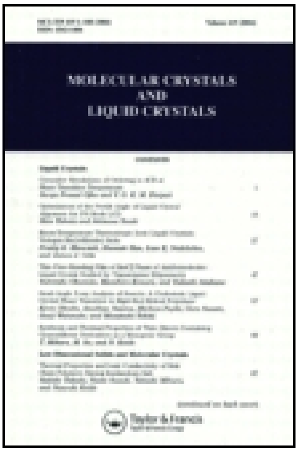

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Structure and Phase Transitions in PEO-KI Complexes

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INTRODUCTION

In the 1970's Wright[1,2] and later Armand *et al.*[3] suggested that poly(ethylene oxide) (PEO) complexed with alkali metal salts could be used as thin film polymeric solid electrolytes. Since this original work we have witnessed a rapid expansion of research and development of this class of conducting polymers.

The original impetus derived from the potential for developing high energy density rechargeable thin film lithium batteries. This was followed by other applications, notably to photoelectrochemical (4) and electrochromic (5) devices where easy-to-prepare large area thin film solid electrolytes with good adhesive properties was desirable.

PEO based electrolytes have high solvating power and very broad redox stability windows with salts like $LiClO_4$ and $LiCF_3SO_3$. The stability of the ether functions and compatibility with lithium electrodes make PEO complexes excellent electrolytes for fabrication of rechargeable lithium batteries. They are also the polymer electrolytes with the highest conductivity at elevated temperatures (> ~80°C).

At lower temperatures, below ~60°C, the tendency of PEO-salt complexes to form crystalline complexes leads to a drastic reduction in ion conductivity due to an almost complete disappearance of the conducting elastomeric phases. The room temperature conductivities are therefore generally in the 10^{-7}–10^{-8} S cm^{-1} range or lower.

The polymer and the salt form a solid solution where the salt is dissolved by the cation complexation by the lone pair electrons of the oxygen heteroatoms. The PEO chain $(CH_2—CH_2—O)_n$ contains a high density of donor heteroatoms and a sufficiently long hydrocarbon segment to allow cation solvation by a "cage" effect where the donor electron doublets of the oxygen are directed inwardly (see Figure 1). This solvation mechanism is reminiscent of that of the well known crown ethers. Unlike crown ethers, however, the cage size formed by the PEO chain can be adjusted to the size of the cation by taking advantage of the high degree of flexibility of the chain.

The solvation mechanism is both intra- and intermolecular and is reversible, a flexibility which allows the presence of ion pairs or multiplets and complex ions. This reversibility and conformational flexibility allows the ions to migrate from one solvating site to another, resulting in ion conductivity.

There are two major competing phenomena which determine the formation of polymer-salt complexes. On the one hand, there is the solvating power of the polymer which involves the density of donor heteroatoms and chain flexibility. The oxygens of the ether function carry the donor electrons and is a strong Lewis base, the complex formation being governed by Lewis acid-base interactions.

Opposing the salt dissolution is the lattic energy or cohesive energy density of the salt.[6] In the case of salts with very high lattic energies no complex formation is observed. However, the threshold for complexation is dependent on the cation used because different cations have different polarizing power.

The original picture of ionic conduction in PEO consisted of cation hopping within the helical PEO structure,[3] a conductivity mechanism

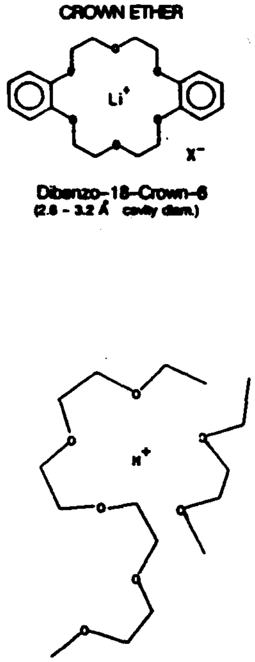

FIGURE 1 Complexation of cations by a crown ether and poly(ethylene oxide).

reminiscent of the hopping mechanism associated with ion conduction in inorganic media. Later, more detailed, studies of PEO-salt complexes demonstrated that the ionic conductivity is associated with the amorphous elastomeric phase.[7–11] In particular, NMR studies[7] showed conclusively that the elastomeric phase dominates in the ionic conduction even if the material is predominantly crystalline as PEO-salt complexes are near room temperature.

