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Polymer Electrolytes

Structure of the Poly(ethylene oxide)–Zinc Chloride Complex**

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Polymer electrolytes consist of salts dissolved in solid coordinating polymers.[1] The development of a new method by which complete crystal structures may be solved ab initio from powder-diffraction data permitted the solution of several key polymer-electrolyte structures that contain monovalent cations. Such structures had resisted being solved by other methods. This breakthrough led directly to the discovery of ionic conductivity in crystalline polymer electrolytes (poly(ethylene oxide)$_6$:LiXF$_6$; X = P, As, Sb; strictly this should be poly(oxyethylene) but is more widely referred to as PEO) when for thirty years all crystalline polymer electrolytes had been regarded as insulators.[2–4] Many polymer electrolytes (polymer–salt complexes) containing multivalent cations (including transitional metals, lanthanides, and actinides) have been prepared.[5] Such materials have potentially important optical, magnetic, and electrical properties in a flexible solid. Solution of their structures has proved difficult even for the ab initio method mentioned above. This has inhibited study, and ultimately exploitation, of their properties. A remarkable early success was the solution of the PEO$_4$:HgCl$_2$,[6] which contains HgCl$_2$ molecules, but such success has not been repeated. Herein we report the first crystal structure of a polymer–salt complex that contains multivalent cations, PEO$_4$:ZnCl$_2$ by growing single crystals of a lower molecular weight polymer–salt complex then using this structure as the basis for elucidating the structure of the equivalent complex of higher molecular weight. This result opens the way to accessing the structures of many other polymer electrolytes that contain multivalent cations, something that is essential if we are to explore and exploit their potentially important properties.

Single crystals of the PEO$_4$:ZnCl$_2$ complex were grown by using a methoxy end-capped ethylene oxide of average molar mass 500, CH$_3$-O(CH$_2$CH$_2$O)$_{11}$CH$_3$, as described in the Experimental Section.[+] Methoxy end-capped material was used to ensure chemical homogeneity throughout the polymer chain. A lower molecular-weight polymer (LMWP) with

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[+] We shall use the term poly(ethylene oxide) in a generic sense to refer to all materials with the (CH$_2$ CH$_2$O) repeating unit, regardless of molecular weight.

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an average of 11 ethylene oxide units was used since this should ensure, on the one hand, a sufficient chain length to permit the complex to adopt a similar structure to that of the higher-molecular-weight polymer (HMWP) while, on the other hand, it is the material with the highest molecular weight from which single crystals may be grown. A single crystal was selected for examination by single-crystal X-ray diffraction (see Experimental Section). The structure was solved by direct methods and subsequently refined by using the SHELXL-97 code.[7] A total of 1196 independently observed reflections with $I > 2\sigma(I)$ were included with six non-hydrogen atoms in the asymmetric unit of the cell, which contained two ethylene oxide units, one Zn^{2+} and one Cl^- ions. Examination of the structure revealed some unrealistic bond lengths. For example, C–O and C–C distances as short as 1.29 Å and 1.35 Å, respectively. The origin of this problem lies in the short ethylene oxide chains of the oligomer, chains that are also distributed in length about a mean of 11 ethylene oxide units, which results in the chain ends being randomly distributed throughout the crystal structure.[8] The structure, determined by single-crystal diffraction, does not identify discrete chains, instead the chains appear continuous. Where two chain ends meet, two CH_3 groups are adjacent to each other instead of a C–C bond. The separation of two covalently bonded carbon atoms and two CH_3 groups are of course different. This introduces disorder along the chains within the average crystal structure, hence the abnormal distances observed from the single crystal diffraction data. The observed C–C and C–O distances are less than expected for such bonds. How might such disorder arise? The structure indicates that Zn^{2+} is coordinated by two neighboring ether oxygen atoms along a chain, the following pair of ether oxygen atoms do not coordinate Zn^{2+}, and this pattern is repeated throughout the structure. It is likely that the chains will end in the region between adjacent Zn^{2+} ions. Given the polydispersity of the polymer, a Zn^{2+} ion could be coordinated by a short chain that then ends leaving one or more missing EO groups and thus introducing disorder. Other mechanisms are also possible, but this example serves to illustrate how such disorder may arise. Of course the effect of chain ends may be reduced significantly by increasing the average molar mass of the polymer, but then single crystals cannot be grown.

