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Modelling lithium ion transport in helical PEO by ab initio calculations

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Abstract

Several potential energy surfaces were calculated for a lithium ion inside a helix of poly (ethylene oxide) (PEO). The calculations were ab initio calculations at the Hartree–Fock level of theory employing the 3-21G* basis set. The model system used was a methyl terminated oligomer chain of PEO, $CH_3O(CH_2CH_2O)_{12}CH_3$. A general chain geometry was used, approximate to that of several experimentally determined crystalline structures of $MXPEO_3$. Preferred lithium ion positions at different levels of intrusion into the PEO helical structure and energy barriers for ion transport inside the helix were calculated. The binding energies were further evaluated using DFT methods, B3LYP/6-31G*//HF/3-21G*, and compared to previously calculated values for coordination of lithium in low M_w PEO oligomer systems. The present results suggest that $LiXPEO_3$ crystalline complexes are poor ion conductors not due to high coordination strengths, but rather due to the high energy barriers, >43 kJ mol^{-1}, and the need for a co-operative motion of lithium ions between the preferred sites. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: PEO; Polymer electrolytes; Ion transport

1. Introduction

Solid polymer electrolytes (SPEs) made from poly (ethylene oxide) (PEO), polymers or oligomers are of great interest for modern electrochemical applications such as high energy density batteries (e.g. lithium-polymer batteries) and electrochromic devices [1]. However, the usage of long-chain PEO or modest chain-length PEO has the disadvantage of the mixed amorphous and crystalline state of the systems, reaching a maximum for pure PEO at $M_w \sim 6000$ Daltons [2].

The equilibrium between crystalline and amorphous regions in the PEO is changed when an inorganic salt, often with a lithium cation, is dissolved into the polymer, creating a SPE. New crystalline complexes may appear or almost completely amorphous materials can be obtained by choosing an appropriate salt and concentration, even at room temperature. The complex multiphase morphology behaviour is from a scientific point of view troublesome, most measurements do not reveal the phases' properties separately, but rather averages or superpositions.

One of the most important properties of the SPEs is ion conductivity. Consensus is now that ion conduction take place mainly in the amorphous regions, as first shown by Berthier et al. [3], but early in the history of the SPEs ion transport inside crystalline PEO-helices was believed to be the prime contributor [4]. Crystalline salt–polymer phases are thus considered the main obstacles lowering the ion conduction. However, mechanical properties may benefit from crystalline phases being present and they may also serve as useful salt reservoirs in the systems. We feel that the question *why* the crystalline regions do not conduct ions has been somewhat neglected. Some insight was, however, given by Wright et al. by their studies on $NaIPEO_3$ [5,6]. The main conclusion from those studies is that the intra-helical contribution to the 'locking' of the cation is substantially larger than the inter-helical. An excellent discussion on conduction in the crystalline phase can be found in Ref. [7]. However, these studies do not deal with lithium as the cation and there is no quantitative comparison with amorphous phase results.

Two important crystal structures of PEO and lithium salts with large and highly 'non-coordinating' anions, both with an ether oxygen/lithium ratio of 3, have been determined by the St Andrews group: $LiCF_3SO_3PEO_3$ [8] and $Li[N(CF_3SO_2)_2]PEO_3$ [9]. Both these structures have helical PEO units. Furthermore, by melting the crystalline $LiCF_3SO_3PEO_3$, an amorphous sample with about the same local structure has been obtained [10]. In the crystalline

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structures, the lithium ion is coordinated by three consecutive ether oxygen from the same PEO strand and the total coordination number for lithium is five. Our model for studying the lithium ion coordination in helical PEO uses these observations.

A previous work dealing with the intra-helical transport of Li^+ (and Cu^{2+}) inside a PEO-helix by ab initio molecular dynamics has been reported [11]. However, the study deals with transport inside a PEO-helix with the conformational sequence of pure crystalline PEO, and not the conformation found in the $MXPEO_3$ complexes. The main advantages of that work are that the calculations are made on a neutral system, and that the helix is relaxed, and thus provides a better coordination environment for the cation. In many other respects, the methodology is similar to the present work.

