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ARTICLES

Ab initio solution of a complex crystal structure from powder-diffraction data using simulated-annealing method and a high degree of molecular flexibility

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The previously unknown crystal structure of the polymer/salt complex poly(ethylene oxide):$NaSO_3CF_3$ was solved from a powder-diffraction pattern collected on a laboratory x-ray diffractometer. The solution was performed starting from a random arrangement of constituent molecular fragments in the unit cell using a full-profile-fitting technique and a simulated-annealing method for finding the global minimum of the figure-of-merit function. Unlike the only other structure solution using this approach, the procedure was successful only when the highest degree of flexibility was applied to stereochemically constrained species. [S0163-1829(97)02217-0]

I. INTRODUCTION

The first example of the successful determination of a previously unknown crystal structure comprising flexible molecules from powder-diffraction data by means of the simulated-annealing procedure was carried out on poly(ethylene oxide)$_3$: $LiN(SO_2CF_3)_2$. It showed considerable promise for such an approach to the solution of complex structures.[1] It has also demonstrated considerable advantage compared with methods based on Monte Carlo randomized-grid-search approaches which are restricted to rotations and translations of rigid molecules in crystallographic space.[2–4]

Polymer/salt complexes belong to a family of polymer electrolytes which are composed of salt dissolved in solid high-molecular-weight polymers. In the case of the previously determined system, the polymer is composed of linear chain with the repeat unit (CH_2-CH_2-O) and the molecular anion comprises two -SO_2CF_3 moieties bridged by a nitrogen atom.

Three important distinctions may be drawn between the previous case and that presented here. First, it was known that the poly(ethylene oxide) chains in $(PEO)_3$: $LiN(SO_2CF_3)_2$ adopted a helical conformation. Second, the approximate location of the helices within the unit cell was known from the lattice parameters and requirement for the helical axis to coincide with the 2_1 screw axis (space group $P2_1/c$). Third, the bond lengths and angles associated with chemically similar moieties (e.g., C-F and S-O bond lengths and C-S-O and F-C-F angles) could be constrained to be equal. In the present study no assumptions concerning chain conformation, orientation, position, or equivalence of bond lengths and angles were made, and indeed attempts to invoke the last of them inhibited a successful structure determination.

II. STRUCTURE SOLUTION AND REFINEMENT

A sample of the complex was prepared by mixing appropriate amounts of dried poly(ethylene oxide) and sodium triflate powders. For the diffraction studies the mixture was then placed into special glass Lindemann tubes 0.7 mm in diameter, sealed under an argon atmosphere, melted at 275 °C for 4 h and then annealed at 70 °C for 7 days, the latter made to promote crystallization.

The diffraction pattern (Fig. 1) was collected in 2θ steps of 0.02° in transmission mode on a STOE STADI/P powder diffractometer, using Cu $K\alpha_1$ radiation and a position-sensitive detector. Indexing and subsequent refinement of lattice parameters by means of the TREOR program[5] yielded the monoclinic cell with the lattice parameters listed in Table I. Systematic absences of reflections allowed unambiguous identification of the space group as $P2_1/c$. The contents of the unit cell were determined on the basis of density. For the given cell volume, the density of the complex predicted on the basis of four formula units in the cell gives a value of 1.53 g cm^{-3}, and this agrees well with the density range for solid polymer electrolytes with similar salt/polymer ratios. This being so, it is most likely that all atoms of the complex should occupy $4e$ general positions of the space group with unit probability. The structure solution proceeded on the basis of moving each of the constituent fragments as a whole within an asymmetric unit, being one-quarter the volume of the unit cell.

The computational procedure used to solve the structure of poly(ethylene oxide):$NaCF_3SO_3$ was similar to that involved in the solution of poly(ethylene oxide)$_3$:$LiN(SO_2CF_3)_2$.[6] The asymmetric unit is composed of the basic repeat unit CH_2-CH_2-O, one Na^+ ion, and one molecular triflate anion $CF_3SO_3{}^-$. The outer geometry of the constituent molecular fragments is shown in Figs. 2.

