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ChemComm
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The structure of poly(ethylene oxide)$_8$: NaBPh$_4$ from a single crystal oligomer and polycrystalline polymer†

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Received (in Cambridge, UK) 24th September 2003, Accepted 11th November 2003
First published as an Advance Article on the web 25th November 2003

We show that the structure of a polymer electrolyte may be solved by growing single crystals of an oligomeric (short chain) complex which provided an adequate starting model for refinement of the equivalent polymeric structure using powder diffraction: the efficacy of this method has been demonstrated by determining for the first time the structure of an 8 : 1 complex, poly(ethylene oxide)$_8$: NaBPh$_4$.

Polymer electrolytes consist of salts, *e.g.* LiI, dissolved in solid polymers, *e.g.* poly(ethylene oxide) [PEO, $(CH_2CH_2O)_n$].[1] Such materials are of considerable interest because they uniquely exhibit ionic conductivity in a solid yet flexible membrane, rendering them key to the realisation of all-solid-state electrochemical devices.

Traditionally, amorphous polymer electrolytes have been the focus of attention, however the recent discovery of ionic conductivity in crystalline polymers, specifically the 6 : 1 complexes PEO$_6$: LiXF$_6$, X = P, As, Sb,[2–4] has inspired interest in crystalline polymer electrolytes. Solving polymer electrolyte structure is important but notoriously difficult, in part because it has generally proved impossible to prepare polymer electrolytes in a form suitable for single crystal diffraction methods. Significant progress has been made by developing innovative methods by which complete crystal structures may be solved *ab initio* from powder diffraction.[4–6] In fact this led directly to the discovery of ionic conductivity in the crystalline 6 : 1 complexes, as well as to understanding of the structure of amorphous polymer electrolytes, such as the PEO : LiCF$_3$SO$_3$ system, by using the crystal structures as models for the interpretation of amorphous structures.[7,8]

Powder methods, however powerful, are limited in the available data and hence the complexity of polymer-electrolyte structures that may be solved. Therefore it is important to go beyond such methods. Here we show, for the first time, that it is possible to grow single crystals of an oligomer : salt complex then use this as a model for refinement of the equivalent polymer : salt complex using powder data. By so doing we have solved the first 8 : 1 polymer electrolyte complex, PEO$_8$: NaBPh$_4$ (Ph = phenyl C$_6$H$_5$), something that proved impossible from powder data alone.

Single crystals of the 8 : 1 complex formed between the oligomer, methoxy-end-capped ethylene oxide of average molar mass 500 [$CH_3O(CH_2CH_2O)_{10}CH_3$], and NaBPh$_4$ were grown for the first time.[9] Note that this material was methoxy end-capped rather than OH terminated to ensure chemical homogeneity. On average there are 10 ethylene oxide units in a chain and this proved to be sufficiently long to ensure that the structure adopted is similar to that in the high molar mass polymeric analogue.

Single-crystal X-ray diffraction data were collected from a colourless crystal of average size 0.1 mm using Mo K$_\alpha$ on a Bruker SMART diffractometer equipped with a fine-focus sealed tube, a graphite monochromator and a CCD detector. Although the basic structure was evident, examination of the bond lengths and angles revealed some unrealistic values; for example, C–O distances as high as 1.72 Å and C–C distances as low as 1.14 Å for some bonds, compared with typical values for PEO of 1.41–1.46 Å (C–O) and 1.52–1.56 Å (C–C). This remained so despite collecting data on several crystals and attempts to improve the refinement, including modelling the disorder by introducing multiple chains with partial occupancies. 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, resulting in the chain ends being randomly distributed throughout the crystal structure. Fig. 1 presents mass-spectrometry data collected on the single crystal highlighting the distribution of chain lengths.

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 carbons 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. 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. However, powder diffraction data of excellent quality may be obtained even using high molar mass polymers while the oligomer structure can serve as an adequate starting model for elucidation of the polymer structure by refinement.

Films of poly(ethylene oxide)$_8$: NaBPh$_4$ were prepared by solvent casting using poly(ethylene oxide) of average molar mass 100000[10] and X-ray powder diffraction data collected. Refinement of powder diffraction data was carried out starting from the single crystal structure of the oligomer. The GSAS program package was used for refinement.[11]‡

The final structure obtained by refinement using the powder diffraction data is shown in Fig. 2.

Each poly(ethylene oxide) chain folds such as to present a ring of 5 ether oxygens with one ether oxygen above and another below the plane of the ring. The Na$^+$ ions are located within this ring and are therefore coordinated by 7 ether oxygens. All the sodium–ether oxygen distances lie within the range 2.45–2.50 Å, which is typical for such distances in other complexes. There exists one ethylene oxide unit linking neighbouring rings along the chain, Fig. 2. The tetraphenyl borate anions are located between the chains and do not

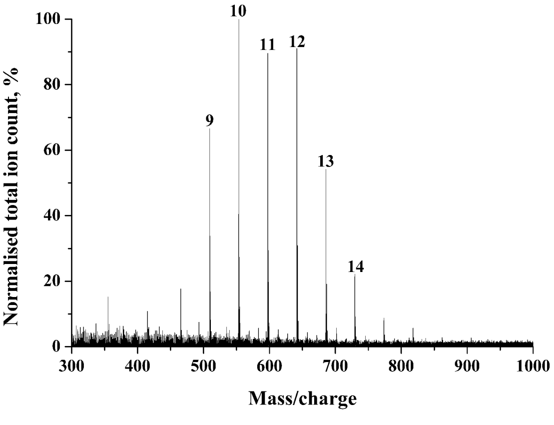

Fig. 1 Mass spectrum of a single crystal of PEO$_8$: NaBPh$_4$, average molar mass 500. As sodium formate was used as calibrant, all masses correspond to the ethylene oxide chain and one Na. Numbers above the peaks represent the number of EO units in the corresponding chains.

