Structural conformation in a poly (ethylene oxide) film obtained from X-ray emission spectroscopy (XES)

*Stepan Kashtanov^{1, 2}, Guorong V. Zhuang¹, Andreas Augustsson^{3, 4}, Jinghua Guo³,
Joseph Nordgren⁴, Y. Luo² and Philip N. Ross^{1*}*

¹ Material Sciences Division, Lawrence Berkeley National Laboratory, Berkeley,
California 94720, USA

² Theoretical Chemistry, Royal Institute of Technology, AlbaNova University Center SE-
10691, Stockholm, Sweden

³ Advanced Light Source Division, Lawrence Berkeley National Laboratory Berkeley,
California 94720, USA

⁴ Department of Physics, Uppsala University Box 530 S-75121, Uppsala, Sweden

*To whom correspondence should be addressed. e-mail: pnross@lbl.gov (PNR)

Abstract: The electronic structure of poly(ethylene oxide) (PEO) in a thin (< 1 μ) film sample was experimentally probed by X-ray emission spectroscopy. The emission spectra from this film were much sharper with more resolved fine structure than the spectra from the bulk polymer from which it was cast. Both non-resonant and resonant X-ray emission spectra were simulated 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 , $\text{M}=\text{P}$, As, or Sb) had been removed. This conformation is different from that in 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 with or without the salt present.

Introduction

Much attention has been paid to solid electrolytes during 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 electrolytes, in which ion-polymer and ion-ion interactions play an important role in the ion transport mechanism. Cation-polymer interactions in PEO electrolytes have been the subject of numerous recent theoretical studies¹⁻⁸. The polymer conformation and its relation to the electronic structure are particularly relevant to understanding the mechanism of ionic conduction in polymer electrolytes. Many polymer electrolytes have been studied and their physical properties, such as ionic conductivity, for example, have been obtained. Nevertheless, there is a lack of information about their detailed structures. One of the issues is that the quality of the diffraction data obtained from polymer electrolytes is often quite poor. Due to that new techniques should be used either instead of or in addition to modern methods of X-ray diffraction (XRD), e.g. as developed recently by Andreev *et al.*⁹ to provide insight to the polymer structure.

In the present paper, we present the application of another technique - the X-ray emission spectroscopy – which gives direct information about the electronic structure of

the polymer that can be analyzed using modern quantum theory to obtain the molecular structure, i.e. polymer conformation. X-ray emission spectroscopy is element specific and sensitive to local electronic structure. Unlike photoelectron spectroscopy, another direct probe of electronic structure in molecules, sample charging is not an issue in XES since it is a photon-in and photon-out technique and can be applied to conducting and insulating samples with equal facility. The non-resonant or normal emission, originating from a valence electron transition to a vacant core-hole, follows the dipole selection rule, and is a direct measure of the occupied partial density of states (DOS) localized to the selected atomic site. Resonant emission, like the more familiar x-ray absorption spectroscopy (XAS), occurs as a result of the decay from a core-excited state where a core electron is excited by an incident photon into one of the unoccupied molecular orbitals, i.e. the LUMO, LUMO+1, etc. XES has recently been used to elucidate the nature of hydrogen bonding in water^{10, 11} and local electronic structure in an alcohol-water mixture^{12,13}. The local electronic structure and associated chemical bonding in fullerenes and conjugated polymers have also been probed in new detail by X-ray emission spectroscopy¹⁴. Though, the XAS itself is a very powerful technique and it has been successfully used to determine different conformation in a gas phase¹⁵, it has limitations in the case of present study, when it is necessary to probe occupied states.

In a previous study¹⁶, we used XES to probe the conformation of PEO in the form of a bulk polymer powder, MW of 600,000. From the differential scanning calorimeter measurements, this sample was characterized as having a 50 % crystalline fraction. XES spectra were simulated using density functional theory (DFT) from four different conformations of the sequence of (CH₂CH₂O) units, including the classical helix structure proposed by Takahashi and Tadokoro from XRD¹⁷. No single conformation fit the

experimental spectra well, with the best fit being mixtures of two conformations that may or may not represent different conformations present in the crystalline versus amorphous phases. In the course of that study, we found that a thin film of PEO cast from this bulk polymer produced “higher quality” spectra than the bulk polymer, i.e. narrower spectra with more resolved fine structure. We hypothesized that the film is more single phase than the bulk polymer and thus may have an electronic structure that may be simulated from a single conformation. We report this analysis in the present work.