Although we were unable to use the single-crystal structure determination from the LMWP complex directly, it does provide a suitable model with which to refine the structure of a HMWP complex, PEO_4:$ZnCl_2$, by using powder-diffraction data collected from the latter material. We have demonstrated previously that structures may be refined by using powder-diffraction data collected from polymer electrolytes ranging in average molar mass from 1000 to 100000. It is clear that the crystallite size is generally larger in polymer electrolytes prepared with materials of molar mass close to 1000. This results in narrower peak widths and hence peaks that are better resolved in the powder diffraction patterns, thus providing data of better quality for refinement. We have elected to refine the structure of PEO_4:$ZnCl_2$ by using methoxy end-capped PEO of average molar mass 2000, which offers a good compromise between the resolution of the powder pattern and the proportion of chain ends.

PEO_4:$ZnCl_2$ of average molar mass 2000 was prepared as described in the Experimental Section. Refinement of powder diffraction data (see Experimental Section) was carried out starting from the model obtained from the single-crystal diffraction of the LMWP. The GSAS program package was used for refinement.[9] The powder pattern consisted of 2498 points and contained 194 reflections. The refinement involved 30 variables with 15 bond-length and bond-angle slack restraints. The final χ^2 was 2.6 and corresponded to a good fit as seen in Figure 1.

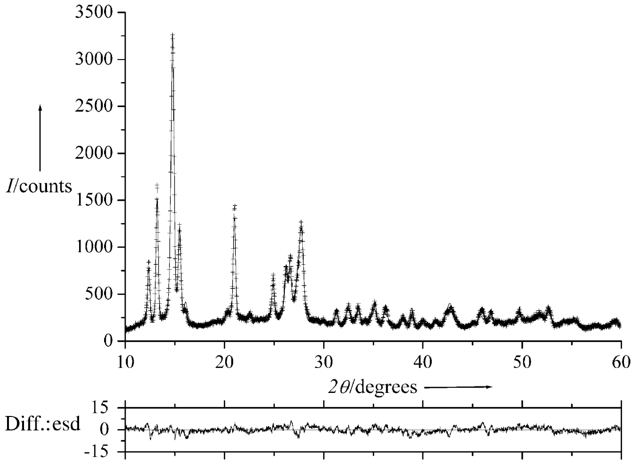

Figure 1. Fitted X-ray powder-diffraction pattern of PEO_4:$ZnCl_2$, average molar mass 2000. Crosses, observed profile; solid lines, calculated (upper) and difference (lower) profiles (esd = estimated standard deviation; Diff. = difference. The unit cell is monoclinic with refined lattice parameters $a = 8.4540(8)$ Å, $b = 13.388(2)$ Å, $c = 11.007(2)$ Å, $\beta = 89.84(3)°$. The space group is $C2/c$.

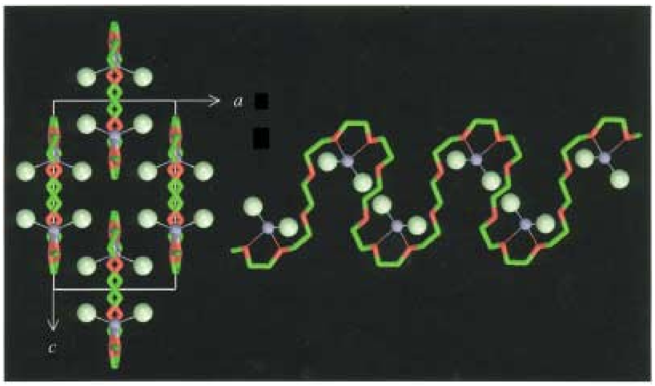

Figure 2. (Left) View of the structure of PEO_4:$ZnCl_2$ showing the stacking of four PEO chains in the unit cell. The chains are located within the bc plane and run along b. (Right) The conformation of an individual chain and the coordination around the Zn^+ cation (thin lines; hydrogen atoms not shown): zinc pale gray; chlorine pale green; carbon green; oxygen red.

