Ion Pairing and Ionic Conductivity in Amorphous Polymer Electrolytes: A Structural Investigation Employing EXAFS

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We would like to report the strong correlation between ion pairing and the bulk ionic conductivity of amorphous poly(ethylene oxide)−$CuCl_2$ polymer electrolytes, aPEO: $CuCl_2$. In addition, we have evidence to suggest that the reduction in conductivity at high salt concentrations is due to the presence of chlorde ion bridges that effectively cross-link the polymer chains. This work represents the first study of the conductivity/structure relationship in aPEO, a completely amorphous polymer at room temperature, by EXAFS[1] and the first conductivity/structure relationship study of a copper salt in any polymer electrolyte.[1k,2] There is increasing interest in the structures of polymer electrolytes since the structure of the salt in the polymer matrix is critical to the performance of the polymer electrolytes. The recent reports by Bruce et al. provide the first diffraction evidence for the structure of the polymer and salt in the crystalline polymer electrolytes $PEO_3LiCF_3SO_3$ and PEO_4MSCN (M = NH_4, K).[3] While studies of crystalline materials are instructive, ionic conductivity occurs in the amorphous phase of polymer electrolytes leading to our structural examination of amorphous polymer electrolytes.

Polymer electrolytes are composed of a salt and a polymer matrix able to solubilize the salt. Such polymer electrolytes can have significant ionic conductivities. aPEO like poly(ethylene oxide), PEO, and other polyethers are such polymers:

$$[CH_2CH_2O]_n \qquad [(CH_2CH_2O)_m CH_2O]_n$$
$$\text{PEO} \qquad\qquad \text{aPEO}$$
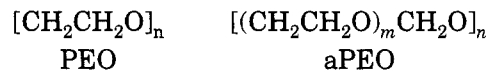
The ether oxygens in the polymer are able to dissolve the salts through Lewis base interactions with the cations. Once dissolved, the ions can move through the polymer matrix under an applied potential. The accepted mechanism of the conduction involves the ions moving from one polymer chain to another by a chain-flexing process called segmental motion.[4] For this to occur, the polymer must be amorphous. aPEO is completely amorphous at room temperature, melting at 17 °C, while PEO is 75–85% crystalline at room temperature with a melt temperature of 65 °C.[5] In addition, EXAFS measurements of salts in aPEO are not complicated by the presence of both crystalline and amorphous regions.[1b] $CuCl_2$ was chosen because copper should have a good transference number[1k] giving the resulting polymer electrolyte reasonable conductivities and the copper K-edge falls in a good energy region for EXAFS analysis. The chloride ion is a simple anion, and it is different in phase shift from oxygen so that the EXAFS can be interpreted. Better understanding of the relationship between structure and conductivity is important for the rational design of new conducting polymers with predictable properties.

aPEO was synthesized using the method of Nicholas et al.[6] and characterized by IR and NMR. From the ^1H NMR, m is 9 in this polymer. The molecular weights were determined by gel permeation chromatography relative to PEO standards and ranged from 30 000 to 110 000 g/mol giving a range in n values from 70 to 250. Vincent[7] has determined that the conductivity of the polymer electrolytes is independent of molecular weight above ∼4000 g/mol, so this range of molecular weights will not affect the results. The polymer electrolytes were prepared by codissolving appropriate amounts of anhydrous $CuCl_2$ (Aldrich, 99.999%) and aPEO in freshly distilled methanol followed by removal of solvent under vacuum. The samples were then dried under high vacuum until the residual pressure was 5×10^{-5} Torr or lower. The resulting polymer electrolytes were dark brown and quite hygroscopic, so they were handled in a Vacuum Atmospheres drybox for all further manipulations. Upon exposure to the atmosphere, they would turn a light blue, indicating the formation of the hydrated Cu^{2+} ion and providing a visible indicator of hydration. A series of five polymer electrolytes were