Experimental and Computational Methods

Commercial poly(ethylene oxide) (PEO) powder with average molecular weight ca.600,000 (Aldrich) was purified to remove inhibitor and silicates (SiO_2). To make PEO films, the powder was first dissolved in acetonitrile (CH_3CN) followed by spin-casting the solutions onto a Silicon (Si) wafer. The thickness of the PEO thin film thus formed was 260 nm. The as-cast film was dynamically pumped in vacuum at ambient temperature for 72 hours. The infrared spectra obtained from the prepared film indicated that it was free (below detection limit) 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 before spectroscopy measurement. The samples were then transferred into the UHV measurement chamber at base pressure of 10^{-9} torr through in inert atmosphere (Ar) loadlock. The non-resonant and resonant X-ray emission spectra were acquired at beamline 7.0¹⁸ of the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL). The Emission spectra were acquired using a high efficiency grazing incidence X-ray spectrometer¹⁹. The combined monochromator and spectrometer energy resolution was estimated to be 0.3 eV and 0.5 eV for carbon and oxygen respectively. The non-resonant or normal C K emission was measured with photon

excitation energy of 320 eV while what we refer to below as the resonant C K emission was obtained with excitation energy of 285.2 eV. The corresponding O K-emission spectra were excited with photon energies of 532.0 eV and 573.3 eV, respectively.

The theoretical framework for simulation of the non-resonant and resonant X-ray emission processes is the same as described in the literature^{20,21} The relative probability of the normal 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 using Kramers-Heisenberg resonant scattering theory. Regarding the “final state rule”, which states 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 emission without including core-hole relaxation effects. Simulated spectra represent intensity only from electron transitions and do not include any additional effects that could be present in experimental X-ray emission data, e.g. absorption and scattering. Resonant 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^{22,23} using the DALTON program²⁴. The atomic site being probed, i.e. core-excited atom, is represented by Sadlej basis set²⁵ while the rest of atoms in the molecules by 6-31G basis. To facilitate comparison with experimental spectra, the calculated emission assumed a Lorentzian profile with full width half maximum (FWHM) of 0.5 eV for non-resonant and 0.3 eV for resonant, respectively. These linewidths are equal to the experimental resolutions. The energy scale of the simulated emission spectra was contracted by a factor of 1.3²⁶.

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 co-planar), and to be gauche (G) if the dihedral angle is non-zero. According to the rotation direction, the gauche can be labeled G^+ or G^- . The X-ray diffraction analysis by Tadokoro²⁷ showed that the PEO uniform helix structure is slightly distorted with respect to the D_7 point group and the monomeric units are repeated seven times in two complete turns of the helix and repeated in T_2G sequences. We will refer to this model as the single helix and the structure is illustrated in Fig. 1.

Figure 1. Models of the polymer chain. Double helix models obtained from PEO-salt complexes: A from $(\text{PEO})_6\cdot\text{LiPF}_6$; B from $(\text{PEO})_6\cdot\text{LiSbF}_6$; C from $(\text{PEO})_6\cdot\text{LiAsF}_6$; and classical helix model for $(\text{CH}_2\text{CH}_2\text{O})$ units in PEO.

Comparison of the simulated non-resonant and resonant X-ray emission spectra for this model with the experimental X-ray emission data from our PEO film sample is presented in Fig. 2 and Fig. 3.

Figure 2. Comparison between simulated and experimental data for oxygen. Simulated non-resonant (a) and resonant (b) X-ray emission spectra from oxygen atoms in the model conformations A, B, C and Helix in comparison with the experimental non-resonant and resonant O K-emission data from PEO film.

Figure 3. Comparison between simulated and experimental data for carbon. Simulated non-resonant (a) and resonant (b) X-ray emission spectra from carbon atoms in the model conformations A, B, C and Helix in comparison with the experimental non-resonant and resonant C K-emission data from PEO film.

As illustrated, experimentally there is shift of ca. 0.7 eV between the most intensive features of non-resonant and resonant emission from oxygen atoms that is absent in the simulated spectra from helix model (Fig. 2a). In addition, the simulated spectra have a number of features that are absent in the experimental data. Similarly, the resonant C K-emission is shifted by ca. 0.5 eV with respect to the non-resonant emission. This shift is presented in the corresponding simulated spectra from helix model (Fig. 3) but the shapes of the simulated spectral profiles are away from these in experiment. Apparently, the helix model proposed by Takahashi and Tadokoro¹⁷ for PEO does not provide adequate representation of the conformation of the polymer chain in the PEO film sample. The same conclusion was reached in our previous study of the PEO bulk polymer from which the present sample was synthesized. Unlike our previous study, we do not invoke a mixture of the helix with other conformations in order to fit the experimental spectra, but we show that another model in itself provides a reasonable simulation of the experimental data from the PEO film.

