polymer complexes were checked for crystallinity by X-ray powder diffraction. The sample, in the form of a film, pressed pellet, or small pieces, was placed on an Al sample holder, and Scotch tape was used to protect the sample from atmospheric moisture.

Thermal properties of the polymer complexes were investigated with a Perkin-Elmer DSC-2 with liquid N_2 cooling. Polymer complexes were hermetically sealed in Al sample pans inside an Ar-filled glovebox. Glass transition temperatures were measured at three heating rates (10, 20, and 40 °C/min), and the T_g for the sample was determined by extrapolating to zero heating rate. The thermal stability and the crystallinity of the polymer complexes also were investigated on an optical microscope equipped with both a hot and polarizing stage. Samples were prepared in an Ar atmosphere by placing a film of the polymer complex between a microscope slide and a cover slip and sealing the assembly with epoxy cement.

Table I
DSC Data for PVP Complexes

PVP[a]	LiTf[a]	PEG[a]	$T_g \pm 2$ °C
1	0	0	180
4	1	0	199
1	1	2	3
2	1	4	−24
3	1	6	−36
4	1	8	−41
5	1	10	−46
1	0	2	−55
0	0	1	−79

[a] The numbers represent the ratios of PVP repeat units to $LiSO_3CF_3$ formula units and to PEG repeat units in each sample.

Results and Discussion

Nomenclature. The composition of the polymer complexes is specified by the ratio of PVP repeat units, the formula units of salt, and the repeat units of PEG. For example, the complex denoted as PVP(4.0)/LiTf(1.0)/PEG(8.0) consists of four repeat units of PVP, one formula unit of LiTf, and eight repeat units of PEG.

Physical Properties of the Polymer Electrolyte Materials. Table I shows the DSC data for both the pure materials and various polymer electrolytes. A single T_g was seen for all of the plasticized polymer complexes (heating from −123 to +327 °C) between the high T_g of PVP (180 °C) and the low T_g of PEG (−79 °C), which indicates a homogeneous plasticized system, at least on the macromolecular level.[7,8] Further qualitative support for the homogeneity of these polymer complexes comes from the clarity of all of the films formed from the PVP complexes.[9]

The amorphous nature of the PVP-based electrolytes is shown by the lack of melting endotherms in the DSC analysis, the lack of X-ray diffraction peaks, and the lack of birefringence by polarized optical microscopy.

The brittle PVP polymer becomes rubberlike when PEG is added to form the PVP(1.0)/PEG(2.0) matrix. In contrast, a complex formed between PVP, LiTf, and dimethyl-capped PEG forms a brittle cloudy polymer system with low ionic conductivity, which indicates the importance of the interactions between the OH groups of PEG and the host polymer to form a homogeneous system, as has been seen in other plasticized polymer electrolytes.[5,6] The polymer complexes from PVP(2.0)/LiTf(1.0)/PEG(4.0) to PVP(5.0)/LiTf(1.0)/PEG(10.0) are all elastomeric solids, and they are similar in their physical properties. A large deviation in physical properties is observed for PVP(1.0)/LiTf(1.0)/PEG(2.0), which forms a very brittle complex. As expected, these physical properties are strongly correlated with the glass transition temperatures and the ionic conductivity. Reproducibility of the temperature-dependent conductivities shows that the polymer electrolytes are thermally stable upon temperature cycling from 30 to 100 °C. Similarly, no phase separation associated with the exclusion of PEG was observed on an optical microscope up to 100 °C.

An ac complex plane analysis of the PVP complexes using Pt blocking electrodes shows the typical arc and spur corresponding to the bulk resistance and capacitance and

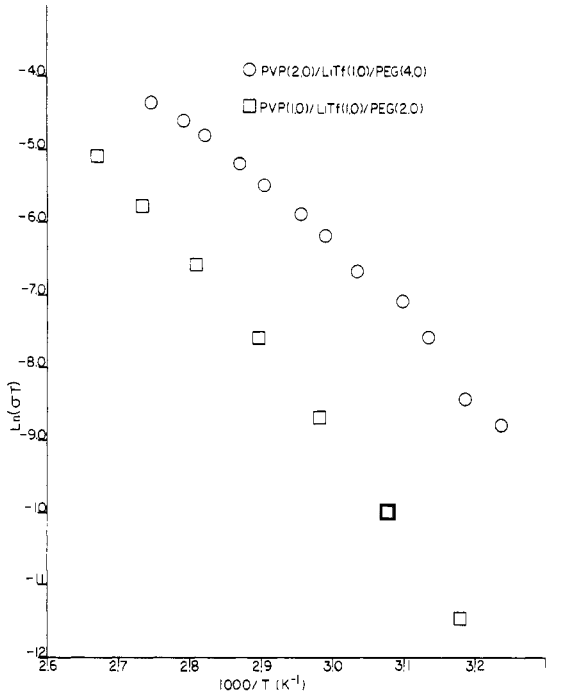


Figure 1. ln (σT) vs. $1000/T$ plot for PVP(1.0)/LiTf(1.0)/PEG(2.0) and PVP(2.0)/LiTf(1.0)/PEG(4.0).

