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First principles modelling of amorphous polymer electrolytes: Li^+–PEO, Li^+–PEI, and Li^+–PES complexes

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Abstract

Several structures of the 1:1 (cation:molecule) complexes of a lithium ion with linear oligomers, $CH_3X(CH_2CH_2X)_nCH_3$, ($n = 0$–5; X = O, NH or S) have been shown to be stable with ab initio calculations at the Hartree–Fock level of theory employing the 6-31G* basis set. Total energies and binding energies were further evaluated using single-point density functional theory calculations (B3LYP/6-311++G**//HF/6-31G*). The total binding energy is found to increase with increasing glyme length and follows: NH > O > S. The binding energy for the different glymes reaches a maximum of ~582 kJ mol^{-1} for the Li^+–PEI pentaglyme ($n = 5$, X = NH) complex. From the present results we conclude the donicity of the heteroatom to be the dominant factor for the relative coordination strength, further supported by the suitability of the coordination geometry provided. Furthermore, transition states and associated energy barriers have been calculated for the conformational changes leading to changes in coordination number for lithium from three to two. The large energy barrier decreases as: O > NH > S. Implications for lithium ion transport and lithium salt solvation are discussed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ab initio; Polymer electrolytes; Ion transport

1. Introduction

Polymer electrolytes (PEs) based on poly ethylene oxide (PEO), $(CH_2CH_2O)_n$, polymers and/or oligomers and a lithium salt are of great interest in the context of developing modern and environmentally friendly large secondary lithium batteries and of fundamental scientific interest [1–3]. Some examples of current technological developments beyond the pure polymer/salt based electrolytes are polymer gel electrolytes or nano-particle modified PEs [1,2,4,5]. Regardless of choice of concept, these types of PEs to a large extent still rely on the ability of the repeated ethylene oxide unit to coordinate lithium cations. However, the lithium transference number in the pure PEs is often too low for technological applications due to strong lithium–oxygen interactions; the materials are in fact mainly anion conductors — not cation conductors [6]. A more labile lithium–polymer bond would be of interest for cation transport, but the interaction must clearly still be strong enough to solvate the salts by cation coordination.

According to the literature the ethers are expected to bind strongly to alkali metals on a 'hard and soft acid and base' (HSAB), basis, but the corresponding imine based polymers could compensate and perhaps even compete by a higher donicity [7]. However, the latter is believed to be more important for transition metals as the coordinated cations. Surprisingly no study dealing with this subject for multidentate species such as PEO, PEI $(CH_2CH_2NH)_n$ or PES $(CH_2CH_2S)_n$, on a molecular level exists. In this perspective it is a challenging task to find out the relative coordination strengths fragments or solvents of PEO, PEI and PES, impose on the lithium cations. Clearly not only the type of electronegative centres matters, their interspacing drastically impact the coordination strength, e.g. $(CH_2O)_n$ (PMO) and $(CH_2CH_2CH_2O)_n$ (PTMO) are both poor solvents compared to $(CH_2CH_2O)_n$ [7]. Further differences might also influence, as in the present case with other electronegative centre atoms, i.e. N or S, resulting in other backbone bond lengths and angles.

Early experimental studies using both linear and branched PEI doped with NaI or $NaCF_3SO_3$ reported lower conductivities than the corresponding PEO-complexes [8–10]. Extensive H-bonding was suggested in the low salt concentration mixtures as well as in the pure polymer, and also a delicate crystalline/amorphous phase balance. In 1993 a similar study with $LiClO_4$ and $LiCF_3SO_3$ as dopants was reported with similar conclusions [11]. A study on Ag coordination to PES has also been undertaken [12]. No systematic study has been performed.

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The salts used in PEs preferably have weakly coordinating anions like BF_4^- or $[(CF_3SO_2)_2N]^-$ (TFSI) to decrease the cation–anion interactions. Such interactions are routinely monitored by molecular spectroscopy, but the corresponding cation–polymer interactions are more demanding and less conclusive experimentally. It is, therefore, interesting to computationally investigate solely and single-handedly how different cations, and then especially lithium ions, are coordinated to polymers and hereby gain information about the ion–polymer complex energetics in these systems.

