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Iodine L-Edge X-Ray Absorption Fine Structure Studies of Polymer- Iodide Salt Complexes

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We report measurements of extended x-ray absorption fine structure (EXAFS) and x-ray absorption near edge structure (XANES) of the L edge of iodine in the polymer electrolytes PPO_6NaI , PPO_6LiI , and $\text{PEI}_{10}\text{NaI}$. The EXAFS indicates a disordered environment for the iodine, although the PEI complex does exhibit several weak oscillations indicating a significantly less disordered environment of the anion in this complex. The XANES results suggest that the iodine is becoming more covalent in the sequence PPO_6LiI - $\text{PEI}_{10}\text{NaI}$ - PPO_6NaI , implying there are substantial interactions between the anions and cations.

INTRODUCTION

Recognition of the fact that ion transport in solid polymer electrolytes occurs primarily in the amorphous phase of a complex which may also possess a crystalline phase has led to the synthesis and study of a great number of amorphous compounds based on poly(ethylene oxide)(PEO) and its analogues.¹ Several experimental techniques such as vibrational spectroscopy,^{2,3} nuclear magnetic resonance (NMR),^{4,5} and extended x-ray absorption fine structure (EXAFS)^{6,7} have been employed to attempt to probe the structural environment of the ions within the disordered host medium. EXAFS measurements of the Rb K edge in PEO-Rb salt complexes,⁶ the Ca K edge in PEO- CaI_2 ,⁷ and the potassium K edge in PEO-KI⁸ have shown that the cations exist within a reasonably well defined oxygen coordination shell, in agreement with early x-ray diffraction studies of crystalline PEO complexes.^{9,10}

Several issues in polymer electrolyte science remain controversial. Principal among these is the widely held belief that the high salt concentrations (up to 4 M) in these materials must lead to substantial

cation-anion interactions, perhaps resulting in the existence of ion pairs or higher multiplets within the complex. With regard to structure and dynamics, considerably less attention has been given to the anions than the cations in polymer electrolytes. This is perhaps surprising in view of the fact that transport number measurements often show that the anionic contribution to the total ionic conductivity can be substantial.¹

In order to study the structural and chemical environments of the anions, we have performed both EXAFS and X-ray absorption near edge structure (XANES) measurements on the iodine L_1 , L_2 , and L_3 edges in poly(propylene oxide)(PPO) complexed with NaI and LiI, and poly(ethyleneimine) (PEI) complexed with NaI. The XANES technique provides information on bond energies through analysis of the position and shape of the absorption spectrum. The L_1 -edge shape is determined by transitions from the 2S core level state to final states of p symmetry with respect to the absorbing atom, while the L_2 ($2p_{1/2}$) and L_3 ($2p_{3/2}$) edges arise from transitions to d -like final states.

EXPERIMENTAL

The starting material for the PPO complexes was PAREL-58 Elastomer (Hercules, Inc.) which is a sulfur-vulcanizable copolymer of PPO and allyl glycidyl ether containing about 95% PPO. The PAREL was then dissolved in methanol and mixed with either NaI or LiI in the ratio of eight oxygens per metal cation. The viscous solutions were poured into teflon molds and placed in a (roughing) vacuum oven at 80°C for 60 hours. The resulting homogeneous films of about 0.5 mm thickness were mounted in metal sample holders sandwiched between two layers of Kapton tape. The mounting procedure was performed in a nitrogen glove bag, and the samples were kept in a dessicator immediately prior to the x-ray measurements, which in turn were taken under flowing helium conditions. The PEI complex ($\text{PEI}_{10}\text{NaI}$) was prepared at the National Bureau of Standards.

X-ray absorption spectra were measured in transmission at both the National Synchrotron Light Source at Brookhaven National Laboratory and at the Cornell High Energy Synchrotron Source at Cornell University. At the NSLS, beam line X23B of the Naval Research Laboratory was used; this is a focussed line with a separated Si(111) crystal monochromator and about 3 eV resolution at the iodine L edge. After appropriate calibration, shifts in absorption edges can be monitored with about 0.5 eV resolution. At CHESS, beam line C1,

which employs a similar monochromator, operated with comparable resolution. The absorption coefficient was taken as the log of the ratio of the measured incident flux to the transmitted flux.