We consider three different models of the polymer chain. These models are constructed from the structures 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 recently^{28, 29}. The reason why we have chosen these structures among variety of PEO-salt complexes is that the conformation of PEO chains within the crystal unit cell for these

three models belongs to $P2_1/a$ space group, quite similar to the distorted D_7 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 are shown in Fig. 1 along with the helix model. The new models consist of two chains of PEO, with each chain having three (CH_2CH_2O) units. Oxygen atoms have different spatial arrangements in all of these new models both within one single chain and between two separate chains.

Calculated resonant and non-resonant X-ray emission spectra for these three models are represented in Figs. 2 and Fig. 3 in comparison with experimental emission spectra measured for the PEO film. It is clear (Fig. 2a) that the worst agreement with experiment is with model C (derived from the $(PEO)_6:LiAsF_6$ polymer-salt complex). As with the helix model, this model does not reproduce the energy shifts observed experimentally between the resonant and non-resonant emission spectra for oxygen atoms. Spectra for carbon atoms (Fig. 3) do not agree with experiment either. Model B illustrates better agreement for oxygen K-emission, but the energy shift is much smaller than it is experimentally observed, and the simulated resonant emission from this model exhibits a strong feature around 525.5 eV which is absent in the experimental resonant spectrum. Among these three models, the best agreement with the experimental X-ray emission data for both carbon and oxygen atoms is achieved using model A (from the $(PEO)_6:LiPF_6$ polymer-salt complex). It reproduces the experimentally observed energy shift between non-resonant and resonant X-ray emission spectra quantitatively, and has relatively few “extra” features that are not present in the experimental spectra. The low-energy tailing in both calculated non-resonant and resonant X-ray emission spectra for carbon atoms is

missing, but such a tailing is due to vibronic coupling, which is not included in the present simulations of X-ray emission spectra.

To discover the origin of the energy shift between non-resonant and resonant X-ray emission spectra, and why only model A reproduces this phenomenon, we examined the symmetry and charge distribution of the lowest unoccupied molecular orbital (LUMO) in various models. The LUMO plays an important role in the resonant emission process. In the resonant emission, the C or O 1s core electron is promoted into the LUMO forming a core-hole excited state, and the emission is primarily the decay from this excited state to the optical excited state, equivalent to the normal emission induced by the decay of a valence electron into the core hole.

LUMO: Lateral view Axial view

Figure 4. Electron density maps. Plots of the lowest unoccupied molecular orbital (LUMO) of Model A, B, C and Helix structures superimposed on the atomic arrangement.

The charge density distribution on the LUMO, shown in Fig. 4, illustrates the contribution of particular atomic centers to this orbital. Model A is the only model that has a highly non-uniform charge density distribution across the (CH₂CH₂O) strands. The atomic centers that have a larger contribution to the LUMO have a 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 density towards one end of the conformation, making the LUMO very sensitive to the coordination of the two strands. The origin of experimentally observed mutual spectral shift between non-resonant and resonant X-ray emission spectra for carbon atoms in PEO film also becomes clear in the light of above.

Conclusions

Unique structural details of the conformation of polymer chains in a PEO thin film sample have been discovered by means of X-ray emission spectroscopy. In particular, the resonant X-ray emission spectroscopy is used to probe the lowest unoccupied orbitals (LUMO, LUMO+1, etc.) in the polymer chains. Quantum chemical calculations showed that these orbitals are particularly sensitive to the conformation of the polymer chains, and that simulated emission spectra can be used to discriminate among different models of the conformation. The best fit was obtained with the chain conformation in PEO electrolytes from which the salt (LiMF₆, M=P, As, or Sb) had been removed. This conformation is different from that in the crystalline bulk polymer and implies that film casting, commonly used to form electrolytes for Li polymer batteries, can induce the same conformation in the polymer with or without the salt present.

Acknowledgement

We thank Dr. Y. G. Andreev in Prof. P. G. Bruce's group at University of St. Andrews for sending us the coordinates of the PEO-salt complex structure. This work was supported by Chemical Sciences Division of the U.S. Department of Energy under contract No. DE-AC02-05CH11231. The Advanced Light Source (ALS) is supported by the Office of Basic energy Sciences, Materials Science Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. Supports from the Swedish Research Council are also acknowledged.