This suggests that the ion transport properties of the polymer-salt complex are strongly dependent on the freedom of movement and rearrangement of the polymer chain. This is described by the free-volume theory (VTF) equation which gives an expression for the conductivity:

$$\sigma = AT^{-1/2} \exp\left[-E_a/(T - T_o)\right]$$

where E_a is a pseudo activation energy, T_o is related to the experimentally measured glass transition temperature, T_g, by a constant, and A is proportional to the carrier concentration.

This relationship generally describes the behavior of amorphous polymers. Polymers with a high degree of crystallinity have temperature dependent conductivities which more often follow Arrhenius type behavior. The conductivities of polymers with a high degree of crystallinity are generally substantially lower than those of amorphous materials.

A third type of observed electrolyte behavior consists of a combination of the first two, with Arrhenius type behavior below a transition temperature and VTF type behavior for higher values. The VTF relationship between the conductivity and the glass transition temperature suggests that high room temperature ionic conductivity would be associated with a low T_g and the prevention of crystallinity.

It is now generally accepted that PEO electrolytes are not single-phase homogeneous materials in the ranges of composition and temperature of interest for batteries and other low temperature devices. The polymer-salt mixtures often contain multiple phases: normal PEO crystallites; one or more PEO-salt crystalline complexes; and one or more amorphous phases containing dissolved salt. A number of studies have suggested that the amorphous, or liquid-like domains dominate conductivity.[7–10] However, detailed studies of the liquid-like domains are rendered difficult because of the simultaneous presence of crystalline regions.

There has been a number of recent studies using binary phase diagrams to describe the interactions between PEO and various salts.[7–10] The binary phase diagrams can sometimes reveal the presence of more than one definite compound with well defined stoichiometries. They also offer an explanation for the shape of the DSC curves.

The relationship between the phase diagrams and conductivity is highly complex and no straightforward explanation in terms of volume fraction of the coexisting phases can be given. The anion plays an important role and can account for many of the observable differences.

This paper concerns a study of complexes formed from solid solutions of PEO and KI. Measurements of ac conductivity, DSC and x-ray diffraction were made and the results are correlated with microscopic structural information obtained by x-ray absorption near edge structure (XANES) experiments at the National Synchrotron Light Source (NSLS). KI was chosen as the complexing salt because the core level absorption of potassium is accessible with the present beamlines at the NSLS. Iodide gives strong backscattering, which makes the results less ambiguous.

RESULTS AND DISCUSSION

Sample preparation

The polymer electrolytes were prepared from PEO having an average molecular weight of 900,000 (Aldrich). Stoichiometric quantities of KI salt and PEO were dissolved in acetonitile. The salt concentrations studied were in the range $4 < 0/M < 20$ and designated as $PEO_n \cdot KI$ for $O/M = n$. The sample films were solution cast and dried at 70°C under dynamic vacuum for 24 h. The mounting of the samples in the conductivity measurement cell was carried out in a glove box. The thin films (1–10 μm) used for x-ray absorption experiments were heated additionally to 100°C in a helium atmosphere for ~2 h immediately prior to the experiment.

Experimental

Ac conductivity measurements with stainless steel electrodes were taken with a Hewlett-Packard 4192A Impedance Analyzer in the frequency range from 5 Hz to 13 MHz. Differential Scanning Calorimetry (DSC) measurements were performed using a DuPont 1090 Thermal Analyzer equipped with a 910 Differential Scanning Calorimeter at a heating rate of 20°C/min under nitrogen atmosphere. X-ray diffraction experiments were carried out using a Philips XRG3100 x-ray diffractometer, with CuK_α radiation and x-ray absorption were performed at beamline X-23A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory.