The coordinates of the atoms belonging to the molecular fragments in the asymmetric unit were first described in terms of bond lengths, bond angles, and torsion angles in corresponding local Cartesian frames with origins located at the sulfur atom (in triflate) and one of the carbons (in ethylene oxide). The thus obtained coordinates were then converted into a common Cartesian frame after choosing a po-

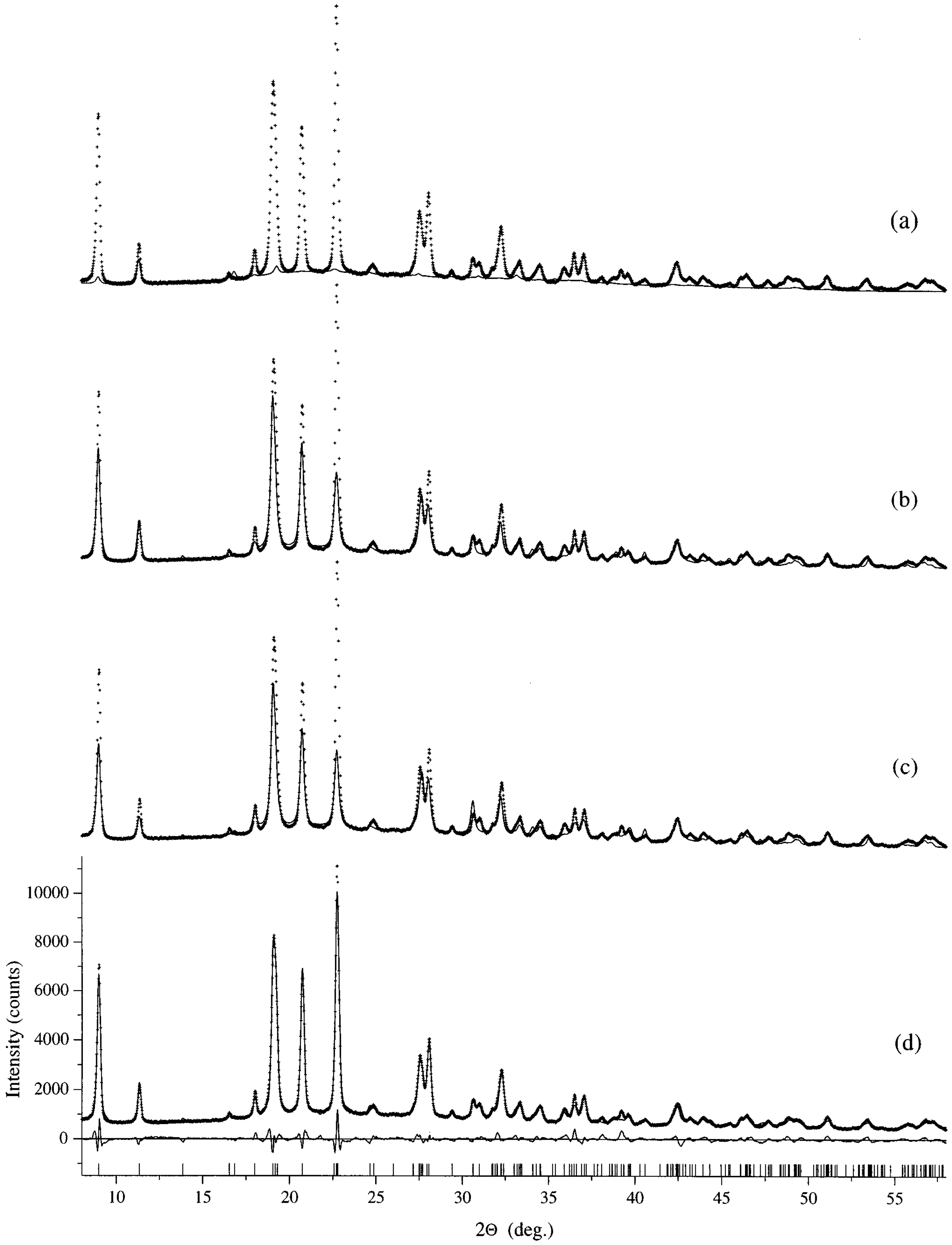

FIG. 1. Diffraction patterns of poly(ethylene oxide):$NaCF_3SO_3$ indicating progress towards the structure solution. Crosses, observed; solid line, calculated. Solid lines oscillating around $y=0$ represent difference profiles. Vertical solid lines indicate positions of reflections. See text for details.