The so-called tetraglyme[1], $CH_3X(CH_2CH_2X)_nCH_3$ ($n = 4$) should be the preferable oligomer models for quantum mechanical studies since lithium is coordinated by five ligands in the first solvation shell in water [13] and calculational results for different ether oxygen containing ligands, including PEO, also suggest a coordination number (CN) of four to five for lithium [14,15]. For computational reasons we here focus on the relative differences (for choices of X) and limit the study to one complex each for $n = 4$ and $n = 5$ — the most stable ones from [15] — but several for $n = 2$–3.

The situation in the amorphous PE systems clearly differs from the known crystal structures e.g. $(PEO)_3LiCF_3SO_3$ [16] and $(PEO)_3Li[N(CF_3SO_2)_2]$ [17]. In these two structures two of the five oxygens coordinating lithium derives from the anions and steric constraints may be imposed. On the contrary, in the amorphous systems in general the O/Li ratio is much higher and thus tetra- or penta-coordination by only ether oxygens or other electronegative X-groups such as -NH- or -S- is suggested. In the context of the local environment of the lithium ion in the amorphous systems, all possible local stable or metastable structures of Li^+–polymer complexes are of interest as well as the transitions between such structures [18]. Therefore the present study also includes calculated transition states (TSs) for such conformational changes and their associated energy barriers.

A series of model calculations on small PEO oligomers coordinated to metal ions have previously been made [15,18–20]. These calculations were motivated by the need to have additional data, including bonding energies and total energies, on complexes with equilibrium geometries which may not be present in any crystal, but still might be possible in amorphous systems. The present work extends these calculations to include PEI and PES oligomers as the lithium ion coordinating species. Ab initio molecular orbital calculations were performed on 1:1 (cation:molecule) complexes of mono- (M), di- (D), tri- (T), tetra- (Te), and penta- (P) ethylene "glycol" dimethyl ethers, imines and sulfides/thio-ethers with lithium ions.

2. Calculational method

Semi-empirical PM3 calculations, ab initio Hartree–Fock (HF) self-consistent field molecular orbital calculations and density functional theory (DFT) calculations have been performed using the TITAN program [21]. Initial calculations on the starting geometries were made with the semi-empirical PM3 method for Li^+–PEI and Li^+–PES. For Li^+–PEO the geometries from [15,18–20] were used directly. The subsequent final geometry optimisations at HF level used the standard 6-31G* basis set. Vibrational frequency calculations were performed at this level of theory to confirm that the structures obtained were true minima. The optimum usage of computational resources suggests employing DFT methods with large basis sets to finally evaluate the energies, while using a rather small basis set for the geometry optimisations of these floppy and highly flexible systems by HF methods [22]. The energies were therefore finally evaluated by single-point calculations using a larger basis set and gradient corrected DFT methods, Becke3–Lee–Yang–Parr, (B3LYP/6-311++G**//HF/6-31G*) [23,24]. The binding energies are defined as ΔE (bind) $= E$ (Li^+-complex) $-$ [E (glyme (in the complex geometry)) $+ E$ (Li^+)]. Stepwise binding energies are defined as $\Delta\Delta E$ (bind) $= \Delta E\ (\text{bind})_{CN=n} - \Delta E\ (\text{bind})_{CN=n-1}$.

Suitable starting geometries for the cation–oligomer complexes have been selected on the basis of earlier calculations on Li^+–PEO complexes [15,18–20]. The geometries and conformation sequences of the oligomers are thus reported and will not be repeated in full here. For clarity, however, a brief outline of how the complexes were obtained follows: for Li^+–diglyme three different stable complexes were found [19] and also two TSs for conversion between bi- and tri-dentate lithium ion coordination [18]. The diglyme in the conformation $aG^-a\ aG^+a$, referred to as structure **1**, has a sequence of three ether oxygen atoms suitably arranged for coordination to a metal ion. Structure **1** can be considered as a fragment of a general crown ether which has alternating aG^-a and aG^+a conformations. The longer glymes (T and up), are combinations of structures **1** and **2**, while M1 (monoglyme) is a simple aG^+a structure. By changing one of the O–C–C–O dihedrals in **1** from G to a a bidentate complex was obtained [18], and subsequently the TS for this intramolecular reaction. The TS was characterized by a vibrational frequency calculation which yielded one imaginary frequency. The same procedure is utilized in the present work for Li^+–PEI and Li^+–PES.