The structure of PEO_4:$ZnCl_2$ is shown in Figure 2 (left). The PEO chains are located in sets of planes parallel to the *bc* plane of the unit cell, with the chains running along *b*. As can be seen in Figure 2 the chains are remarkably flat within these planes. A single chain is shown in Figure 2 (right). It describes large loops within each of which a Zn^{2+} ion is located. Each Zn^{2+} ion is coordinated by two neighboring ether oxygen atoms along the chain and two Cl^- ions, the coordination number around the Zn^{2+} ion is therefore four, and these four atoms form a slightly distorted tetrahedron. A mixed oxygen-chlorine environment for zinc as seen here in the crystalline phase, is probably retained in the amorphous phase as seen by EXAFS studies.[10] There are two noncoordinating ether oxygen atoms between each Zn^{2+} ion along the chain. Each chain is isolated from its neighbors. The Cl^- ions protrude from each chain but are more than 2.5 Å from the atoms of the neighboring chains, therefore there is no evidence of interaction between the Cl^- ions, or indeed any other parts of the chain, with neighboring chains. The chains are held together in the solid state by only weak Van der Waals forces. It is instructive to compare the structure of PEO_4:$ZnCl_2$ with the structure of the complex formed between PEO and $HgCl_2$ molecules, PEO_4:$HgCl_2$.[6] The structure of PEO_4:$HgCl_2$ is orthorhombic ($a = 8.58$ Å, $b = 13.55$ Å, $c = 11.75$ Å) with flat PEO chains located within the *bc* plane of the unit cell. The conformation of the chain is different from that in PEO_4:$ZnCl_2$. The chains in PEO_4:$HgCl_2$ are three times more stretched, thus forming a zigzag, compared to an almost square-wave shape in PEO_4:$ZnCl_2$. Unlike the {Cl–Zn–Cl} unit in PEO_4:$ZnCl_2$, the covalently bonded {Cl-Hg-Cl} moiety in PEO_4:$HgCl_2$ preserves the linear geometry of the $HgCl_2$ molecule (deviation from linearity in the complex is less than 4°). The shortest Hg–O distance is 2.6 Å compared to the shortest Zn–O distance of 2.14 Å in PEO_4:$ZnCl_2$.

As might have been anticipated for the first structure of a polymer electrolyte that contains divalent cations, the structure is completely different from any of the previously known polymer electrolytes that contain monovalent cations. It would not have been possible to establish the structure of the present material starting from any known monovalent structure or from the structural model of PEO_4:$HgCl_2$. We have used a similar approach to establish the structure of PEO_4:$ZnBr_2$. The structure is very similar to that of the chloride and will be reported elsewhere.

The combination of single-crystal growth by using a LMWP, single-crystal-diffraction methods, and the use of the single-crystal structure as a model for refining the structure of the material of higher molecular weight by using powder-diffraction data, provides a powerful tool with which to access polymer-electrolyte crystal structures that cannot be solved from powder data alone. In particular by solving the first crystal structure of a polymer of a multivalent-cation electrolyte, we have demonstrated that it is possible to establish such structures, which opens the way to investigate other multivalent-cation polymer electrolytes.

Experimental Section

Methods: Single crystals of the 4:1 complex formed between 500 molar mass methoxy-end-capped ethylene oxide and $ZnCl_2$ were grown by first dissolving $ZnCl_2$ (0.32 g, 2.35 mmol, Fluka, ≥98%) and oligomer (0.41 g, 0.77 mmol, Aldrich, >98%) in anhydrous methanol (5 mL, Aldrich, 99.8%). This corresponded to an ethylene oxide:salt ratio of 4:1. All constituents were dried prior to use and all manipulations were carried out in a high-integrity argon-filled MBraun glove box. Once the salt and polymer had completely dissolved, the methanol was removed by slow evaporation, which yielded a clear solution from which crystals were seen to precipitate. PEO_4:$ZnCl_2$ was prepared for powder X-ray diffraction by first dissolving poly(ethylene glycol) dimethyl ether of average molar mass 2000 (Aldrich, >98%) and $ZnCl_2$ in methanol at room temperature. After dissolution, the solution mixture was allowed to evaporate slowly to remove the methanol and yield a powder product.

Single crystal X-ray diffraction data were collected at 125 K from a colorless crystal of average size 0.1 mm by using Mo K_α on a Bruker SMART diffractometer equipped with a fine-focus sealed tube, a graphite monochromator and a CCD detector. Powder X-ray-diffraction data were collected at room temperature, in transition mode by using a STOE STADI/P diffractometer with Cu $K_{\alpha 1}$ radiation and a position-sensitive detector. The sample was placed into a sealed Lindeman tube 0.7 mm in diameter. The data were collected with a step size of 0.02° in 2θ.

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