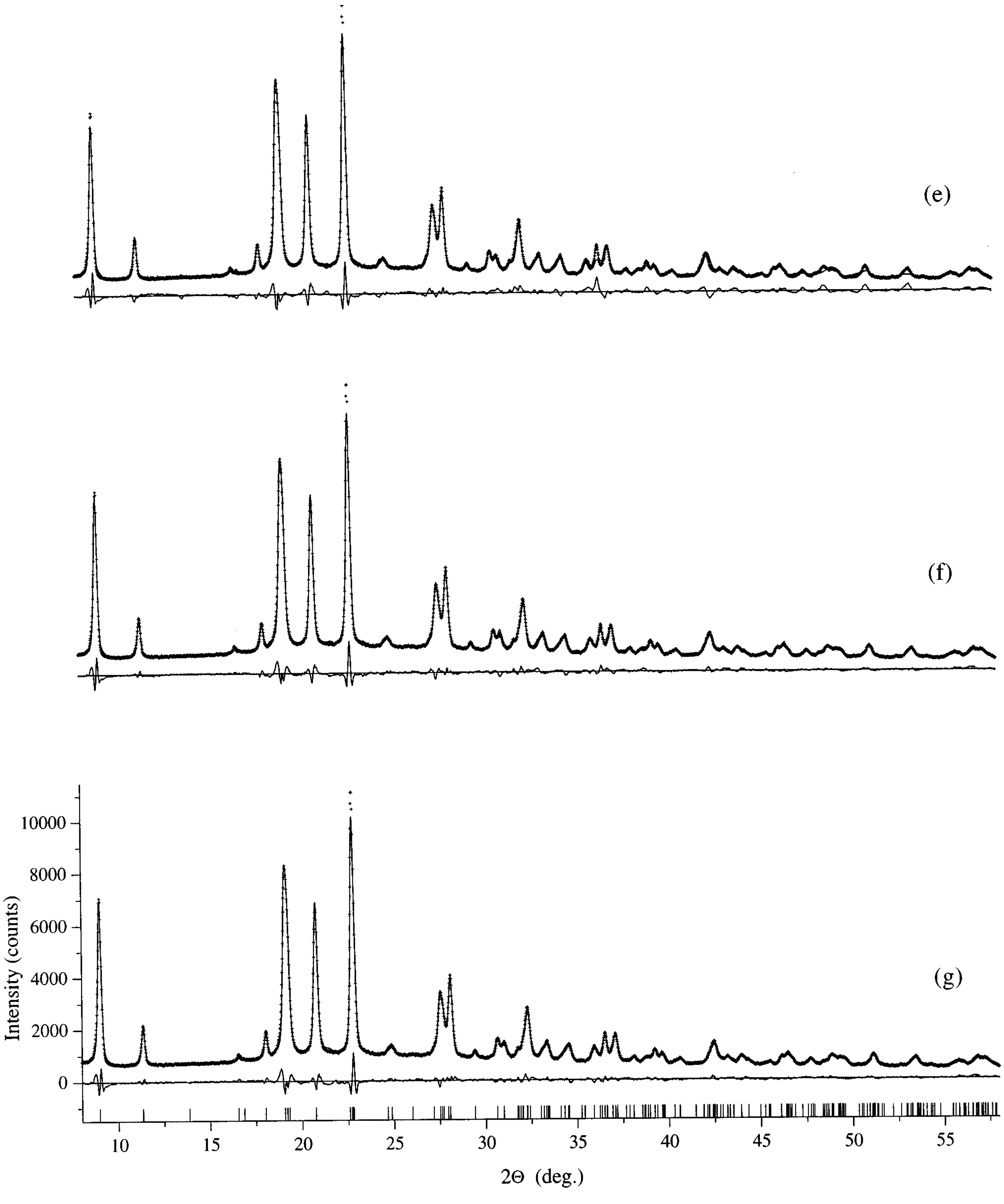

FIG. 1. (*Continued*).