RESULTS AND DISCUSSION

Figure 1(a) shows EXAFS data $[X(k)]$ in the vicinity of the L_3 absorption edge of iodine in the complexes PPO_8LiI , PPO_8NaI , and $\text{PEI}_{10}\text{NaI}$. A smooth background has been subtracted from the data

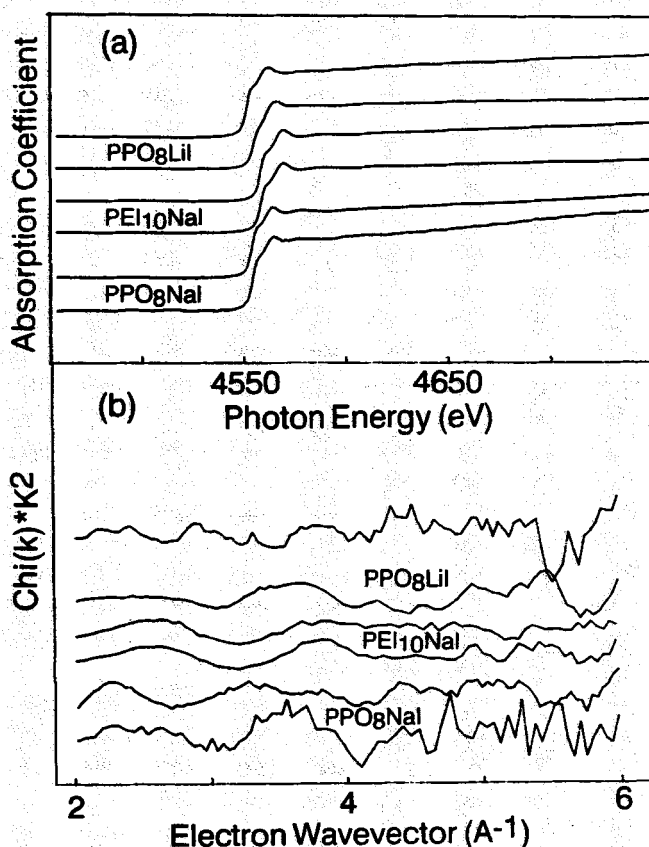


FIGURE 1 (a) X-ray absorption structure in vicinity of the L_{III} edge of I in several ion conducting polymers as indicated. Two spectra are shown for each material. (b) The EXAFS extracted from the spectra in (a) by fitting a smooth background, converting to k , the outgoing electron wavevector, and weighting by k^2 . Only in the $\text{PEI}_{10}\text{NaI}$ is there evidence of significant EXAFS.

and it is normalized to unit edge jump, in accord with conventional practice in EXAFS analysis.¹¹ The quantity $k^2 X(k)$, where k is the wavevector of the outgoing photoelectron, is plotted in Figure 1(b). It is immediately evident that there are few well defined EXAFS oscillations, suggesting an appreciable lack of order in the vicinity of the iodine atom, particularly for the PPO complexes. The $\text{PEI}_{10}\text{NaI}$ does, however, exhibit several weak EXAFS oscillations which implies that the iodine may be somewhat more ordered in this complex. An earlier study by Chiang and co-workers of PEI complexes¹² suggested that $\text{PEI}_{10}\text{NaI}$, which did not show powder x-ray diffraction peaks, did in fact exhibit DSC and conductivity features associated with the presence of a crystalline phase. Therefore it is not surprising that the iodine EXAFS in the PEI complex contains some structure, in contrast to the fully amorphous PPO complexes. However, even in the most favorable case, $\text{PEI}_{10}\text{NaI}$, there is evidently very little order in the vicinity of the iodine. In sharp contrast to the cation EXAFS studies mentioned above, the anion is clearly in a highly disordered environment.

The near edge absorption (XANES) spectra potentially contain much chemical information as they are very sensitive to the details of the local band structure. However, these spectra are difficult to calculate from first principles and interpretation in terms of a particular (unique) chemical bonding arrangement is usually problematic. Therefore it is advantageous instead to measure a series of simple compounds in which a particular parameter such as bond ionicity can be systematically varied. In Figure 2 we display the near edge spectra (the L_1 , L_2 , and L_3 edges respectively in (a), (b), and (c)) of such a series, namely I_2 , CuI , MgI_2 , and NaI , arranged top to bottom in order of increasing I-ionicity. From these results there is evidently a total shift in core level binding energies of about 8 eV from the most ionic (NaI) to the least ionic (I_2) compound. The L_1 results in Figure 2(b) are slightly complicated by the presence of a strong excitonic feature in the I_2 spectrum just below the edge.