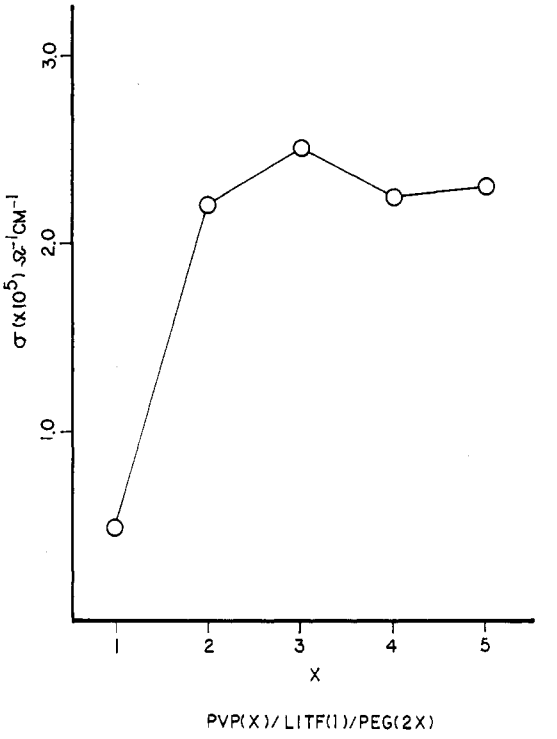


Figure 2. Plot of ionic conductivity vs. plasticized polymer complex concentrations at 80 °C.

to a double-layer capacitance of the polymer electrolyte–Pt electrode interface, respectively.[3,10,11] Attempts to employ ion-reversible Li or Li/Hg electrodes were unsuccessful, owing to the reaction of Li with the hydroxyl groups of PEG.

The concentration dependence of the conductivity data is qualitatively understandable in terms of eq 1, which is empirically observed for the transport of small molecules[12] and ions in polymers.[13] This equation may be derived

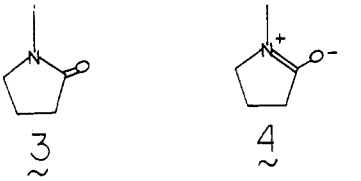
$$\sigma = AT^{-1/2} \exp[-B/(T - T_0)] \quad (1)$$

from either free-volume or excess entropy models.[14] In this equation the preexponential A term is proportional to the charge carrier concentration, the B term is a heat of transport, and T_0 is a parameter closely related to T_g. In the absence of other effects, an increase in salt concentration should increase the A term and hence the conductivity. Changes in composition of the electrolyte that increase the T_g (and therefore T_0) should decrease conductivity.

Figure 1 shows ln (σT) vs. $1/T$ plots for PVP(1.0)/LiTf(1.0)/PEG(2.0) and PVP(2.0)/LiTf(1.0)/PEG(4.0), both display curvature that is characteristic of amorphous electrolytes and the behavior indicated in eq 1.[1,2,13] Similar ln (σT) vs. $1/T$ plots are seen for the complexes ranging from PVP(2.0)/LiTf(1.0)/PEG(4.0) to PVP(5.0)/LiTf(1.0)/PEG(10.0). The conductivities of various PVP complexes at 80 °C are shown in Figure 2. The complexes from PVP(2.0)/LiTf(1.0)/PEG(4.0) to PVP(5.0)/LiTf(1.0)/PEG(10.0) have similar conductivities, which may originate from a balance between T_g and the carrier concentration. Values of low T_g are associated with materials having high segmental polymer motion and high conductivity.[1,2,15] As the salt concentration of a polymer increases, the charge carrier concentration is increased, but apparently this favorable influence on conductivity is offset by the lower polymer flexibility associated with an increased T_g. Decreasing T_g, by adding more plasticizer at a constant carrier concentration, should increase conductivity, and this is seen for PVP(4.0)/LiTf(1.0)/PEG(12.0), which has an ionic conductivity an order of magnitude higher than PVP(4.0)/LiTf(1.0)/PEG(8.0).

The complex PVP(1.0)/LiTf(1.0)/PEG(2.0) differed from the others in all of its physical properties; it forms a brittle complex with low ionic conductivity, and it has a high activation energy for ion transport. Apparently the influence of high T_g for PVP(1.0)/LiTf(1.0)/PEG(2.0) dominates over the increased carrier concentration to produce a complex with low conductivity.