sition and spatial orientation of each moiety as a whole. Simultaneously, a trial position of the Na^+ ion in the same frame was chosen. Thus a set of parameters was obtained which was necessary and sufficient to calculate the crystallographic coordinates of each atom in the asymmetric unit by yet one more frame transformation. The set of crystallographic coordinates together with a randomly chosen and averaged (for all atoms) amplitude of isotropic mean-squared displacements was then used to calculate integrated intensities of diffraction peaks. Finally, the whole profile for a trial structural model was calculated using a set of profile parameters which were determined in advance using a profile-fitting procedure of the CPSR program package.[7] The profile parameters were varied during structure refinements that followed simulated annealing runs. The Monte Carlo (MC) procedure necessitates random generation of coordinates, i.e.,

TABLE I. Structural parameters of poly(ethylene oxide):$NaCF_3SO_3$ and profile parameters of its x-ray-diffraction pattern.

		Structural parameters		
Atom	x	y	z	U (Å^2)
S(1)	0.6636(5)	0.0813(5)	0.243(1)	0.054(3)
C(1)	0.855(1)	0.096(1)	0.297(2)	0.03(1)
F(1)	0.9163(8)	0.0376(9)	0.153(2)	0.10(2)
F(2)	0.879(1)	0.2018(8)	0.224(2)	0.10(2)
F(3)	0.8681(9)	0.0897(9)	0.514(2)	0.10(2)
O(1)	0.633(1)	−0.0215(9)	0.339(2)	0.084(6)
O(2)	0.600(1)	0.158(1)	0.390(2)	0.084(6)
O(3)	0.641(1)	0.088(1)	−0.004(2)	0.084(6)
Na(1)	0.4991(8)	0.3331(6)	0.2412(2)	0.077(5)
O(4)	0.317(1)	0.224(1)	0.026(2)	0.08(1)
C(2)	0.270(2)	0.1544(8)	0.200(3)	0.071(6)
C(3)	0.215(1)	0.218(1)	0.405(2)	0.071(6)
H(1)	0.201(4)	0.111(3)	0.137(6)	0.4(1)
H(2)	0.344(4)	0.111(3)	0.249(7)	0.4(1)
H(3)	0.152(3)	0.267(3)	0.345(6)	0.4(1)
H(4)	0.173(4)	0.173(3)	0.511(5)	0.4(1)
$a=9.8491(4)$ Å	$b=12.7862(5)$ Å	$c=5.7750(3)$ Å	$\beta=90.638(5)°$	Space group $P2_1/c$
		Profile parameters		
$2\theta_{\min}$	5°		Half width parameters	
$2\theta_{\max}$	85°		G_U	819.7(5)
Step width	0.02°		G_V	−121(32)
Timer per step	700 sec		G_W	49(3)
Peak shape	pseudo-Voigt		L_X	10.6(2)
Number of peaks	543		L_Y	0
Rp	0.040			
Rwp	0.052		Asymmetry	−0.13(3)
R-Bragg	0.089			

the generation of new trial structures, and for the molecular moieties this is most easily accomplished by random steps of the bond lengths, bond angles, and torsion angles. The agreement between the calculated and experimental profiles was quantitatively evaluated using the χ^2 Pearson-distribution function after appropriate rescaling of the calculated intensities. The same value served as an energy analog in a standard Metropolis importance sampling algorithm[8] for simulated annealing. A randomized search in crystallographic space for the trial models is carried out with a gradually decreasing ''temperature,'' i.e., marginal change of the χ^2 value, for as long as the system is ''frozen.'' Full computational details can be found in Ref. 6.