Thermodynamic properties

Figure 2 shows DSC thermograms of two samples, one untreated sample and one sample annealed at 100°C after solution casting, which corresponds to the treatment of the x-ray absorption samples. In the annealed sample the low temperature melting peak corresponding to melting of pure PEO is absent, indicative of a fully complexed material. The broad endothermic feature corresponds to the melting of the complex. The absence of a sharp melting point indicates that the complex is basically amorphous.

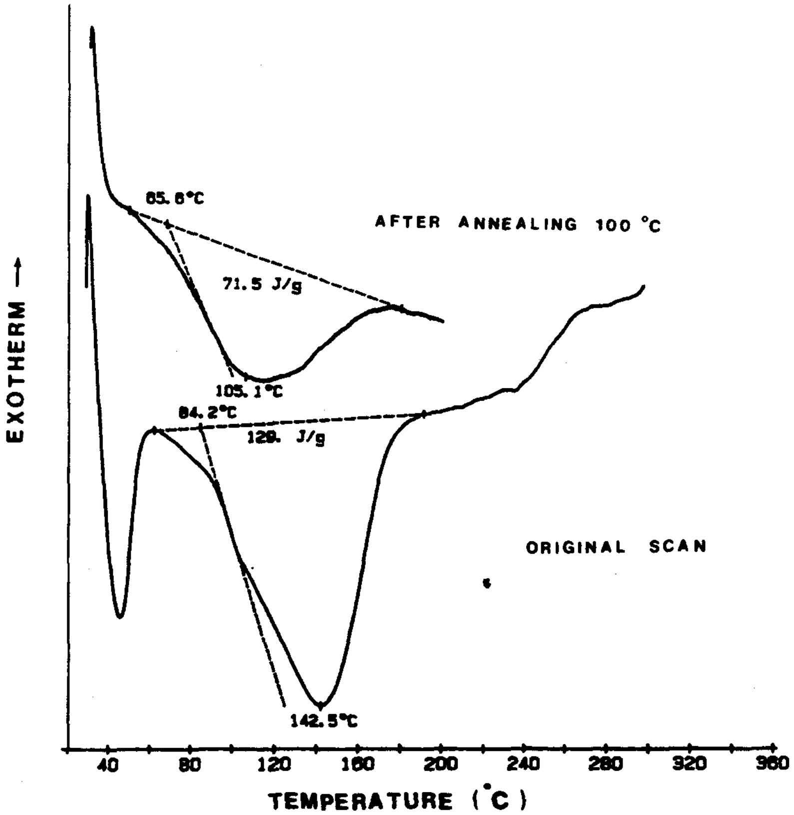

FIGURE 2 DSC thermograms of two samples of PEO_8-KI. The bottom scan is for a sample solution cast at room temperature from acetonitile. The top scan corresponds to a sample which had been annealed at 100°C.

X-ray diffraction

As can be seen from Figure 3, the x-ray diffraction patterns of annealed PEO-KI complexes have no peaks in the range of concentrations we consider. Neither pure PEO nor pure KI salt can be detected in the PEO_8-KI complex. This indicates that the complex is amorphous, supporting the conclusions of the DSC measurements.

ac Conductivity

The conductivity as a function of temperature for three different concentrations of KI salt is shown in Figure 4. Two general conducting regimes can be distinguished with the transition around 60–80°C

