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Structural Conformation in a Poly(ethylene oxide) Film Determined by X-ray Emission Spectroscopy

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The electronic structure of poly(ethylene oxide) (PEO) in a thin ($<1\ \mu$) film sample was experimentally probed by X-ray emission spectroscopy. Both nonresonant and resonant X-ray emission spectra were simulated by using density functional theory (DFT) applied to four different models representing different conformations in the polymer. Calculated spectra were compared with experimental results for the PEO film. It was found that the best fit was obtained with the polymer conformation in PEO electrolytes from which the salt (LiMF_6 , $M = \text{P, As, or Sb}$) had been removed. This conformation is different from the crystalline bulk polymer and implies that film casting, commonly used to form electrolytes for Li polymer batteries, induces the same conformation in the polymer not depending upon the presence of salt.

Introduction

Much attention has been paid to solid electrolytes during the past several decades due to their important ionic conducting roles in electrochemical devices such as high-energy density batteries, fuel cells, and other electrochemical devices. One of the most studied solid electrolytes is polyethylene oxide (PEO)/alkali metal salt electrolyte, in which ion–polymer and ion–ion interactions play an important role in the ion transport mechanism.^{1,2} Cation–polymer interactions in PEO electrolytes have been the subject of numerous theoretical studies.^{3–10} The polymer conformation and its relation to the electronic structure are particularly relevant for understanding the mechanism of ionic conduction in polymer electrolytes. Many polymer electrolytes have been studied and their physical properties, such as ionic conductivity, have been obtained. Nevertheless, there is a lack of information about their microscopic structure. One of the crucial issues is that the quality of diffraction data obtained from polymer electrolytes is often not satisfactory. Thus, new techniques are called to use in addition to modern methods of X-ray diffraction (XRD), e.g., as developed recently by Andreev et al.¹¹ to provide insight into the polymer structure.

In this study, we apply X-ray emission spectroscopy (XES) to probe the electronic structure of polymer that is analyzed using modern quantum theory to obtain the molecular structure, i.e., polymer conformation. XES is element specific and sensitive to local electronic structure. Unlike photoelectron

spectroscopy, another powerful probe of electronic structure, sample charging is not a problem in XES based on the photon-in and photon-out scheme that can be applied to both conducting and insulating samples. The nonresonant emission, originating from a valence electron transition to a vacant core-hole, follows the dipole selection rule, and thus is a direct measure of the occupied partial density of states (DOS) localized to the selected atomic site. Resonant X-ray emission occurs as a result of the decay from a core excited state where a core electron is selectively excited to an unoccupied molecular orbital, i.e., the lowest unoccupied molecular orbital (LUMO), LUMO+1, etc. Such a technique has recently been used to elucidate the nature of hydrogen bonding in water^{12,13} and alcohol–water mixtures.^{14,15} The local electronic structure and associated chemical bonding in conjugated polymers have been investigated in detail by X-ray absorption and emission spectroscopy.^{16,17}

Previously,¹⁸ we used XES to determine the conformations of PEO in its powder form with a molecular weight of 600 000. From the differential scanning calorimeter measurements, the sample was characterized to have a fraction of 50% crystalline. XES spectra were simulated by using density functional theory (DFT) from four different conformations of the sequence of $(\text{CH}_2\text{CH}_2\text{O})$ units, including the classical helix structure proposed by Takahashi and Tadokoro from XRD.¹⁹ None of the single conformations fit the experimental data, and the best fit was the mixtures of two conformations. We found that a thin PEO film spin casting from this bulk polymer produced a narrower spectral profile with more resolved fine spectral features. We hypothesized that the PEO film is more in a single phase than the bulk polymer and thus has an electronic structure simulated from a single conformation.

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Experimental and Computational Methods