Using these spectra as standards, we display in Figure 3 the iodine L_1 and L_3 edges as measured in the polymer complexes PPO_8LiI , $\text{PEI}_{10}\text{NaI}$, and PPO_8NaI . The polymer spectra are bracketed by the corresponding spectra for I_2 and MgI_2 replotted from Figure 2. The polymers exhibit a shift to higher binding energies in the sequence PPO_8LiI – $\text{PEI}_{10}\text{NaI}$ – PPO_8NaI , the total shift being about 3 eV. This result implies that the iodine is becoming more covalent (or less ionic) in the same sequence, assuming that bond length variations among

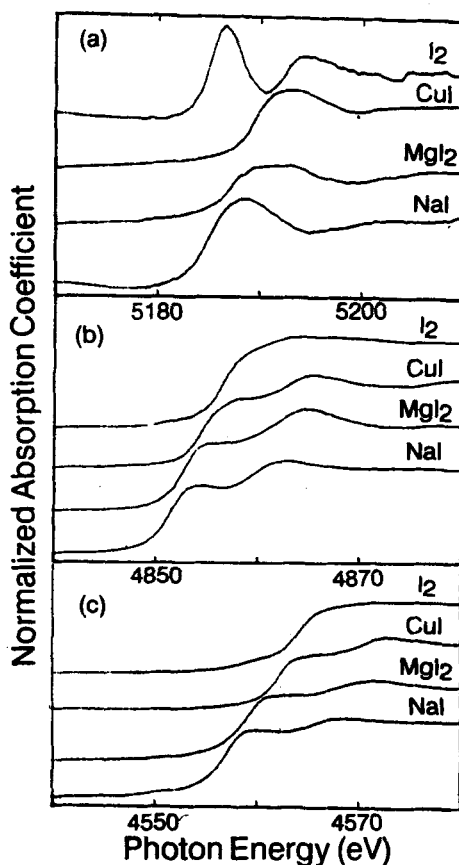


FIGURE 2 High resolution plot of the near edge absorption spectra of several I-based compounds in order of increasing bond ionicity from top to bottom: (a) L_1 edge; note the shakeup feature in the I_2 spectrum; (b) L_2 edge; (c) L_3 edge. The edge consistently shifts to lower binding energy by about 8 eV (total range) as increasing ionicity increases the charge at the I site.

the compounds are not sufficiently great to complicate this simple interpretation.

Two important conclusions can be drawn from the above XANES data. The first is that the near edge peak position is clearly quite sensitive to details of the local environment, displaying large energy shifts and thus offering a powerful means of probing the chemical environment of the anions in polymer electrolytes. This is particularly attractive as the near-edge data is relatively easy to measure precisely.

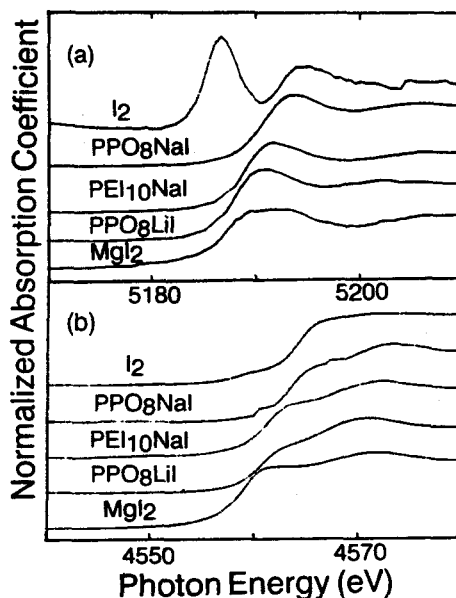


FIGURE 3 The near edge x-ray absorption spectrum of the polymer complexes of Figure 1 compared to appropriate reference compounds extracted from Figure 2.

The second conclusion, which is somewhat tentative due to the limited number of samples, is that the iodine core levels in the complexes seem to be determined to a greater extent by the cationic species than by the host polymer, as indicated by the observation that the I edge in PPO₈NaI is closer to I in PEI₁₀NaI than it is to I in PPO₈LiI. This result implies a significant degree of interaction between the cations and anions in the polymer complexes, a result perhaps to be expected from the relatively high salt concentration in these materials. These measurements are currently being extended to other PPO-iodide complexes as well as corresponding PEO-based materials.

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