Structure of the polymer electrolyte poly(ethylene oxide)$_3$: LiN(SO_2CF_3)$_2$ determined by powder diffraction using a powerful Monte Carlo approach

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The crystal structure of the polymer electrolyte, poly(ethylene oxide)$_3$: LiN(SO_2CF_3)$_2$ is solved using a newly developed Monte Carlo approach capable of solving the structures of flexible molecules.

Introduction of the rechargeable lithium battery represented one of the greatest revolutions in power sources this century.[1–4] However these cells are still based on a conventional configuration composed of a liquid electrolyte separating two solid electrodes. In the future, solid polymer electrolytes will replace liquid electrolytes in commercial batteries yielding all-solid-state devices with the very significant advantages which accrue from such a construction.[1,4–7] Poly(ethylene oxide) [$(CH_2CH_2O)_n$] containing the salt LiN(SO_2CF_3)$_2$ possesses one of the highest conductivities at room temperature of any such solvent-free lithium polymer electrolyte. As a result poly(ethylene oxide) : LiN(SO_2CF_3)$_2$ and its closely related derivatives have made possible the development of new room-temperature lithium batteries entirely free from low molecular mass solvents. Therefore, there is considerable interest in determining the structure of this most highly conducting polymer electrolyte. This is especially so since comparison of the structure with that of related systems which possess significantly lower conductivities, *e.g.* poly(ethylene oxide)$_3$: $LiCF_3SO_3$,[6] should not only reveal factors responsible for suppression of the melting point and hence promotion of highly conducting amorphous phases in the poly(ethylene oxide) : LiN(SO_2CF_3)$_2$ system, but in addition should offer direction to the design of new anions that can yield polymer electrolytes with yet higher ionic conductivities. Since no single crystals of appropriate quality were available we have now succeeded in determining the structure of poly(ethylene oxide)$_3$: LiN(SO_2CF_3)$_2$ from powder X-ray data. This is the largest polymer electrolyte structure to be solved so far. In contrast to our previous structure elucidation of the simpler poly(ethylene oxide)$_3$: $LiCF_3SO_3$ which was carried out by Rietveld refinement and difference Fourier techniques, the structure of poly(ethylene oxide)$_3$: LiN(SO_2CF_3)$_2$ could not be obtained by any established approach to the analysis of powder diffraction data. This is due in part to the flexible conformation of the $N(SO_2CF_3)_2^-$ anion.[8] Instead it was necessary to develop a new and powerful Monte Carlo approach to the *ab initio* determination of crystal structures from powder diffraction data. Furthermore, our results demonstrate that with this new approach it is possible, for the first time, to solve the structures of flexible molecules in general. Our new approach differs from previous implementations of the Monte Carlo method, by us and by others, which were restricted to rigid molecules.[9,10]

Poly(ethylene oxide)$_3$: LiN(SO_2CF_3)$_2$ was prepared by grinding together appropriate proportions of the anhydrous polymer (Aldrich, M = 100 000) and salt (3 mol dm^{-3}). The sample, once sealed in a Lindemann tube, was heated at 150 °C for 6 h then annealed at 55 °C for 4 days.[11] Powder diffraction data were collected on a Stoe STADI/P diffractometer operating in transmission mode with Cu-Kα_1 radiation. The peaks were indexed using the program TREOR[12] and then refined to yield the monoclinic cell with a = 12.0343(9), b = 8.6605(7), c = 19.139(2) Å, β = 128.11(3)° in space group $P2_1/c$. Trial structures were calculated and in each case a powder pattern was generated and compared with the observed data by calculating the agreement factor, $\chi^2 = [\Sigma(y_i^{obs} - y_i^{calc})^2/y_i^{obs}]/N$, where y_i^{obs} and y_i^{calc} are the observed and calculated intensities at the ith profile point, N is the number of degrees of freedom. Minimisation of χ^2 was carried out using standard Metropolis importance sampling.[13] A new move is accepted if $\chi^2_{new} < \chi^2_{old}$ or if $\exp[-(\chi^2_{new} - \chi^2_{old})/(\Delta\chi^2_{cur})] > r$, where r is a random number between 0 and 1; χ^2_{new} and χ^2_{old} are respectively the goodness of fit for the current and preceding moves and $\Delta\chi^2_{cur}$ is the analogue of temperature in a Boltzmann expression. Simulated annealing was employed, which means that the value of $\Delta\chi^2_{cur}$ is reduced automatically during the course of the run so that the system moves efficiently towards the lowest minimum. This is shown in Fig. 1 where convergence to a minimum in χ^2 is clearly evident. The used simulated annealing increases the probability of this minimum being global. A unique feature of our approach, which is crucial to its power and success, is that we describe the position of each atom in the model structures in terms of bond lengths, bond and torsion angles. This permits us to check that each model is chemically reasonable by ensuring that the bond lengths and angles fall within constrained values, otherwise the move is rejected. A total of 25 atoms were located in the asymmetric unit by the Monte Carlo approach. Finally the best trial structure was subjected to conventional refinement by the Rietveld method using the GSAS code,[14] and including chemical constraints. The weighted profile R factor for the fit R_{wp} = 0.056 and the fit is excellent. The final refined structure of poly(ethylene oxide)$_3$: LiN(SO_2CF_3)$_2$ shown in Fig. 2.