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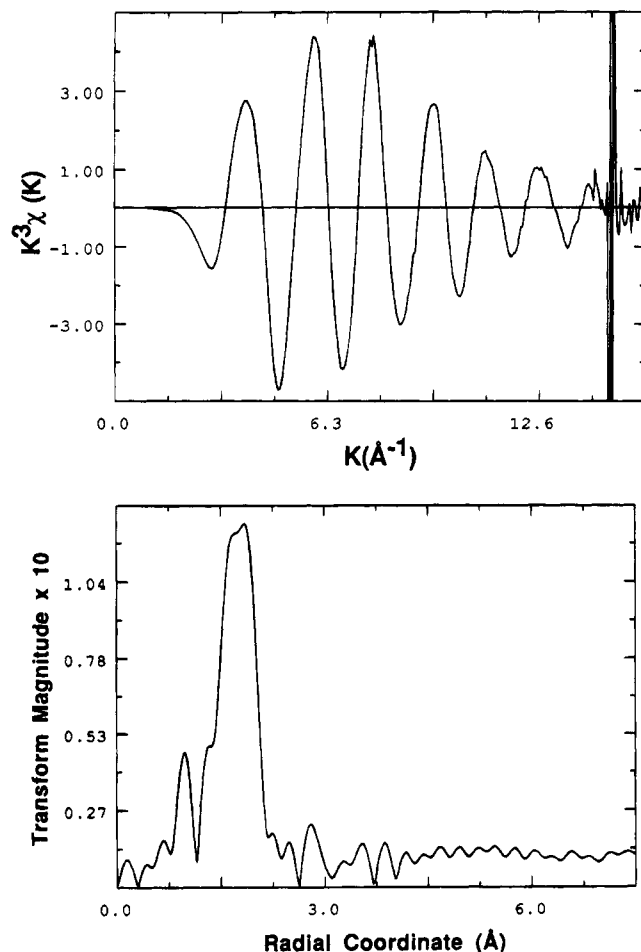
Figure 1. (a, top) Raw (after background substraction) Cu EXAFS data for (aPEO)$_8$CuCl$_2$. (The large-amplitude rise at 14.6 K is presumably due to a monochromator "crystal glitch" and is observed in all data files.) (b, bottom) Fourier transform of the Cu EXAFS for (aPEO)$_8$CuCl$_2$.

Figure 2. Correlation of copper coordination environment to the bulk ionic conductivity of the polymer electrolytes (aPEO)$_x$-CuCl$_2$ where x is the number of ether oxygens to one copper ion.

prepared: 2:1, 4:1, 8:1, 20:1, 44:1. The ratios indicate the number of polymer ether oxygens:1 copper, so the 2:1 represents the highest concentration. The conductivities were measured by impedance spectroscopy and the glass transition temperature, T_g, were determined by DSC.

EXAFS measurements were performed at the National Synchrotron Light Source (Brookhaven National Laboratory) on beamline X-9A at ~30 K.[8] The samples were sealed in Mylar sample holders with Kapton tape windows in an Ar drybox and transported to NSLS in a desiccator. The samples were quenched from room temperature to 77 K to freeze the room-temperature coordination environments and then cooled further to ~30 K to minimize thermal motion. Figure 1 shows the raw background subtracted EXAFS data and the Fourier transform of the EXAFS for the 8:1 sample. As with all the polymer electrolyte samples, two large overlap-

ping peaks were observed in the Fourier transforms. The peak corresponding to the shortest distance from the copper center is assigned to oxygen and the other to chloride backscattering. The relative heights of the two peaks changed as a function of composition, higher salt concentration resulted in a higher chlorine peak. The results of the computer fits to the EXAFS data are shown in Table 1. Phase and amplitude functions for both Cu–O and Cu–Cl backscattering were extracted from the EXAFS data from CuCl$_2$·2H$_2$O also measured at ~30 K. There are several observations that can be made based on the trends in the fit results over the series of five polymer electrolytes. First, chloride is present in the copper coordination sphere in all the complexes, demonstrating that Cu–Cl ion pairs form even in the most dilute polymer electrolyte studied. Second, the coordination number of both oxygen and chloride varies systematically over the series. Oxygen coordination increases and the chloride coordination decreases as the salt concentration decreases. A plot of the Cl/O coordination ratio and conductivity vs composition (Figure 2) demonstrates the correlation between the degree of chloride coordination to the copper cation (ion pairing) and the bulk conductivity of the polymer electrolyte. As the degree of ion pairing increases, the conductivity decreases. This same trend was observed in the aPEO:CuBr$_2$ system[9] and in PPO–NaCF$_3$SO$_3$ as determined by Raman spectroscopy.[10] EXAFS studies of Rb salts[1n] and Zn salts[1i] in PEO showed no dependence of the coordination number on composition. In the case of PEO, the pure polymer crystalline phase dissolves as the salt content increases so the composition of the conducting amorphous phase remains constant over a significant range of the overall polymer–salt composition. In our aPEO–CuCl$_2$ system, the total coordination number tends to decrease as the salt concentration decreases. The bond distances for the Cu–Cl bond are comparable to CuCl$_2$·2H$_2$O, ca. 2.275 Å;[11] however, the Cu–O bond distance is longer in all cases than in CuCl$_2$·2H$_2$O, 1.925 Å. The bond distances tend to slightly increase as the salt concentration decreased. Xu et al. observed this same trend in a different polyether by following the absorption maxi-