However, in the present study we use an idealised static conformation of a PEO-oligomer chain, similar to the experimentally determined for $MXPEO_3$ systems, in which a lithium ion is systematically placed at different positions. The most favourable positions of the lithium ion are located and evaluated. Since the calculations do not include any anion, the usage of the exact geometry of the PEO chain from any of the above mentioned structures would be of less value as a general information source. A general PEO-helix does, however, give elementary information about the lithium ion coordination. The calculations were ab initio molecular orbital calculations on 1:1 complexes of $Li^+–CH_3O(CH_2CH_2O)_{12}CH_3$.

2. Calculational method

A methyl-end-capped PEO-oligomer, 'dodeca-glyme', ($CH_3O(CH_2CH_2O)_{12}CH_3$), with the conformation sequence (TTG^+ TTG^+ TTG^-) (T = *trans*, G = *gauche*) was used as the model system (Fig. 1). This conformation is reported for the crystal structures of $NaIPEO_3$ [12], $NaClO_4PEO_3$ [13], $NaSCNPEO_3$ [14], $LiCF_3SO_3PEO_3$ [8] and $Li[N(CF_3SO_2)_2]$-PEO_3 [9]. The values used for the dihedral angles C–C–O–C and C–O–C–C (T) and O–C–C–O ($G^{+/-}$) were fixed to 180° and ±50°, respectively. All internal atomic distances and angles in the helix were kept at fixed values (Table 1). The model system completes two full turns of the helix.

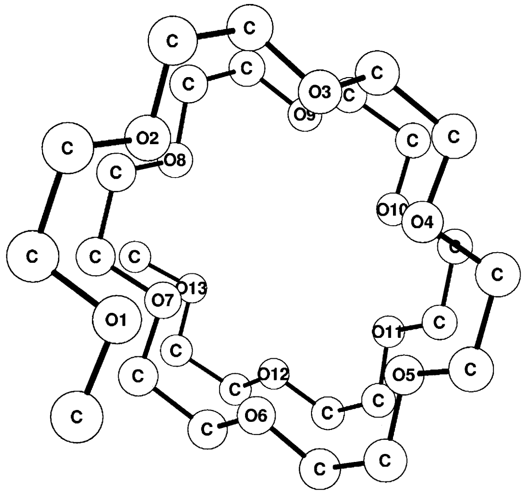

Fig. 1. The geometry of the model compound, $CH_3O(CH_2CH_2O)_{12}CH_3$, used in the study. Hydrogen atoms omitted for clarity.

Table 1
Fixed geometry parameters for the PEO-helix

Bond lengths (*r*) in Å and angles (*a*, dh) in degrees	
r(C–H)	1.096
r(C–O)	1.410
r(C–C)	1.531
a(H–C–X)	109.47
a(C–O–C)	105.00
a(O–C–C)	105.00
dh(O–C–C–O)	(±)50
dh(C–O–O–C)	180.00
dh(C–O–C–C)	180.00

The lithium ion was positioned inside the PEO-helix using a volume-grid, $2.0 \times 2.0 \times 6.0$ Å^3, with a resolution of 0.5, 0.5, and 1.0 Å in the x, y and z directions, respectively (Fig. 2). The z-axis was set parallel to the helix and the first xy-plane ($z = 0$) at the base of the helix. The total number of grid-points was thus $5 \times 5 \times 7$. These positions for the lithium ion were evaluated by single-point energy calculations using ab initio Hartree–Fock (HF) self-consistent field molecular orbital methods employing the 3-21G* basis set. After evaluating the results from the volume-grid, an additional xy surface for $z = 4.5$ Å was calculated. For a full optimisation (HF/3-21G*) of the lithium ion position several