Examination of Fig. 2 indicates that the poly(ethylene oxide) chain adopts a helical conformation with all C–O bonds *trans*, T, but with C–C bonds adopting a *gauche*, G, or *gauche* minus, configuration, *i.e.* TTGTTGTTG$^-$ similar to that found in all 3 : 1 complexes studied so far.[6,8,15] Li$^+$ ions are located in each turn of the helix and are coordinated by three ether oxygens

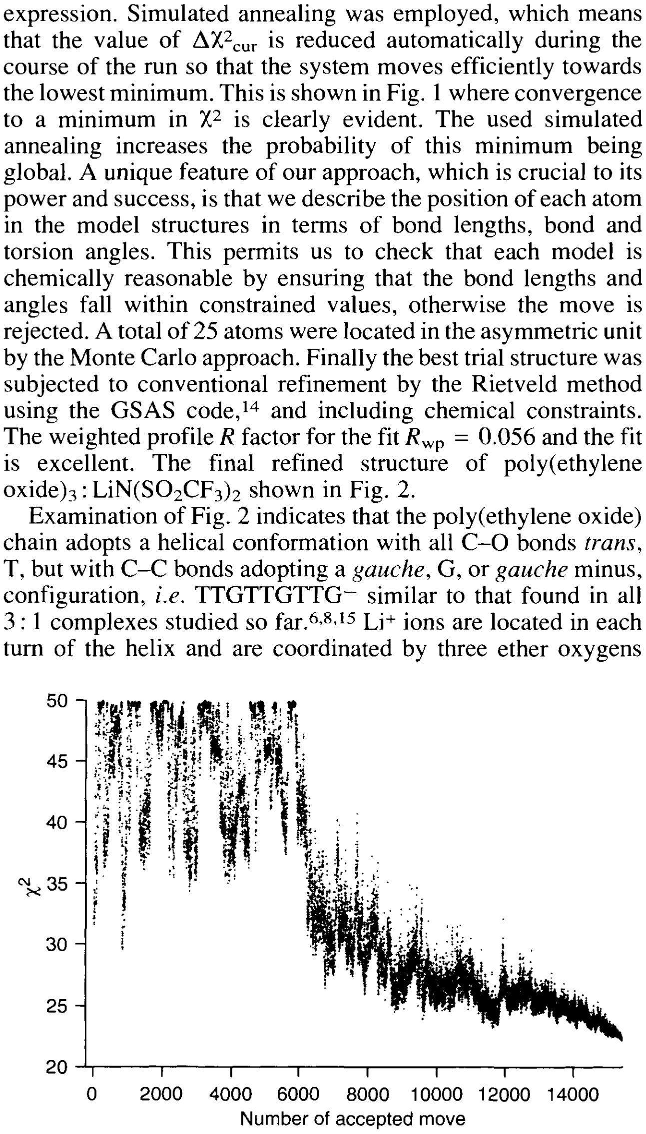

Fig. 1 Variation of χ^2 during Monte Carlo minimisation. Each point corresponds to a different trial structure. As the Monte Carlo process progresses more (lower χ^2) and less (higher χ^2) likely structures are explored. The process terminates at the lowest χ^2 value.