Commercial PEO powder with an average molecular weight of ca. 600 000 (Aldrich) was purified to remove inhibitor and silicates (SiO_2). The PEO was first vacuum dried. The dried powder was dissolved in acetonitrile (CH_3CN) completely, followed by passing molecular sieve before being spin-coated onto the Si wafer. The solvent was allowed to evaporate slowly under vacuum at room temperature for 3 days. The thickness of the PEO thin film thus formed was 260 nm. The film thickness was measured by a Tencor P10 profilometer. The as-cast film was dynamically pumped under vacuum at ambient temperature for 72 h. The infrared spectra obtained from the prepared film indicated that it was free of water and CH_3CN . The prepared sample was stored in a He-filled glove box for three weeks to allow the film to reach an equilibrium conformation. The samples were then transferred into a UHV chamber at a base pressure of 1×10^{-9} Torr through an inert atmosphere of Ar loadlock. The X-ray emission spectra were acquired at beamline 7.0.1.1 of the Advanced Light Source, using a high-efficiency grazing incidence X-ray spectrometer.²¹ The combined monochromator and spectrometer energy resolution was estimated to be 0.3 and 0.5 eV for carbon and oxygen K-edges, respectively. The nonresonant C K-emission was recorded at a photon excitation energy of 320 eV while resonant C K-emission was recorded at an excitation energy of 285.2 eV. The corresponding O K-emission spectra were excited at photon energies of 573.3 and 532.0 eV, respectively.

The theoretical framework for simulation of X-ray emission processes was described in the literature.^{22,23} The relative probability of the nonresonant emission process for arbitrarily oriented sample was computed within the dipole approximation by considering one-electron transitions between occupied orbital and core-hole. Resonant X-ray emission spectra were simulated by using Kramers–Heisenberg resonant scattering theory. Regarding the “final state rule” that accurate X-ray emission spectra can be obtained by considering only final state wave functions of the process, our calculations were performed assuming the ground state as the final state of the resonant X-ray emission without including core-hole relaxation effects. Simulated spectra represent intensity only from electron transitions and do not include any additional effect that could be present in experimental X-ray emission data, e.g., self-absorption and diffusion scattering. Resonant X-ray emission spectra were calculated only from electron transitions to the lowest unoccupied molecular orbital (LUMO). The calculations were carried out within the framework of Density Functional Theory (DFT) at the hybrid B3LYP functional level^{24,25} with the DALTON program.²⁶ The excited atomic site is represented by Sadlej basis set²⁷ while the rest of the atoms in the molecules are represented by the 6-31G basis. To facilitate comparison with experimental spectra, the calculated emission assumed a Lorentzian profile with full width at half-maximum (FWHM) of 0.5 eV for nonresonant XES and 0.3 eV for resonant XES, respectively. The energy scale of the simulated emission spectra was contracted by a factor of 1.3.²⁸

Results and Discussions

The polymer chain in PEO is composed of a sequence of $(\text{CH}_2\text{CH}_2\text{O})$ units; the conformations about the successive OCCO, CCOC, and COCC segments are defined to be trans (T) if the dihedral angle between the four atoms is zero (the atoms are coplanar) and to be gauche (G) if the dihedral angle is nonzero. According to the rotation direction, the gauche can be labeled G+ or G−. The X-ray diffraction analysis by

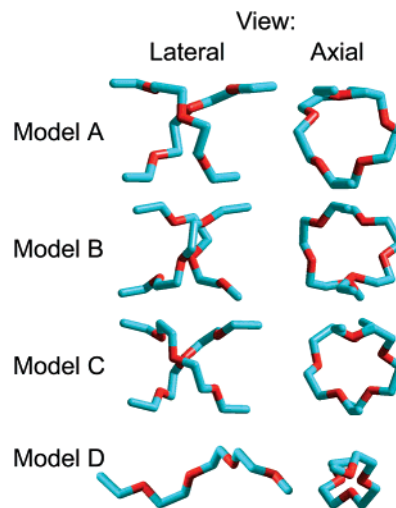


Figure 1. Models of the polymer chains: Model A, from $(\text{PEO})_6\text{:LiPF}_6$; Model B, from $(\text{PEO})_6\text{:LiSbF}_6$; Model C, from $(\text{PEO})_6\text{:LiAsF}_6$; and Model D, classical helix for $(\text{CH}_2\text{CH}_2\text{O})$ units in PEO.

Tadokoro²⁹ showed that the PEO uniform helix structure is slightly distorted with respect to the D7 point group and the monomeric units are repeated seven times in two complete turns of the helix and repeated in T2G sequences. We now refer to this model as Model D (the single helix) and the structure is illustrated in Figure 1.