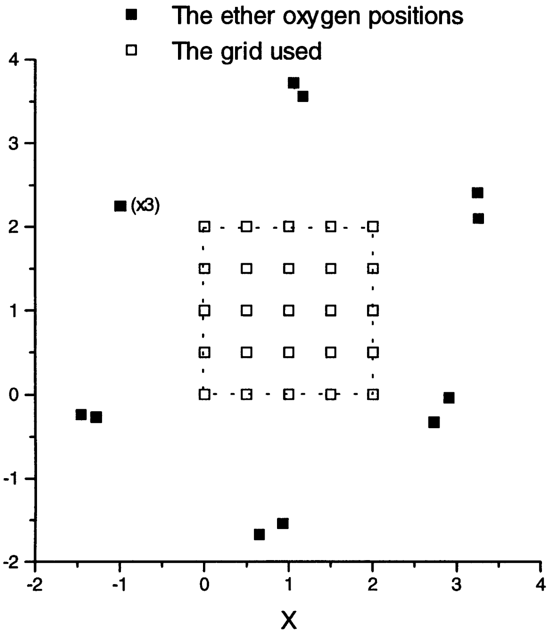

Fig. 2. The grid used for positioning the lithium ion inside the PEO-helix.

different starting positions were used, and all atoms except the lithium ion were kept fixed.

The optimum usage of computational resources suggests employing DFT methods to finally evaluate the energies and using a rather small basis set for the, in this case partial, geometry optimisations by HF methods [15]. Due to the size of the system the energies were finally evaluated using DFT methods (B3LYP/6-31G*//HF/3-21G*). The binding energies are defined as $E(\text{bond}) = E(\text{Li}^+\text{-helix}) - (E(\text{Li}^+) + E(\text{helix}))$. All calculations were made using the GAUSSIAN94 program [16].

3. Results and discussion

3.1. Potential energy surfaces

Consider a slice of the volume-grid in the *xy* plane at $z = 0$ and the corresponding potential energy surface resulting from moving the lithium ion in that plane. The lithium ion position with the lowest energy is found for $x = 0.5$ and $y = 1.0$ (Fig. 3). This position corresponds to the first step of introducing a lithium ion into the helical PEO-model. By following the *z*-axis in the positive direction we mimic a higher level of intrusion into the PEO-helix cavity, a similar concept is used in Ref. [11].

From the potential energy surfaces the preferred lithium ion positions, lowest energies, in each *xy*-plane are extracted (Fig. 3). The preferred positions follow the inside of the helix as it turns and thereby the lithium ion gets bi- or tri-dentately coordinated by the ether oxygen. The total and relative energies for the optimum position in each *xy*-plane are listed in Table 2. The differences in energies between the preferred positions in the different *xy*-planes are rather high (Table 2). However, it seems logical that the *xy*-planes with higher values of *z* get on average lower energies, as more oxygen are brought in the vicinity of the lithium ion.

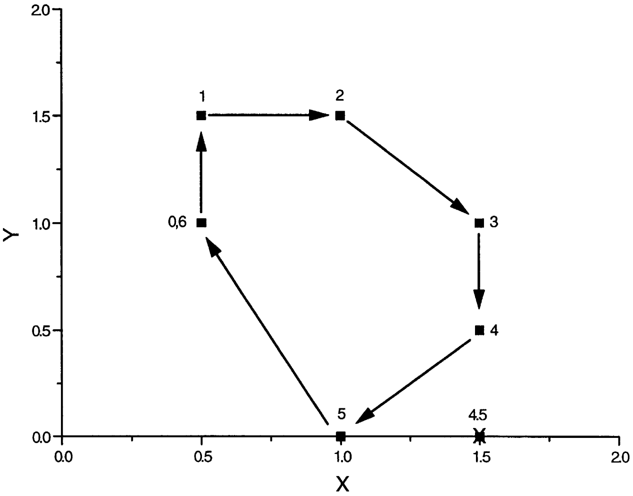

Fig. 3. The preferred positions for the lithium ion in the different *xy* planes. ($z = 0 - 6 + 4.5$).