Additional calculations on Li^+–(CH_3–X–CH_3) complexes were added to calculate the coordination strength without multidentate coordination.

We do not suggest that this study fully covers all the possible complexes of these highly flexible systems — to find all of these would be a truly demanding task. Still, we believe our selection of complexes provides results that are relevant to the comparison of coordination strengths and to the complete set of stable complexes.

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[1] A little sloppily we here refer to all these oligomers as "glymes" although it is commonly only the ethers (X = O) that are meant.

Table 1
Energies and selected geometry parameters for the Li$^+$–PEO complexes

	HF/6-31G*				B3LYP/6-311++G**//HF/6-31G*	
	Av. r (Li$^+$–O) (Å)	CN	E (au)	ΔE bind (kJ mol^{-1})	E (au)	ΔE bind (kJ mol^{-1})
M1	1.879	2	− 314.322049	305	− 316.340745	287
D1	1.931	3	− 467.269858	412	− 470.247539	382
D2	1.933	3	− 467.266816	408	− 470.244584	380
T1	1.982	4	− 620.207099	499	− 624.143096	457
T2	2.008	4	− 620.206819	497	− 624.142549	455
T3	1.993	4	− 620.208577	500	− 624.144647	458
T4	2.014	4	− 620.210367	501	− 624.146507	458
Te9	2.06	5	− 773.140239	566	− 778.035028	517
P7	2.222	6	− 926.060497	596	− 931.916374	543

3. Results and discussion

3.1. Li$^+$–PEO complexes

Selected geometry parameters and energies of the obtained complexes, M1–P7, are presented in Table 1. The total Li$^+$ binding energies are shown in Fig. 1a and b. Fig. 2 shows the P7 complex with a distorted trigonal prism geometry (C_2) — basically the same as in [15], although now optimized with a larger basis set. The complexes show little variation in the lithium ion binding energy for a specific CN, but increases steadily reaching a maximum of 543 kJ mol^{-1} for CN = 6 (P7) (Fig. 1b). The P7 conformation was previously found to be the lowest energy conformation and to bind Li$^+$ strongest [15]. The average Li$^+$–O distances (for each CN) simultaneously increase from 1.88 to 2.22 Å, all in reasonable agreement with the experimentally observed values from neutron diffraction studies on LiI/PEO [25].

Although it is tempting to assume a conformation sequence for the glyme similar to that of a crown ether, as often suggested to be the case for Li$^+$–PEO and a commonly known fact, a previous calculation at HF/3-21G* showed that such a sequence ($aG^-a\ aG^+a\ aG^-a\ aG^+a$) is not stable for Li$^+$ as the coordinating cation [15]. However, we now re-calculated this complex starting at the HF/6-31G* level — and it is in fact a possible sequence. For the present purpose it does not however, provide any significant new data — the binding energy is lower than for the used P7 conformation (536 kJ mol^{-1}) — but is still important from a general complexation point of view.

3.2. Li$^+$–PEI complexes

Selected geometry parameters and energies of the Li$^+$–PEI complexes obtained, M1–P7, are listed in Table 2. In contrast to what was expected a priori the total coordination energy is higher for PEI than for PEO for each CN (Fig. 1a and b). This is true even for higher CNs where steric hindrances might be expected to occur for PEI i.e. for the P7 complex CN becomes 5 not 6 and the binding energy is 582 vs 569 kJ mol^{-1} for the Te9 complex (CN = 5). Note also that the P7 complex was chosen on the basis of the earlier results with PEO, which PEI should not unfairly benefit from. As mentioned in the introduction early attempts using PEI as solvent matrix for PE purposes showed lower ion conductivities than for the equivalent PEO samples [8–11] — and then interpreted as due to a higher contact ion-pair fraction or due to the higher viscosity. The discouraging ion conductivities effectively stopped further use and no progress was thus made for PEI as the matrix. Perhaps a better interpretation of the lower ion conductivity, in the light of the present results, is a stronger cation complexation.