We consider three different models of the polymer chains. These models are constructed from the structure in $(\text{PEO})_6\text{:LiAsF}_6$, $(\text{PEO})_6\text{:LiPF}_6$, and $(\text{PEO})_6\text{:LiSbF}_6$ polymer-salt complexes, i.e., electrolytes, which have been solved ab initio from X-ray diffraction data.³⁰ We have chosen these structures among a variety of PEO–salt complexes because the conformation of PEO chains, within the crystal unit cell for these three models belonging to the $P21/a$ space group, is fairly similar to the distorted D7 space group Takahashi and Tadokoro observed for pure crystal PEO. The new models were derived from these three different PEO–salt complexes by simply removing PF_6^- , AsF_6^- , and SbF_6^- anions and Li^+ cations from the original structure. The resulting polymer chains denoted as Model A, Model B, and Model C are shown in Figure 1 along with the helix model. The new models consist of two chains of PEO, with each chain having three $(\text{CH}_2\text{CH}_2\text{O})$ units. Oxygen atoms have different spatial arrangements in all of these new models both within one single chain and between two separate chains. A comparison of the simulated X-ray emission spectra for these models with the experimental data from the PEO film sample is presented in Figure 2.

The most intensive peak in the oxygen K-emission spectra originates from the transitions of oxygen lone pair electrons. The intensity and the natural width of the peaks in the X-ray emission spectrum reflect the characters of the orbitals. The almost pure p character of the lone pair orbital implies large X-ray intensity for transitions to the 1s orbital. The position of the lone-pair peaks can be used to determine the molecular structure as was shown in the study of liquid water and methanol mixture.¹⁴ As illustrated, experimentally there is a shift of ca. 0.7 eV between the most intensive features of nonresonant and resonant emission from oxygen atoms that is absent in the simulated spectra from the helix model (Figure 2a). In addition, the simulated spectra have a number of features that are absent in the experimental data. Apparently, the helix model proposed by Takahashi and Tadokoro¹⁹ for PEO does not provide adequate conformation representation of the polymer chain in the PEO film. The same conclusion was reached in our previous

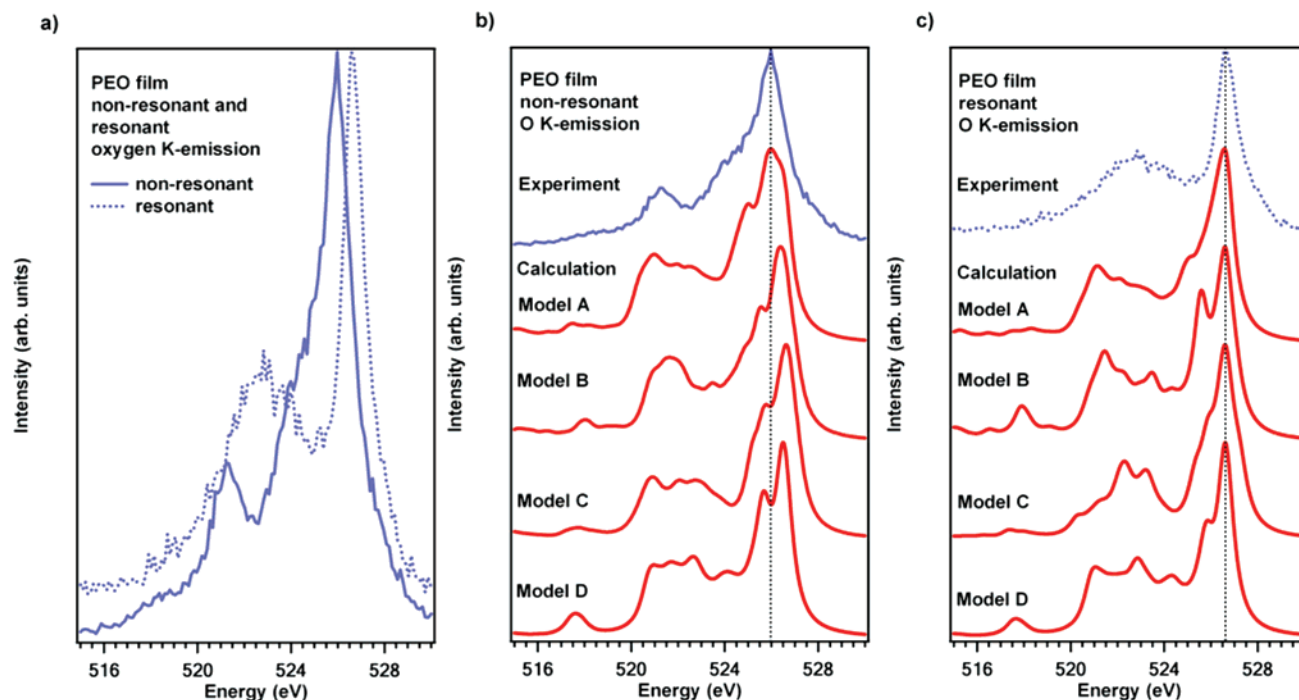


Figure 2. (a) Nonresonant and resonant oxygen K-emission and (b) simulated nonresonant (c) and resonant X-ray emission spectra from oxygen atoms in the model conformations A, B, C, and D in comparison with the experimental data from PEO film.