The initial trial structure [Fig. 2(a)] was randomly chosen and, as can be seen from Fig. 1(a), provided no match of the calculated and observed diffraction patterns. The first MC run starting from this point has altered the arrangement of the fragments significantly [Fig. 2(b)] and improved the fit [Fig. 1(b)]. Twenty-seven parameters were varied simultaneously in each MC step. There were, for the triflate, C-S, S-O, and C-F bond distances, S-C-F, C-S-O, O-S-O, and F-C-F bond angles, the F-C-S-O torsion angle, coordinates of the S atom, and Eulerian angles; for the polymer chain, C-O and C-C bond distances, the O-C-C bond angle, coordinates of the carbon atom adjacent to the ether oxygen, and Eulerian angles. At this stage all distances and angles associated with particular bond types, e.g., all S-C-F1, S-C-F2, and S-C-F3 angles in the triflate, were set to be equal and varied simultaneously in order to reduce the total number of variables. As can be seen from Fig. 2(b), the position of the ethylene oxide unit obtained in the end of the first MC run did not result in a continuous chain at the junctions of neighboring asymmetric units, although there was ample evidence that the continuity could be achieved along the shortest axis (c) with minimal effect on the quality of fit. With this in mind the second MC run was made during which the coordinates of the Na^+ ion and of all the atoms comprising the triflate group were fixed at the values obtained from the previous run, while nine chain parameters were varied. During this MC run, only those trial configurations were allowed that gave a continuous chain along the c axis. As expected, the resulting structure led to a marginal 7% increase in the figure-of-merit function, indicating a slightly inferior quality of fit [Fig. 1(c)], while providing a starting model with a continuous poly(ethylene oxide) chain [Fig. 2(c)] for the profile refinement procedure.

After addition of hydrogens to the carbons of the polymer chain assuming tetrahedral coordination, refinement involving 66 independent profile and structure parameters was performed using the Rietveld method[9] by means of the GSAS program package.[10] In contrast to the MC runs, the crystallographic coordinates of all atoms at this stage were varied