3.3. Li$^+$–PES complexes

In Table 3 selected geometry parameters and energies of the Li$^+$–PES complexes obtained (M1–P7) are presented. A much weaker interaction with Li$^+$ (as expected) can be observed in Fig. 1a and b. This could be advantageous in the light of a more labile polymer–cation interaction providing higher cation transport numbers. The total binding energy reaches a maximum for the P7 complex; 433 kJ mol^{-1}, which is only 80% of the PEO value. No steric hindrances as for PEI can be observed for PES. However, there are severe question marks on the electrochemical stability of the C–S bond.

3.4. Comparison across the different Li$^+$–“glyme” complexes

The total bond energies as a function of glyme length ($n = 1 - 5$) are shown in Fig. 1a and b, allowing general statements about the Li–X binding strength in these systems to be made. The increase in the bond energy is almost linear for the $n = 1$–3 complexes, and the energy differences for a choice of X within the same CN are negligible ($n = 2, 3$). It seems clear, regardless of basis set and theory, that the

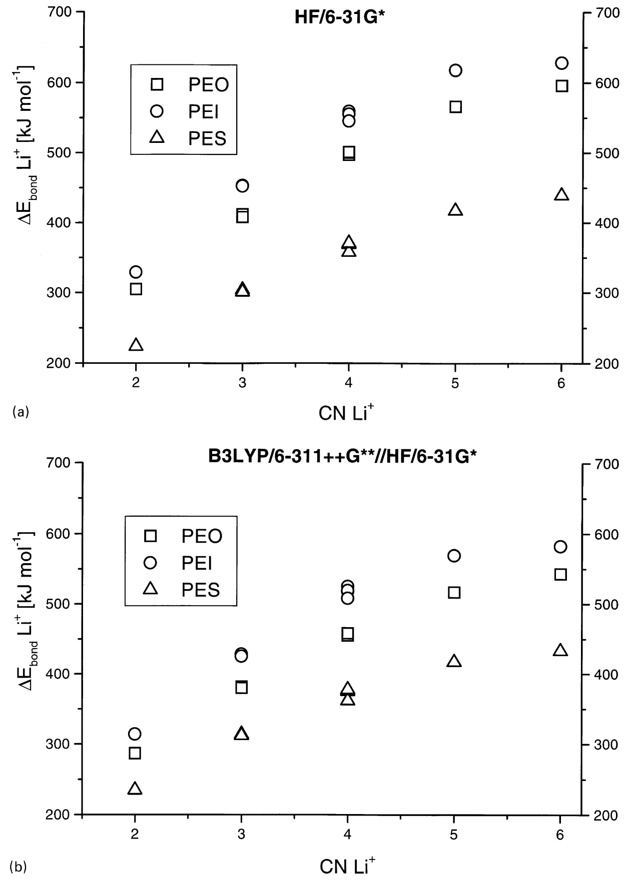

Fig. 1. (a) The total binding energies as a function of CN at HF/6-31G*. (b) The total binding energies as a function of CN at B3LYP/6-311++G**.

strength of Li$^+$ coordination is NH > O > S, contrary to the more expected O > NH > S.

It is important to stress that this result is only valid for Li$^+$ as the cation, a larger alkali cation (such as Na$^+$ or K$^+$ [20]) would perhaps introduce less strain in the PEO polymer backbone, with reference to the pure polymer. The latter should favour PEO before PEI; uncomplexed PEO optimized in structure **1** conformation has a O–C–C–O value of ~73° which should be compared to PEI's N–C–C–N dihedral: ~61°. For Li$^+$ as the complexing cation the PEO dihedral changes to ~49 compared to ~60° for the PEI dihedral. A much larger deviation from the uncomplexed equilibrium is thus required for PEO and Li$^+$. It therefore seems as when the complexing strength is to be evaluated in systems as these, not only the hardness or electronegativity of the heteroatom, or the donicity is crucial, but also the spatial arrangement of the complexing units.