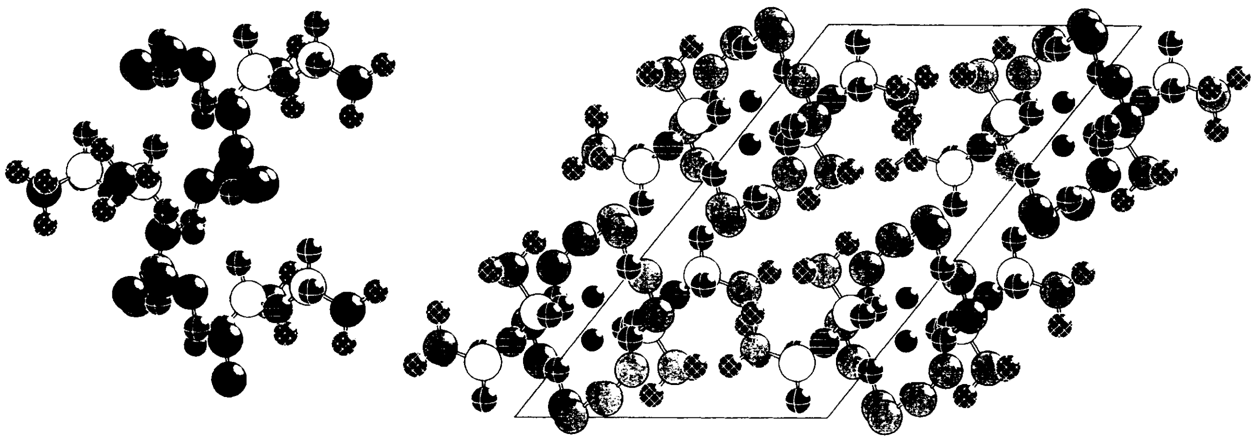

Fig. 2 Left, a portion of the poly(ethylene oxide)$_3$: $\mathrm{LiN(SO_2CF_3)_2}$ structure showing a single polymer chain with associated ions. Right, view of the structure down the fibre axis. Solid black spheres, lithium; lined black, nitrogen; white, sulfur; solid gray, carbon; crossed grey, oxygen; hatched black, fluorine (hydrogen atoms are not shown).

from the chain that do not coordinate to any other ion. The total lithium coordination number of five is completed by one oxygen from each of two imide ions. Only one of the $\mathrm{SO_2}$ groups of each imide is involved in coordinating to the $\mathrm{Li^+}$ ions with each oxygen coordinating neighbouring $\mathrm{Li^+}$ ions along the chain thus forming a continuous sequence $\mathrm{-Li^+-O-S-O-Li^+-}$. The rest of the imide anion projects into the interchain space. Each polymer chain is associated with a dedicated set of cations and anions. There is no significant interaction between neighbouring chains and each chain is essentially an isolated infinitely long coordination complex.

The unprecedented insight that knowledge of the poly(ethylene oxide)$_3$: $\mathrm{LiN(SO_2CF_3)_2}$ crystal structure provides is demonstrated by the following points. First, we can confirm our previous speculation that the poly(ethylene oxide)$_3$: $\mathrm{LiCF_3SO_3}$ and poly(ethylene oxide)$_3$: $\mathrm{LiN(SO_2CF_3)_2}$ structures are related;[6] the essential difference is the replacement of the triflate anion by the flexible imide with the $\mathrm{-SO_2}$ groups coordinating the $\mathrm{Li^+}$ ions in the same fashion in each case but with the additional atoms of the imide projecting further into the interchain space. The unpredictable conformation of the imide is shown in Fig. 2. It differs from that of the imide in the $\mathrm{LiN(SO_2CF_3)_2}$ salt[16] and the lowest-energy configuration calculated for the anion in the gas phase.[17] As a result of the size and conformation of the imide the polymer chains are forced apart thus expanding the unit cell while at the same time weakening the interactions between the chains as well as hindering their ability to pack into a regular crystal structure. This is consistent with the drop in the melting temperature of the crystalline phase from 180 °C in the case of the triflate to 80 °C for the imide. The strained nature of the imide in the crystal structure compared with the imide in the gas phase, as mentioned above, is also likely to reduce the stability and lower the melting point of the crystalline phase. We can see a structural rationale for the preservation of the conducting amorphous phase to low temperatures, something that is impossible for the triflate analogue. We do not suggest that the structure of the poly(ethylene oxide)$_3$: $\mathrm{LiN(SO_2CF_3)_2}$ is necessarily the only factor responsible for the high conductivity of this important polymer electrolyte. The high degree of charge delocalisation and low basicity of the anion must also play a role. Comparison of the crystal structures of the triflate and imide suggests a direction for the improvement of ionic conductivity. The optimum anion should contain at least one $\mathrm{-SO_2}$ group, required for coordination to $\mathrm{Li^+}$, and be of low basicity to ensure high dissociation of the salt. However, of great importance is the inclusion of a moiety which projects outwards from the chains forcing them apart and minimising their interaction while at the same time inhibiting crystal packing. The moiety should be flexible thus increasing the entropy of melting and further reducing the melting point.

The success of this structure determination demonstrates that the Monte Carlo approach is sufficiently powerful to solve crystal structures containing relatively complex molecules that are flexible and therefore may adopt *any* geometry.

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