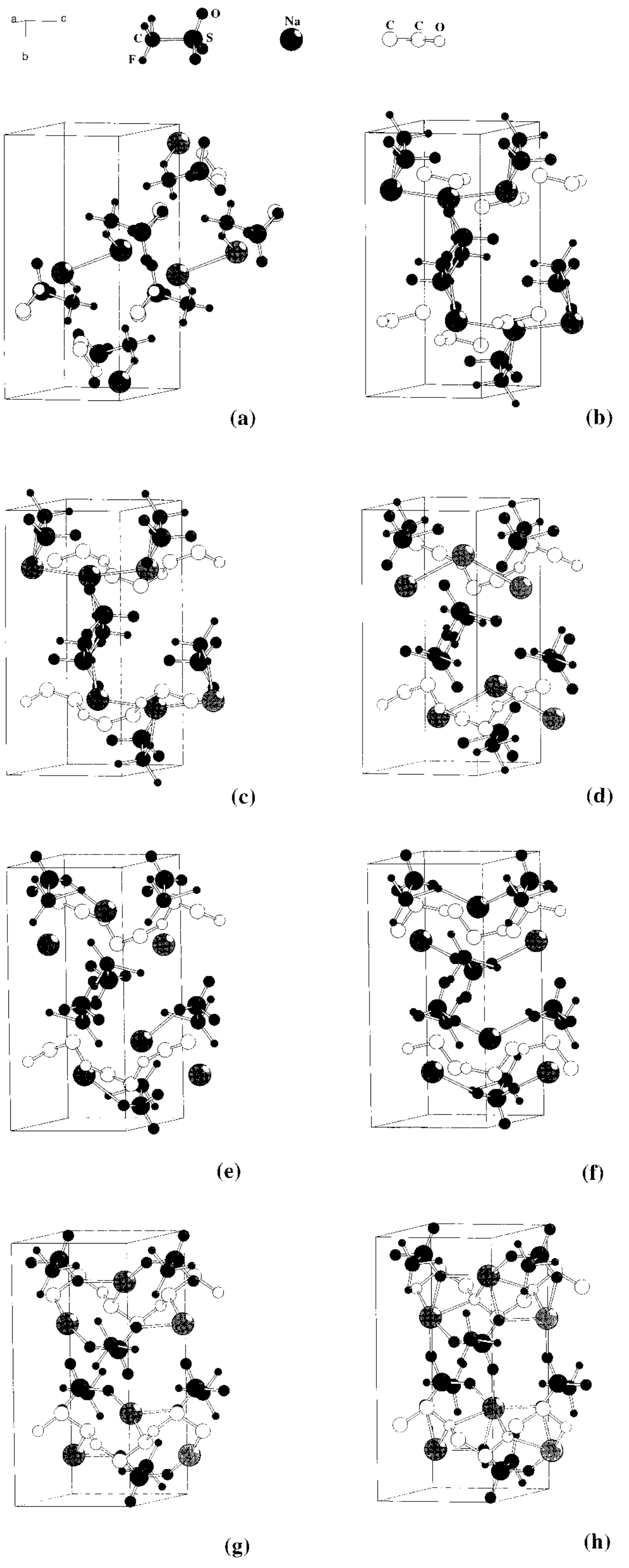

FIG. 2. Structural models of poly(ethylene oxide):$NaCF_3SO_3$ at consecutive stages of structure solution and refinement. Hydrogen atoms are not shown. Bonds between atoms are drawn when interatomic distances become less than the sum of corresponding van der Waals radii. Solid lines show the edges of the unit cell. See text for details.

individually, while the stereochemical configuration of the constituent moieties was preserved by introducing an additional punishment term in the figure-of-merit function for the least-squares procedure. Thus at each iteration selected interatomic distances were recalculated via the new set of coordinates and the target function was vastly multiplied if their values fell beyond preset limits. Such constraints, unlike the first MC procedure, force distances and angles to vary only within predetermined limits with all like distances and angles not necessarily equal in this case. The refinement significantly improved the fit [Fig. 1(d)], although the structure did not change substantially [Fig. 2(d)], the most significant change being in the position of Na^+ in the asymmetric unit. Despite the better fit, all attempts to improve it further by refinement failed. The best χ^2 value which could be obtained was 6, and this was associated with a noticeable misfit in the 2θ range from 35° to 45°. The unsatisfactory fit of the calculated pattern to the observed was not the only indicator that the correct structure had not been yet obtained. The refined model placed the fluorines rather than the oxygens of the triflate anion adjacent to the Na^+ cation [Fig. 3(a)]. This contradicts the expected coordination based on the charge distribution within the $(CF_3SO_3)^-$ ion. Calculations place the negative charge mainly on the oxygens.[11] Furthermore, a survey of the known poly(ethylene oxide)-based polymer electrolytes containing triflate salts indicates that the ether oxygens rather than the carbons invariably coordinate the cations. Such a coordination is also supported by computations which localize a certain amount of negative charge on the oxygens of the poly(ethylene oxide) chain.[12] There was no evidence of this favorable coordination in the structural model obtained. In addition, the Na^+ ions were only 3.26 Å apart from each other, which is hardly possible because of the Coulombic repulsion. Further evidence indicating the inappropriateness of the structural model was found in the value of the mean-square displacement amplitude for the oxygen atom in the polymer chain; this appeared to be a complex number.

Attempts to pursue the refinement approach by inverting the triflate anion thus placing the SO_3 moiety next to the Na^+ ion failed to improve the situation. The resulting model [Fig. 2(e)] exhibits much the same quality of fit [Fig. 1(e)]. Although the separation of the neighboring sodiums was improved, the displacement amplitude turned out to be a complex number for both the chain oxygen and the carbon atom in triflate.