3.2. Lithium ion coordination

The starting grid, with a resolution of 1.0 Å in *z*, revealed that the optimum coordination site for the lithium ion was likely to be found between $z = 4$ and $z = 5$ (Table 2). Therefore, an additional surface for $z = 4.5$ was calculated. In Fig. 4 the local coordination of lithium for $x = 1.5$, $y = 0.0$, $z = 4.5$ is shown, the position with the lowest energy and thus the highest bond energy (Table 2). The cation–oxygen distances are 1.86, 1.84, 2.89 and 2.94 Å, thus a bi-dentate structure, in agreement with the work of Palma et al. [11]. They report their two minima to be bi-dentate with average distances Li–O = 1.9 Å. Comparable distances from Ref. [8] are 1.72, 2.01, and 2.38 Å and from Ref. [9]; 2.12, 2.16 and 2.20 Å. All other lithium–ether oxygen distances are >3.0 Å, i.e. outside the first coordination sphere of the lithium ion. The binding energy is 436 kJ mol^{-1}, which is comparable to the values

Table 2
Total, relative and bond energies

Grid point			HF/3-21G* and **B3LYP/6-31G*//HF/3-21G***		
z	*x*	*y*	Energy (au)	ΔE (kJ mol^{-1})	*E* (bond)[a] (kJ mol^{-1})
0.0	0.5	1.0	−1985.183282	243.9	435
1.0	0.5	1.5	−1985.226051	131.7	547
2.0	1.0	1.5	−1985.235686	106.4	572
3.0	1.5	1.0	−1985.229775	121.9	556
4.0	1.5	0.5	−1985.248159	73.6	605
5.0	1.0	0.0	−1985.248389	73.0	606
6.0	0.5	1.0	−1985.235614	106.5	572
4.5	1.5	0.0	−1985.251853	63.9	615
			−2008.350535	**45.0**	**436**
	Fullopt		−1985.276181	0.0	679
			−2008.373920	**0.0**	**481**

[a] E(Li^+) = −7.187095 (**−7.284544**) and E(helix) = − 1977.830432 (**−2000.905988**).

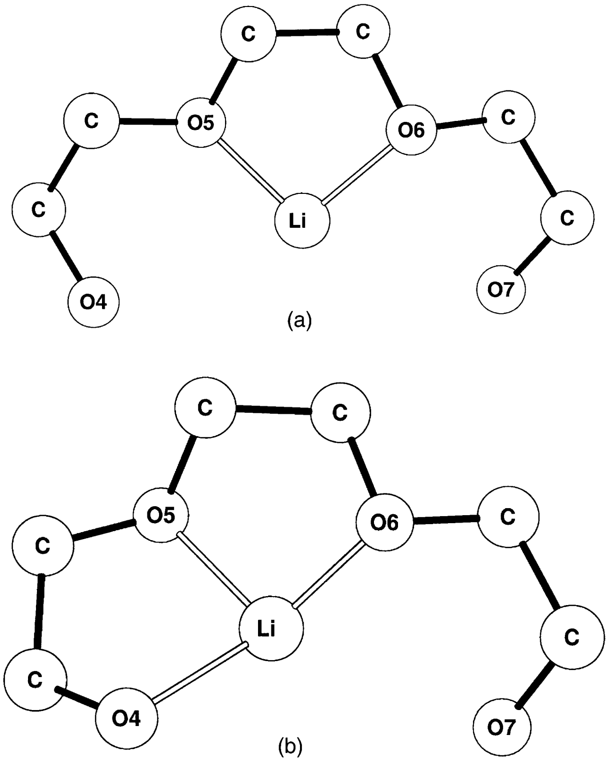

Fig. 4. (a) The local coordination geometry of the lithium ion at $x = 1.5$, $y = 0.0$, $z = 4.5$. (b) The local coordination geometry of the lithium ion after the full position optimisation. Hydrogen atoms omitted for clarity.

for the tri-dentate Li^+–$CH_3O(CH_2CH_2O)_2CH_3$ complexes, ~430 kJ mol^{-1}, calculated by us previously [17,18]. It is also clearly lower, by 1–200 kJ mol^{-1}, than binding energies calculated for tetra- [18,19], penta- and hexa-coordination [18] of lithium by flexible PEO-oligomers. In Ref. [11] no binding energies were reported.