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† Electronic supplementary information (ESI) available: powder diffraction data for PEO$_8$: NaBPh$_4$. See http://www.rsc.org/suppdata/cc/b3/b311800b/

DOI: 10.1039/b311800b

coordinate to the cations. Although located between the chains, each BPh_4^- anion is slightly closer to one PEO chain with one Ph moiety situated opposite an ethylene oxide link between two rings that coordinate Na^+ ions, Fig. 2.

The structure is quite different from all previously known polymer electrolyte crystal structures. Only one chain is involved in coordinating the cations whereas in the 6 : 1 structures each PEO chain folds to form a half cylinder with pairs of chains interlocking to generate tunnels within which the Li^+ cations reside; there is no coordination of the cations by the anions. As the salt content is increased and we reach the 4 : 1 and 3 : 1 complexes, each chain folds to form a helix with a cation being located in each loop of the helix.[5,12] At these salt concentrations the anions also coordinate the cations unlike the situation in the 6 : 1 or 8 : 1 complexes.[4] In the case of the even more concentrated 1 : 1 complexes the PEO chains adopt a zig-zag confirmation with the cations being coordinated by only 2 ether oxygens and either 4 or 5 anions depending on the particular salt, the anions bridge to cations associated with neighbouring chains thus generating a 3-dimensional network.[13] Therefore it is clear that ion association increases with increasing salt content. We can see that extending the boundaries of our polymer electrolyte structure to include the 8 : 1 complexes has revealed quite new polymer-chain conformations. Also for the first time we observe a chain that describes two conformations which repeat alternately along its length. One ($tgg\overline{gg}t\overline{gg}t\overline{g}gtt\overline{gg}t\overline{gg}t$) involves chain folding to form a coordination site for the cation and the other ($ct\overline{ggg}$) links these coordination sites along the chain.[14] This is in contrast to structures determined previously that exhibit the same single repeating confirmation throughout the structure.

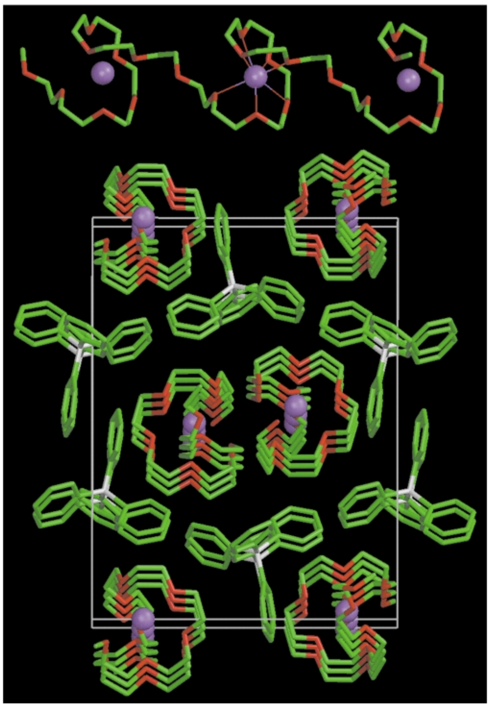

Fig. 2 The structure of PEO_8:$NaBPh_4$. (Top) View showing the conformation of the PEO chain and the coordination around the Na^+ cation (thin lines) (hydrogens not shown). Purple, sodium; white, boron; green, carbon; red, oxygen. (Bottom) View of the entire structure along the chain axis.

The approach described here opens the door to the establishment of many polymer electrolyte structures that were too complex to access by other means. The approach is applicable to other crystalline polymers and hence has potential impact beyond the field of polymer electrolytes.

P. G. B. is indebted to the Royal Society and the EPSRC for financial support. We thank Dr Catherine Botting for help with the MS data.

Notes and references

‡ STOE STADI/P diffractometer, Cu $K_{\alpha 1}$, room temperature, 2θ range 5–60°, step size 0.02°, chemical formula $PEO_8 : NaBPh_4$, $M = 694.65$, $a = 22.737(2)$, $b = 17.117(1)$, $c = 9.8903(8)$ Å, $\beta = 101.286(7)°$, $P2_1/n$, $Z = 4$, 1159 reflections, $R_{wp} = 0.076$, $R_{exp} = 0.032$, $R_I = 0.098$, background approximated by a 5-term cosine series.

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9 Single crystals of the oligomeric 8 : 1 complex formed between 500 molar mass methoxy-end-capped ethylene oxide and $NaBPh_4$ were grown by first dissolving 0.31 g of dry $NaBPh_4$ (Fluka, ≥99.5%) and 0.33 g of the dry oligomer (Aldrich, >98%) in 5 ml of acetonitrile (Aldrich, 99.8%). Once the salt and oligomer had completely dissolved, the acetonitrile was removed by slow evaporation, yielding a clear solution from which crystals were seen to precipitate.

10 Poly(ethylene oxide)$_8$: $NaBPh_4$ was prepared as a film for powder X-ray diffraction by dissolving dried PEO of average molar mass 100000 (Aldrich, >98%) and dry $NaBPh_4$ in acetonitrile at room temperature. After dissolution, the solutions were cast into Teflon moulds and the solvent allowed to evaporate until polymer electrolyte films formed.

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14 The conformation was derived assuming that torsion angles in the range 0 ± 45° are *cis* (*c*), 180 ± 45° are *trans* (*t*), the rest are either *gauche* (*g*) or *gauche*-minus ($\overline{g}$).