(8) Three to four EXAFS scans were collected for each sample over the energy range 8.700–9.975 keV, which encompasses the copper K absorption edge. The EXAFS data are analyzed using Robert Scott's XFPAK programs. All files were calibrated relative to the absorption edge for copper metal. To directly compare the different compositions, the same preedge and spline points were used except for slight variation in the first spline point which was adjusted so that the curvature of all the spline fits were similar. In addition, the FT and reverse FT regions were also very similar. The FT k space limits were 3–15.6 with a half–Gaussian of 0.1 while in the RFT fits the R-space limits were 1.37–2.15 and the half-Gaussian value was 0.08.
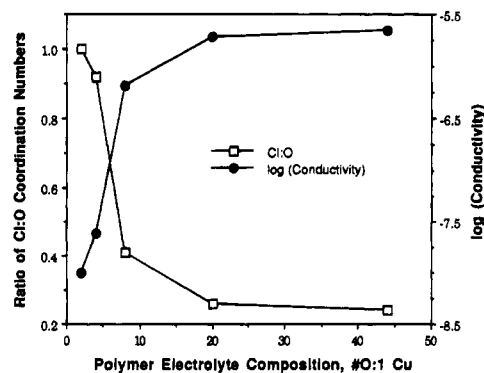
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Table 1. Fits of the Cu EXAFS Data in a PEO:CuCl₂

composition[a] shell	2:1		4:1		8:1		20:1		44:1	
	O	Cl	O	Cl	O	Cl	O	Cl	O	Cl
bond length (Å)	2.01	2.27	2.01	2.26	2.03	2.27	2.04	2.31	2.03	2.29
coordination no.	2.5	2.6	2.6	2.4	3.4	1.4	3.8	1.0	3.4	0.83
Debye–Waller factor, σ^b	0.065	0.053	0.059	0.062	0.056	0.043	0.052	0.040	0.051	0.021
ΔE^c (eV)	1.3	−0.03	0.05	−1.3	6.0	−9.1	−8.6	−18	−8.7	−15
F^d	0.026		0.021		0.007		0.16		0.023	
Cl:O^e	1.0		0.92		0.41		0.26		0.24	

^{a} The ratio refers to the number of oxygens from the polyether chain:1 copper cation. ^{b} Set to 0.05 for the CuCl₂·2H₂O model. ^{c} Energy correction. ^{d} Minimization function value or sum-of-squares-of-errors between the observed and simulated data. ^{e} Ratio of the Cl coordination number to the O coordination number.
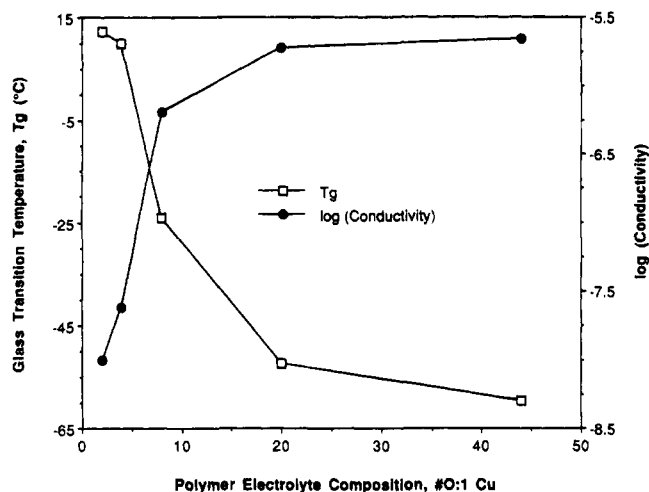

Figure 3. Comparison of T_g to the bulk ionic conductivity of the polymer electrolytes as a function of composition.

mum of lithium picrate.[12] Given the observed coordination numbers, we can postulate structures of ion aggregates in these polymer electrolytes. At low concentration a simple ion pair [Cu–Cl]⁺ is consistent with our data while at high concentration [Cu(μ-Cl)₂] networks may be forming.

T_g represents the temperature at which the polymer chains in the amorphous phase start undergoing segmental motion. Both pure high molecular weight aPEO and PEO have a T_g of −60 °C. The presence of the CuCl₂ in the polymer increases the T_g as shown in Figure 3, a plot of ionic conductivity and T_g vs composition. This plot shows that T_g varies in a similar way as the Cl/O ratio does with conductivity. In other words, as the Cu–Cl ion-pairing increases, T_g also increases,

resulting in the conductivity falling. This suggest that the chloride ions may be serving to cross-link the polymer, thus reducing the ability of the polymer chains to undergo segmental motion and therefore increasing T_g. Possibly a Cu²⁺ associated with one or two polymer chains is ion paired to another Cu²⁺ associated with other polymer chains via a chloride bridge which locks the chains together and prevents segmental motion. Interestingly, the 2:1 and 4:1 compositions have a chloride coordination number exceeding 2, which indicates that the chloride ion is associating with more then one Cu²⁺, and these complexes have much lower conductiviites than the other compositions again suggesting the formation of Cl⁻ ion bridges.

In summary, we have observed ion pairing in all of the polymer electrolytes we examined, including the very dilute polymer electrolytes using EXAFS. We have been able correlate ion pair formation with decreasing bulk ionic conductivities and increasing glass transition temperatures.

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