Infrared Spectroscopy. Infrared spectra of PVP and its complexes were determined to clarify the nature of the interactions between polymer, salt, and plasticizer. There is abundant physical data available on amide–alkali metal interactions. Enniatin B and valinomycin, two naturally occuring polyamides, complex alkali metal salts via their carbonyl groups, as shown by X-ray single-crystal structures.[16,17] Similarly, complex formation between *N*-methyl-2-pyrrolidone, **3**, and $LiNO_3$ or $LiClO_4$ leads to



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lower carbonyl stretching frequency from 1690 to 1650 cm^{-1}, indicating that coordination occurs through the carbonyl.[16,17] These results are consistent with the greater importance of resonance structure 4 in the Li^+ complex. Solution IR and NMR studies indicate that four *N*-methyl-2-pyrrolidone molecules are coordinated to one Li cation.[19]

Table II shows the infrared data for various PVP systems. There is no significant change in the position or shape of the carbonyl peak upon addition of PEG to form PVP(1.0)/PEG(2.0), which suggests that there is no hydrogen bonding between the OH moiety and the carbonyl. The infrared band associated with the carbonyl group of PVP was observed to decrease by 20 cm^{-1} upon addition of LiTf, demonstrating that Li^+ is coordinated to the carbonyl as was described above for *N*-methyl-2-

Table II
IR Data for PVP and Its Complexes

PVP[a]	LiTf[a]	PEG[a]	$\nu_{CO} \pm 2$ cm^{-1}
1	0	0	1676
1	0	2	1677
4	1	0	1660
10	1	20	1679
7	1	14	1679
5	1	10	1664
4	1	8	1659
3	1	6	1659
2	1	4	1660
1	1	2	1658

[a] The numbers represent the ratios of PVP repeat units to $LiSO_3CF_3$ formula units and to PEG repeat units in each sample.

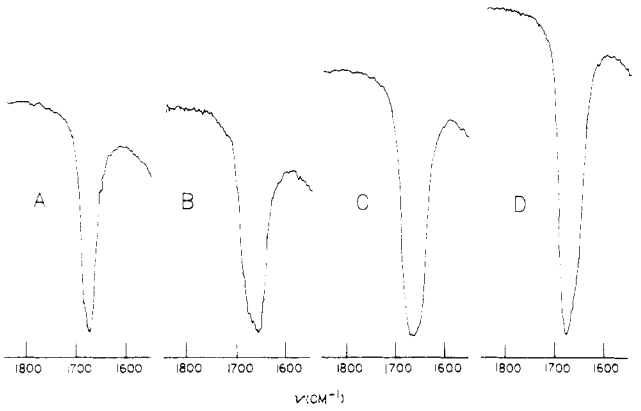

Figure 3. Infrared spectra in the carbonyl region for PVP and various plasticized polymer complexes: PVP (A); PVP(4.0)/LiTf(1.0)/PEG(8.0) (B); PVP(5.0)/LiTf(1.0)/PEG(10.0) (C); PVP(7.0)/LiTf(1.0)/PEG(14.0) (D). The varying intensities of the CO bands are due to differences in the thickness of the films used for the infrared spectra.

pyrrolidone solutions of lithium salts.

The concentration dependence of the CO stretching frequencies provides some insight into the stoichiometry of interaction. The dilute-salt complex PVP(7.0)/LiTf(1.0)/PEG(14.0) shows a low-frequency shoulder on the main carbonyl band, which is attributed to coordination of the carbonyl to Li^+. (Figure 3). Addition of more LiTf to form PVP(5.0)/LiTf(1.0)/PEG(10.0) causes the CO band to broaden and shift to lower frequencies due to the increased concentration of coordinated CO. The CO stretching band for PVP(4.0)/LiTf(1.0)/PEG(8.0) is sharp and centered at 1658 cm^{-1}, indicating that most of the CO is coordinating Li^+; in addition a high-frequency shoulder shows the presence of uncomplexed CO. All the complexes from PVP(1.0)/LiTf(1.0)/PEG(2.0) to PVP(4.0)/LiTf(1.0)/PEG(8.0) have similar CO bands, which implies that the Li cation is coordinated by four carbonyls as was seen for *N*-methyl-2-pyrrolidone.

Increasing the salt concentration beyond the PVP(4.0)/LiTf(1.0)/PEG(8.0) ratio requires PEG to coordinate excess LiTf, since all the coordination sites in PVP are filled. Therefore, infrared spectral evidence was sought for perturbation of PEG by added LiTf. A small shoulder is seen at ca. 3200 cm^{-1} on the main OH bond for all of the complexes, indicating that some of the lithium cations are coordinated to the OH moieties of PEG. In all cases the main OH stretching bond is seen at 3392 ± 5 cm^{-1}. The C–O and C–C stretching modes of PEG are good indicators of coordination of metal salts to PEG,[20] but for the PVP-based electrolytes these regions of the infrared spectrum were blocked by bands due to PVP and the triflate anion.

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