In such a situation when two different structural models give approximately the same reasonable but not satisfactory quality of fit to the experimental data, it is likely that multiple minima of the χ^2 occur in crystallographic space. In each case the least-squares procedure located the nearest minimum which was not the deepest. This in turn applies to the MC run which had failed to place the structure near the global minimum of χ^2 (Ref. 13) presumably because of insufficient flexibility of the triflate in which all like distances and angles were restricted to be equal. Some idea of the impact such an averaging might make can be gained from comparison of the fits presented in Figs. 1(c) and 1(d). We therefore returned to the MC procedure, but now allowing all distances and angles in the triflate to vary independently. During this run, 37 parameters were varied in the same ran-

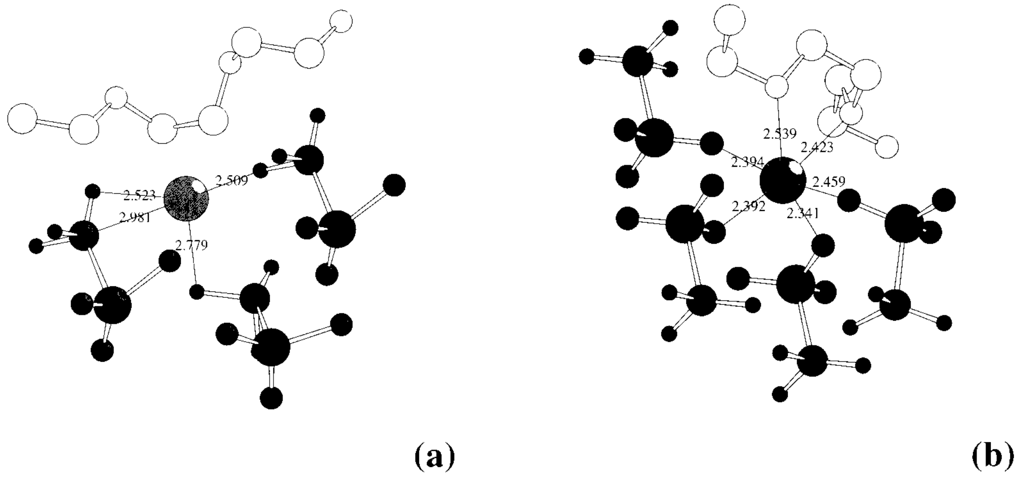

FIG. 3. Coordination around the sodium ion in the intermediate (a) and the final (b) structural model of poly(ethylene oxide):$NaCF_3SO_3$. Hydrogen atoms are not shown. Bonds between atoms are drawn when interatomic distances become less than the sum of corresponding covalent radii. Numbers indicate distances in Å between the sodium ion and its nearest neighbors. See text for details.

domized fashion as the first MC run with continuity of the poly(ethylene oxide) chain imposed. The resulting structural model is shown in Fig. 2(f). This MC run further increased the separation of the Na^+ ions, simultaneously coordinating them by the oxygens belonging to the surrounding triflates and those of the polymer chain. Subsequent refinement further improved the quality of fit [Fig. 1(f)], especially in the 2θ region where it was particularly poor before and resulted in a $\chi^2=3.0$. However, the Na^+ ions in this model [Fig. 2(g)] were also coordinated by the chain carbons rather than the oxygens. After reversing the ordering of atoms in the chain backbone within the asymmetric unit and carrying out one further refinement run, the Na^+ ions appeared to be neatly coordinated by six equidistant oxygens [Figs. 2(h) and 3(b)]. The quality of the final fit is excellent [Fig. 1(g)] (Ref. 14) with $\chi^2=1.1$ in 2θ range 8°–85° and all the displacements amplitudes are real numbers. Such a result gives confidence in the validity of the final structural model. Atomic coordinates and displacement factors are listed in Table I together with profile-defining parameters.