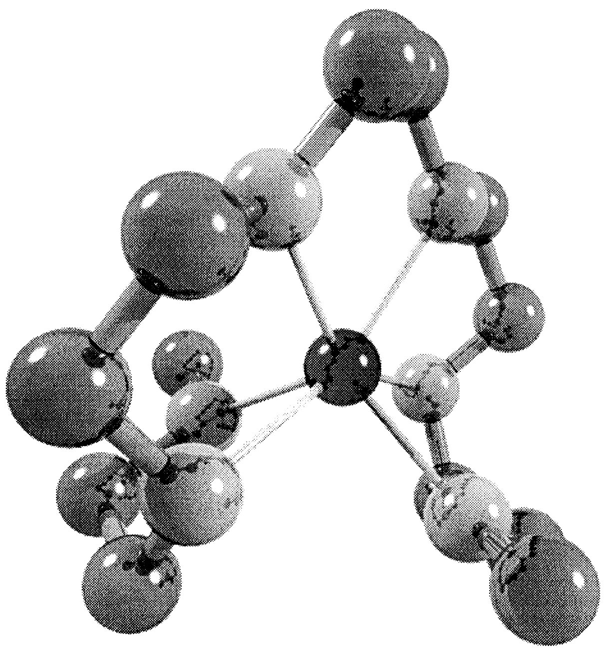

Fig. 2. The hexacoordinated Li$^+$–PEO P7 complex. Hydrogens omitted for clarity.

An obvious series of calculations to clarify the different sources relative importance is to further reduce the oligomer chain length by setting $n = 0$. Additional calculations were thus made on Li$^+$–(CH_3–X–CH_3). The results are summarized in Table 4. For $n = 0$ PEI still shows slightly higher Li$^+$ coordination strength than PEO. This is in accordance with the recent work of Kim and Oh on donicity [26]. The coordination environment in terms of geometry provided by the $(CH_2CH_2NH)_n$ chains cannot disturb this coordination strength sequence.

Table 2
Energies and selected geometry parameters for the Li$^+$–PEI complexes

	HF/6-31G*				B3LYP/6-311++G**//HF/6-31G*	
	Av. r (Li$^+$–N) (Å)	CN	E (au)	ΔE bind (kJ mol^{-1})	E (au)	ΔE bind (kJ mol^{-1})
M1	2.028	2	− 274.675766	329	− 276.610828	314
D1	2.074	3	− 407.796016	453	− 410.648574	428
D2	2.066	3	− 407.795256	452	− 410.64856	425
T1	2.124	4	− 540.909484	559	− 544.681138	525
T2	2.155	4	− 540.904684	555	− 544.675766	518
T3	2.154	4	− 540.906015	555	− 544.676601	519
T4	2.174	4	− 540.902674	545	− 544.67361	508
Te9	2.259	5	− 673.998653	617	− 678.689379	569
P7	2.526	5	− 807.085897	628	− 812.697175	582

Table 3
Energies and selected geometry parameters for the Li$^+$–PES complexes

	HF/6-31G*				B3LYP/6-311++G**//HF/6-31G*	
	Av. r (Li$^+$–S) (Å)	CN	E (au)	ΔE bind (kJ mol^{-1})	E (au)	ΔE bind (kJ mol^{-1})
M1	2.452	2	− 959.62604	224	− 962.295836	235
D1	2.501	3	− 1435.223347	304	− 1439.178356	314
D2	2.5	3	− 1435.224114	301	− 1439.179767	312
T1	2.548	4	− 1910.818445	369	− 1916.058175	375
T2	2.61	4	− 1910.812271	358	− 1916.051726	362
T3	2.555	4	− 1910.8167	370	− 1916.056702	376
T4	2.564	4	− 1910.815793	371	− 1916.056079	378
Te9	2.648	5	− 2386.402856	417	− 2392.926237	417
P7	2.824	6	− 2861.978876	439	− 2869.786164	433

Table 4
Binding energies and Li$^+$–X distances for the $n = 0$ complexes

X	HF/6-31G*		B3LYP/6-311++G**//HF/6-31G*
	r (Li$^+$–X) (Å)	ΔE bind (kJ mol^{-1})	ΔE bind (kJ mol^{-1})
O	1.827	179	171
NH	1.992	188	182
S	2.415	132	141

Table 5
Stepwise binding energies for the Li$^+$–PEX complexes (B3LYP/6-311++G**//HF/6-31G*)

Step (CN)	PEO (kJ mol^{-1})	PEI (kJ mol^{-1})	PES (kJ mol^{-1})
1–2	116	132	94
2–3	94	112	78
3–4	76	91	60
4–5	60	52	44
5–6	26		16

Stepwise binding energies decrease from initial 79 to 16 kJ mol^{-1} for PES (Table 5). Consequently, the energy per bond decreases to a minimum of ∽72 kJ mol^{-1} for PES. High CNs are thus less driven by gains in binding energy for PES than for PEO where the lowest stepwise energy is 26 kJ mol^{-1}, but on par with PEI (13 kJ mol^{-1}) due to the steric hindrances occurring for the latter for the highest CN. The onset of steric hindrances for PEI seems to occur for $n = 4$ (CN ≥ 5), whereafter the PEO value is higher than for PEI. The complete set of values is also reported in Table 5.