References

1. Neyertz, S.; Brown, D.; Thomas, J. O. *Electrochim. Acta* **1995**, *40*, 2063.
2. Forsyth, M.; Payne, V. A.; Ratner, M. A.; de Leeuw, S. W.; Shriver, D. F. *Solid State Ionics* **1992**, *53-56*, 1011.
3. Lonergan, M. C.; Shriver, D. F.; Ratner, M. A. *Electrochim. Acta* **1995**, *40*, 2041.
4. Johansson, P.; Gejji, S. P.; Tegenfeldt, J.; Lindgren, J. *Solid State Ionics* **1996** *86-88*, 297.
5. More, M. B.; Glendening, E. D.; Ray, D.; Feller, D.; Armentrout, P. B. *J. Phys. Chem.* **1996**, *100*, 1605.
6. Ray, D.; Feller, D.; More, M. B.; Glendening, E. D.; Armentrout, P. B. *J. Phys. Chem.* **1996**, *100*, 16116.
7. Smith, G. D.; Jaffee, R. L.; Partridge, H. *J. Phys. Chem. A* **1997**, *101*, 1705.
8. Bruce, P. G. *Electrochim. Acta* **1995**, *40*, 2077.
9. Andreev, Y. G.; Lightfoot, P.; Bruce, P. G. *J. Appl. Crystallogr.* **1997**, *30*, 294.
10. Guo, J.-H.; Luo, Y.; Augustsson, A.; Rubensson, J. -E.; Sthe, C.; gren H.; Siegbahn, H.; Nordgren, J. *Phys. Rev. Lett.* **2002**, *89*, 137402.

11. Kashtanov, S.; Augustsson, A.; Luo, Y.; Guo, J.-H.; Sthe, C.; Rubensson, J. -E.; Siegbahn, H.; Nordgren, J.; gren H. *Phys. Rev. B* **2004**, *69*, 024201.
12. Guo, J. -H.; Luo, Y.; Augustsson, A.; Kashtanov, S.; Rubensson, J. -E.; Shue, D. K.; gren H.; Nordgren, J. *Phys. Rev. Lett.* **2003**, *91*, 157401.
13. Kashtanov, S.; Augustsson, A.; Rubensson, J. -E.; Nordgren, J.; gren H.; Guo, J.-H.; Luo, Y. *Phys. Rev. B* **2005**, *71*, 104205.
14. Guo, J. -H.; Nordgren, J. *J. Electr. Spectr. Relat. Phenom.* **2000**, *110-111*, 105.
15. Wang, J.; Cooper, G.; Tulumello, D.; Hitchcock, A. P. *J. Phys. Chem. A* **2005**; *109*; 10886.
16. Brena, B.; Zhuang, G. V.; Augustsson, A.; Liu, G.; Nordgren, J.; Guo, J. -H.; Ross, P. N.; Luo, Y. *J. Phys. Chem. B* **2005**, *109*, 7907.
17. Takahashi, Y.; Tadokoro, H. *Macromol.* **1973**, *6*, 672.
18. Warwick, T.; Heimann, P.; Mossessian, D.; McKinney, W.; Padmore, H. *Rev. Sci. Instrum.* **1995**, *66*, 2037.
19. Nordgren, J.; Bray, G.; Cramm, S.; Nyholm, R.; Rubensson, J. -E.; Wassdhl, N. *Rev. Sci. Instrum.* **1989**, *60*, 1690.
20. Gel'mukhanov, F.; gren, H. *Phys. Rep.* **1999**, *312*, 87.
21. Luo, Y.; gren, H.; Gel'mukhanov, F. *J. Phys. B: At. Mol. Opt. Phys.* **1994**, *27*, 4169.
22. Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
23. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
24. "DALTON, a molecular electronic structure program, Release 1.2 (2001), see <http://www.kjemi.uio.no/software/dalton/dalton.html>"
25. Sadlej, A. J. *Theor. Chim. Acta* **1991**, *79*, 123.
26. Luo, Y.; gren, H.; Gel'mukhanov, F.; Guo, J. -H.; Skytt, P.; Wassdhl, N.; Nordgren, J. *Phys. Rev. B* **1995**, *52*, 14479.

27. Tadokoro, H. *Polymer* **1984**, 25, 147.
28. Gadjourova, Z.; Marero, D.; Andersen, K. H.; Andreev, Y. G.; Bruce, P. G. *Chem. Mater.* **2001**, 13, 1282.
29. MacGlasshan, G. S.; Andreev, Y. G.; Bruce, P. G. *Nature* **1999**, 398, 792.

Structural conformation in a poly (ethylene oxide) film obtained from X-ray emission spectroscopy (XES)

Stepan Kashtanov, Guorong V. Zhuang, Andreas Augustsson, Jinghua Guo , Joseph Nordgren, Y. Luo and Philip N. Ross