III. CRYSTAL STRUCTURE

Although determined without any reference to the structures of other polymer electrolytes, the crystal structure of PEO:$NaSO_3CF_3$ is found to be similar to PEO:NaSCN.[15] In both cases the structures are distinctive when compared with the more well-studied 3:1 and 4:1 complexes.[16–18] In every 3:1 and 4:1 complex investigated to date, a helical PEO chain is ubiquitous with all C-O bonds adopting the *trans* (t) conformation and with C-C bonds either *gauche* (g) or *gauche*-minus ($\bar{g}$). The 3:1 complexes exhibit the repeat $ttgttgtt\bar{g}$, while 4:1 is $ttgttgtt\bar{g}tt\bar{g}$. In contrast, the PEO chain in the 1:1 complexes adopts a stretched zigzag conformation running along the c axis of the unit cell, in which the C-O bonds are either *trans*, *gauche*, or *gauche*-minus and the C-C bonds are either *gauche* or *gauche*-minus, i.e., $tggt\bar{g}\bar{g}$. There are two such chains in parallel, associated with each cell. Like the 3:1 and 4:1 complexes, each Na^+ ion is associated with only one chain, i.e., there is no interchain cross-linking by the cation. However, unlike the 3:1 or 4:1 complexes, the zigzag PEO conformation is unable to envelop the cations. In PEO_3:$NaClO_4$ each Na^+ ion is coordinated by ether oxygens from the chain and one oxygen from each of two ClO_4^- anions. Na^+ ions in PEO:$NaCF_3SO_3$, in contrast, are coordinated by two ether oxygens of the chain separated by one C-C bond. The Na^+ ions form two zigzag rows in each cell running parallel to the PEO chains. The anions may also be described as forming two zigzag rows within each cell, and these are parallel to the PEO chains and Na^+ rows. Four $CF_3SO_3^-$ anions coordinate each Na^+ ion with one oxygen from each anion being directly coordinated to the sodium, yielding a total coordination of six oxygens around the sodium. All three oxygens of the SO_3 group are involved in coordinating the Na^+ ions. Two oxygens, O(1) and O(3) in Table I, each coordinate a Na^+ ion, whereas the third oxygen, O(2), coordinates two Na^+ ions simultaneously, both of which belong to the same row of Na^+ ions. The O(1) oxygen coordinates a Na^+ ion, which belongs to a different row from those to which the O(2) and O(3) oxygens are linked.

In the 3:1 and 4:1 complexes, each PEO chain is associated with a dedicated set of cations and anions, thus forming an isolated unit from the neighboring chains. In particular, there is no ionic cross-linking. In the 1:1 complex, the anions cross-link by simultaneously coordinating Na^+ ions that are themselves coordinated to neighboring PEO chains. Such interchain cross-linking provides an explanation, at least in part, for the much higher melting point of the PEO:$NaSO_3CF_3$ complex (melting point 330 °C) compared with PEO_3:$NaClO_4$, which melts incongruently at 150 °C. In the latter case only weak van der Waals interactions between neighboring chains must be overcome to achieve the molten state.

IV. CONCLUDING REMARKS

The present example of a structure solution by minimizing residuals of a full-profile fit to an experimental powder-diffraction pattern clearly shows that the simulated annealing method presented here is capable of finding the right structural model in a situation when only an approximate stereochemical configuration of constituent molecular fragments is known from the outset. At first glance the new structure solved is less complicated than that of poly(ethylene oxide)$_3$:LiN(SO$_2$CF$_3$)$_2$, as far as the number of nonhydrogen atoms in the asymmetric unit is concerned (12 versus 25). However, this is not the case when the number of parameters varied in a randomized fashion (37 versus 36) is considered. Unlike the previous structure solution, the concept of treating all like distances and angles as equal during the MC run was misleading. This is at first sight surprising since the same constraints were used for finding the internal configuration and position of the imide ion N(SO$_2$CF$_3$)$_2^-$ in the structure of the previously solved polymer/salt complex with almost twice as many all like distances and angles as in triflate set to be equal. Further, all like distances and angles within the helical conformation of the poly(ethylene oxide) chain were treated as equal during the MC run in the former case. Nevertheless, the distribution of the scattering power among the constituent atomic species in the case of poly(ethylene oxide):NaCF$_3$SO$_3$ was such that a random search using the constrained model of the triflate was biased from the start and could not possibly give the correct solution.

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