A full geometry optimisation of the lithium ion position, with all other atoms fixed, results in a local coordination as depicted in Fig. 4(b). The energy is listed in Table 2. Cation–ether oxygen distances for this geometry are 1.77, 1.93 and 2.00 Å, clearly in better agreement with the experimentally determined structures. The binding energy is 481 kJ mol^{-1}, which is ~50 kJ mol^{-1} lower than for tetra-dentate coordination of lithium by a flexible PEO-oligomer [18], but also ~50 kJ mol^{-1} higher than for tri-dentate coordination [17,18]. Thus the non-coordinated oxygen also contributes to the binding energy, or the helix itself provides a lower energy position for the lithium ion than the flexible glymes do. The latter may be due to the presence of methyl end-groups close to the coordinating oxygen in case of the glyme models, which may cause steric hindrances.

Each move in the z-axis direction, and the resulting minimum energy positions, can be compared to the bifurcation point observed in Ref. [20]. Relaxation from the bifurcation point for the Li^+–diglyme system results in two *energetically* equivalent tri-dentate structures, but with unique lithium positions if a longer chain system is taken as reference.

3.3. Lithium ion transport or not?

As mentioned in Section 1, the ion conduction takes place mainly in the amorphous phase. Why is there no ion conduction in the crystalline phase? The results above show that the coordination strength to the helical polymer in fact is lower than for a lithium ion coordinated by a flexible PEO-oligomer. This may be an effect of the exclusion of an anion in the model, too low coordination number, but the lower ion conduction may also be explained from more general physical chemistry. The ion conductivity should depend more on the energy barriers to overcome, than on the binding strengths in the stable positions. Our model allows us to estimate those barriers using the present potential energy surfaces.

The preferred grid-position for the lithium ion is (1.5, 0.0, 4.5). The next equivalent position occurs at $z = 6.5$ since there is symmetry in the helix conformation about the O6–C–C–O7 dihedral angle (G^-) and one full turn of the 7/2 helix is ~6.0 Å along z. The second next equivalent site is found at $z = 7.5$. The reaction path, or lithium ion movement, we want to consider can thus be simplified as passing $z = 4.5$ to $z = 6.0$, using the lowest energy points in each surface. This *very* simplistic path then uses only three unique points: (1.5, 0.0, 4.5), (1.0, 0.0, 5.0) and (0.5, 1.0, 6.0). Thus, using the values in Table 2, the energy barrier to overcome is ~43 kJ mol^{-1} for each step of 2.0 Å along z. If the fully optimised lithium ion position is used the value rises to ~100 kJ mol^{-1}.

In reality, apart from likely anionic interaction, this next site ($z = 6.5$) may already be occupied by a lithium ion. But, using the stoichiometry of O/Li = 3 and the structural helix data, the distance Li–Li should be ~3.0 Å along z, and therefore this site ideally should be empty. However, it is very close to the next, presumed occupied, site at $z = 7.5$, which certainly makes ion transport less probable, as some co-operative mechanism is required.

The present value of ~43 (100) kJ mol^{-1} for the activation energy should be compared to that of the amorphous phase, measured by pfg-NMR to be ~38 kJ mol^{-1} [21] for $LiTFSIPEO_{10}$. Our value is thus higher, which agrees with the notion of less ion conduction in the crystalline phase. Palma et al. report closer values to the experiment cited above, and thus seem to mimic the *amorphous* phase of lithium salt/PEO systems better. However, our model does seem to partially explain why the *crystalline* phase has significantly lower ion conductivity than the amorphous phase, even if it clearly is (too) simple and can be expected to have serious quantitative errors.

4. Conclusions

The lithium ion is bi- or tri-dentately coordinated by the ether oxygen within the PEO helix in each *xy*-plane calculated, in agreement with the relevant crystal structures. The binding energy is comparable to that from calculations on Li^+–diglyme tri-dentate complexes. A complete optimisation of the lithium ion position resulted in binding energies much lower than those obtained for lithium ions coordinated to flexible oligomers of PEO, but higher than those for the specific coordination number (3). Even if the energy barriers between the preferred sites seem to be one cause for the low ion conductivity in the crystalline systems, the need for a co-operative mechanism in the ion conduction may be a more severe restriction.

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