To qualitatively compare all the Li$^+$–X distances obtained in the oligomer complexes ($n > 0$) histograms over the "radial distribution functions" (RDFs), are shown in Fig. 3. By fitting a single Gaussian to each we extract peak values at ~1.99, ~2.13 and ~2.55 Å, respectively. The values for PEO we can compare with the reported experimental RDF on LiI dissolved in PEO by Londono et al. [25], a system which however, contains some Li$^+$–I$^-$ interactions. Their peak value is ~2.1 Å, our value is lower mainly due to the complexes with unrealistically low CNs such as 2 and 3. This should also be true for PEI and PES for which we have been unable to find appropriate experimental studies to compare with.

3.5. Transition states and energy barriers

In Fig. 4 the reaction paths for the intramolecular reactions leading to a lowering of the CNs from 3 to 2 mainly via a changed X–C–C–X dihedral from gauche to anti are

Table 6
Energies, dihedral angle and imaginary frequencies along the reaction paths

	X–C–C–X (°)	E (au)	ΔE (kJ mol^{-1})	Imaginary frequency (cm^{-1})
PEO				
D1	− 50.4	− 467.269858	0	
TS	− 131.2	− 467.233319	96	− 111
Bi	− 179.1	− 467.235754	89.6	
PEI				
D1	− 60.1	− 407.796016	0	
TS	− 134.8	− 407.759712	95.3	− 94.9
Bi	− 179.5	− 407.761684	90.2	
PES				
D1	− 68.7	− 1435.223347	0	
TS	− 134.6	− 1435.198014	66.5	− 78.8
Bi	− 182.6	− 1435.200563	59.8	