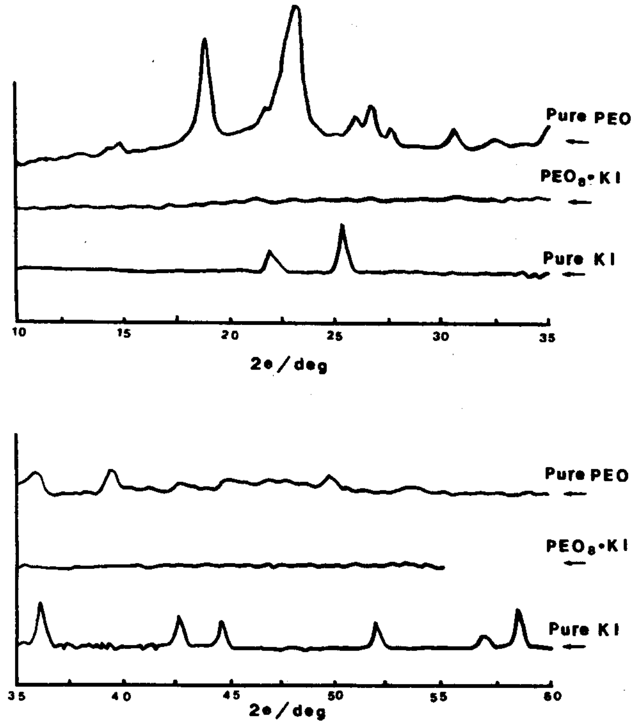

FIGURE 3 X-ray diffraction patterns of pure PEO, annealed $PEO_8 \cdot KI$, and pure KI salt.

corresponding to the onset of the broad endothermic feature in Figure 2. This is most pronounced in the most dilute sample with 0/M = 20. The curvature observed in the conductivity plots at all concentrations suggests that the mechanism of conduction can best be described with a free volume theory (VTF), in which the transport of carriers cooperates with the segmental motion of the host polymer in an amorphous phase.

X-ray absorption near edge structure (XANES)

X-ray absorption techniques using synchrotron radiation have unique advantages for studying amorphous materials since they probe the local environment of a particular atom type, and the material, therefore, does not need to be crystalline.

The Extended X-ray Absorption Fine Structure (EXAFS) technique takes advantage of the fact that the oscillations observed on the high energy side of absorption edges in the x-ray absorption

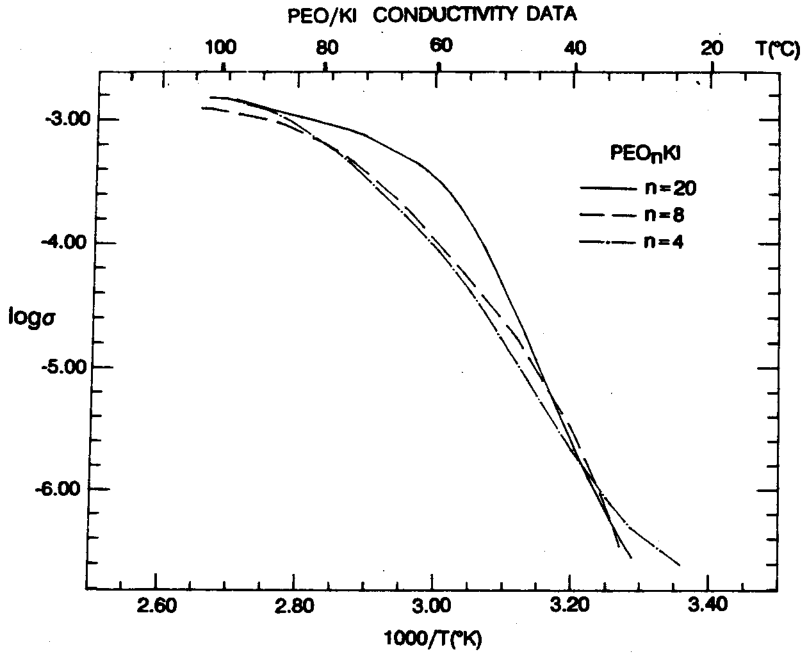

FIGURE 4 Ac conductivity of PEO$_n$-KI complexes for n = 4, 8, 20.

spectra of condensed materials are a function of the distance from, and number and type of atoms surrounding the atom undergoing the x-ray transition. In the EXAFS regime, beyond 30–40 eV from the absorption edge, it is assumed that only single scattering of the photoelectron occurs. This assumption makes it possible to analyze the data with a relatively simple mathematical treatment.[12] However, in the near-edge, or low energy, region of the spectrum the full series of structures extending over a ~30–40 eV energy range and defined as XANES are directly determined by the local structure.[12,13]

The XANES peaks have been identified as multiple scattering resonances of the excited photoelectron scattered by neighboring atoms in the continuum part of the spectrum. The multiple scattering nature gives XANES the potential for determining local geometry of atomic arrangements giving unique information complementary to EXAFS in complex systems.