study of the PEO bulk polymer from which the present sample was synthesized. We now show that another model in itself provides a reasonable description of the PEO film.

Calculated nonresonant and resonant X-ray emission spectra for these three models are represented in Figures 2 in comparison with experimental spectra of the PEO film. It is clearly seen (Figure 2a) that the worst agreement with experiment is Model C (derived from the $(\text{PEO})_6\text{LiAsF}_6$ polymer-salt complex). With the helix model, it does not reproduce the energy shift observed experimentally between the nonresonant and resonant X-ray emission spectra of oxygen. Model B illustrates better agreement for oxygen K-emission, but the energy shift is much smaller than that in experiment, and the simulated resonant emission from this model exhibits a strong feature around 525.5 eV that is absent in the experimental resonant spectrum. Among these three models, the best agreement with the experimental X-ray emission data is achieved with Model A (from the $(\text{PEO})_6\text{LiPF}_6$ polymer-salt complex). It reproduces the experimentally observed energy shift between nonresonant and resonant X-ray emission spectra, and has relatively few "extra" features that are not present in the experimental spectra.

To determine the origin of energy shift between nonresonant and resonant X-ray emission spectra, and why only Model A reproduces this phenomenon, we have examined the symmetry and charge distribution of the lowest unoccupied molecular orbital in all four models. The LUMO plays an important role in the resonant X-ray emission process.

The charge density distribution of LUMO (shown in Figure 3) illustrates the contribution of particular atomic centers to this orbital. Model A is the only model that has a highly nonuniform charge density distribution across the $(\text{CH}_2\text{CH}_2\text{O})$ strands. The atomic centers, having a larger contribution to LUMO, have the higher probability of electron transitions in the process of resonant X-ray emission. Therefore, the contribution of some atomic centers into particular spectral features in the resonant X-ray emission spectrum is more significant than that for other atomic centers. For Model A, there is an accumulation of charge

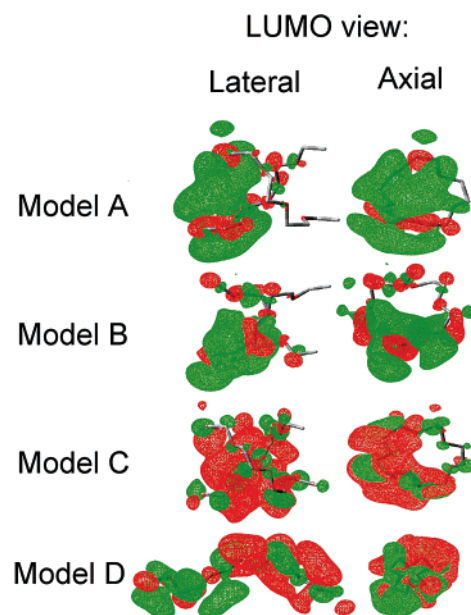


Figure 3. Electron density maps illustrating the lowest unoccupied molecular orbital of Models A, B, C, and D superimposed on the atomic arrangement.

density toward one end of the conformation, making the LUMO very sensitive to the coordination of the two strands.

Conclusions

Unique structural details of the conformation of polymer chains in the PEO thin film have been determined by means of X-ray emission spectroscopy. In particular, the resonant X-ray emission spectroscopy is used to probe the lowest unoccupied orbitals in the polymer chains. Quantum chemistry calculation shows that LUMO is very sensitive to the conformation of polymer chains, and also simulated emission spectra can be used to discriminate different conformations. The best fit was found to be the chain conformation in PEO electrolytes from which

the salt (LiMF_6 , $M = \text{P, As, or Sb}$) was removed. This conformation is different from the crystalline bulk polymer. This study indicates that film casting, commonly used to form electrolytes for Li polymer batteries, can induce the same conformation in the polymer not depending upon the presence of salt.

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