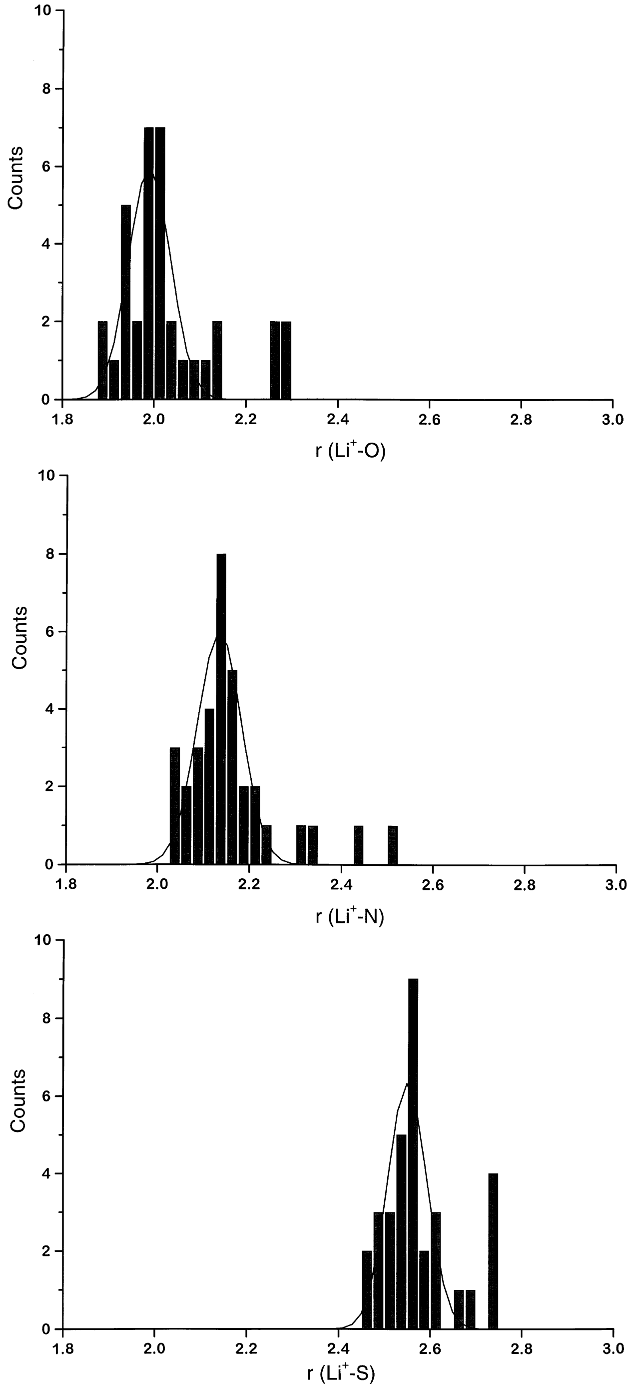

Fig. 3. (a) Histogram (RDF) of Li^+–O distances. (b) Histogram (RDF) of Li^+–N distances. (c) Histogram (RDF) of Li^+–S distances.

depicted for PEO, PEI, and PES. The starting geometries for the TS searches were initially constructed by changing one X–C–C–X dihedral to −135°. All TSs were found rather easily and confirmed by vibrational frequency calculations, all rendering one low-lying imaginary frequency (~100 cm^{-1}) and the mode being mainly due to a changing X–C–C–X dihedral as dectected by visualization. The tridentate structures are type **1** and the bidentate structures

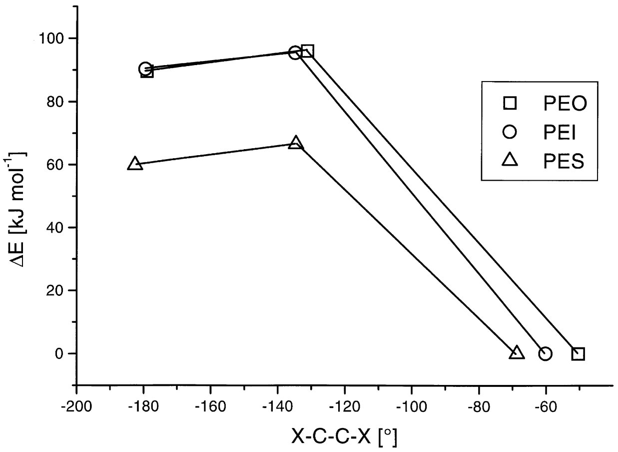

Fig. 4. Calculated relative energies along the CN 3 ⇛ 2 reaction paths.

have one X–C–C–X ∽ −180°. Selected geometry parameters and energies are reported in Table 6. Although these complexes all have unrealisticly low CNs for Li^+, it was previously shown [18] that the small energy barrier differs little upon increasing the system size, while the large barrier becomes somewhat lower. The latter is most probably due to the lower energy per bond as CN increases. For the purpose of lithium ion transport a co-operative mechanism as outlined in [18] might facilitate ion transport along a single polymer chain. Such a mechanism, being an S_N^2 type reaction, is still dependent on an initial decrease in CN, which should be related to the large energy barrier in the present cases. Therefore, one can envisage a faster lithium ion transport along a PES chain than for both PEI and PEO. Also the synthesis of new polymers for PE purposes, if this mechanism dominates, should aim to find systems with as low large barriers as possible.

4. Conclusions

From the present calculations the sequence of coordination strength of Li^+ seem to be NH > O > S — partly in disagreement with earlier belief. The reason is mainly the donicity of the nitrogen heteroatom in conjunction with the spatial arrangement provided by the imine oligomer. Suitable experiments to verify or dismiss these results are highly desirable. We will continue and extend this study to other cations e.g. Na^+, K^+, Mg^{2+}. From an ion conductivity point of view PES show more labile Li^+–X bonds, while still providing high CNs for Li^+. However, the electrochemical stability and the solubility of the lithium salts could then be a more severe problem. The large flexibility of the oligomer chain backbones appear to allow numerous stable structures within narrow energy ranges for different choices of electronegative groups. Steric hindrances do not seem to play a vital role in determining the relative energies for the different choices of X. For all choices of X five or six seem to be the CN of preference on pure binding energy basis, while five might be expected on the basis of the number of possible complexes (as for already stated for PEO [15]).

Acknowledgements

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