The information on stereochemical details contained in XANES spectra (coordination geometry and bond angles) are particularly important for complex systems, like most polymeric systems, which are generally characterized by weak order and low symmetry.

The multiple scattering nature of XANES poses a formidable challenge to formulating a coherent mathematical treatment, which generally are practical only in highly symmetric systems. However, even in the absence of a detailed mathematical analysis, the spectral features can be used to fingerprint unknown sites from spectra of model compounds of known chemical structure.[14]

Figure 5 shows XANES spectra for three model coupounds in which the K^+ ion is coordinated with 1, 2, and 6 oxygen atoms, respectively. Immediately apparent in this figure is a monotonic change in the relative peak heights at the edge as the coordination number decreases.

A similar trend can be observed in the spectra of PEO-KI complexes as the temperature is increased. Figure 6 shows the data for PEO_4-KI as the temperature is increased from room temperature to 100°C. At 60–70°C a spectral change can be observed. Comparing this transition with the spectra of Figure 5, we see that the spectral change corresponds to decreasing the coordination number of the K^+ ion as the temperature increases. This coordination number decrease means that the K^+ ion will be less strongly bound to the host polymer chain and become increasingly mobile. This transition corresponds to that observed in the DSC and conductivity measurements.

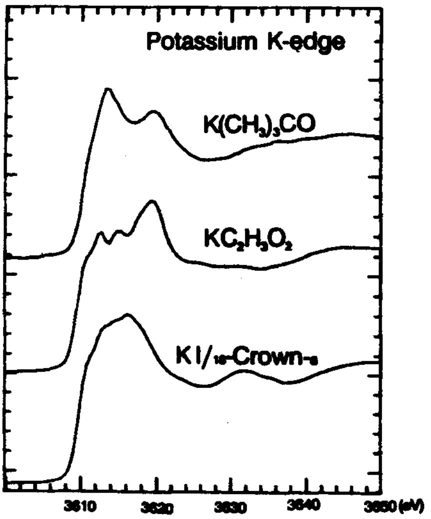

FIGURE 5 Potassium K-edge XANES spectra of model compounds where the K^+ ion is coordinated with 1, 2, and 6 oxygen atoms.

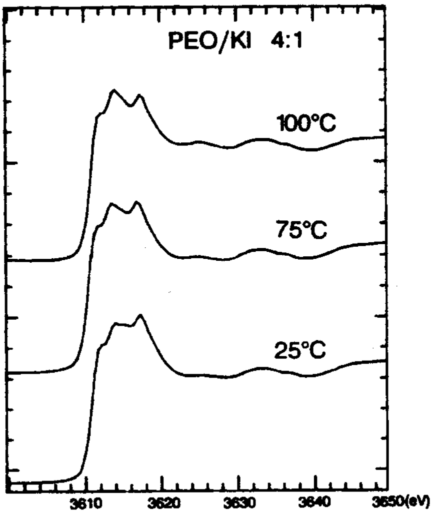

FIGURE 6 Potassium K-edge XANES spectra of PEO_4·KI as a function of temperature.

Conclusions

It is generally accepted that PEO electrolytes are not single-phase, homogeneous materials in the ranges of composition and temperature of interest for batteries and other low temperature electrochemical devices. The polymer-salt mixtures often contain multiple phases, which makes detailed analysis of structure and transport properties difficult.

In this paper we have shown that x-ray absorption experiments can be used to study the microscopic structural parameters of these materials, and that microstructural information thus obtained can be correlated with macroscopic thermodynamic and transport data.

The conclusion we can draw from our studies of PEO·KI complexes is that the transition to a higher conductivity phase at elevated temperatures is associated with a decreasing oxygen coordination number of the K^+ ion. However, the complexity of this class of materials and the differences between various polymer-salt combinations which have been observed in the macroscopic parameters, make it difficult to draw conclusions about the relationship between coordination numbers and transport properties which can be generalized to other polymer-salt systems.

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