Computational Molecular Modeling of Polymer Solid Electrolytes I: *ab initio* Calculation of Polyethylene oxide and its Alkali Salt Complexes

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ABSTRACT

The *ab initio* calculation on the conformation of a single PEO chain and the structure of PEO/salt complexes were reported. First, the conformational properties and new Rotational Isomeric State (RIS) model have been derived, based upon both semi-empirical (PM3) and *ab initio* (HF-SCF and MP2) electronic structure calculation of the three representative segments of PEO (semi-empirical) and 1,2-dimethoxyethane, DME (*ab initio*). The RIS model, with all the parameters derived from the conformational geometries and energies of DME, predicts the chain dimensions, the dipole moments, and their temperature coefficients for PEO in good agreement with experiments. At a more local scale, the model reproduces the fraction of bond conformers in close agreement with the data from electron diffraction and NMR coupling constants. Next, several stable structures of the 1:1 complexes of an alkali ion with di-, tri-, tetra-, penta- and hexaglyme [$CH_3O(CH_2CH_2O)_nCH_3$, n=2–6] were obtained at HF level of theory employing the 3-21G* basis set. Various different stable complexes were found with coordination numbers ranging from two to six. The total energies and the binding energies were evaluated by using density functional theory (DFT) calculations (B3LYP/6-31G*//HF/3-21G*) and showed the total binding energy to increase with the chain length. The average binding energy per bond for a specific coordination number for alkali cation shows only minor changes when extending the oligomer.

INTRODUCTION :

Polymer solid electrolytes (PSE) based on polyethylene oxide (PEO), $(CH_2CH_2O)_n$, polymers and/or oligomers and an alkali salt are of great interest in the context of developing modern and environmentally friendly large secondary batteries and of fundamental scientific interest. These types of PSE to a large extent still rely on the ability of the repeated ethylene oxide unit to coordinate cations. PEO is known to be one of the most flexible polymers characterized by a small value of the unperturbed dimension. The polymer is soluble in various organic solvents as well as in water. It has long been established that PEO chains have a large fraction of bonds in *gauche* conformations. This is a specific example of the *gauche* effect in which polar substituents cause the preferred conformation about a C—C bond to switch from *trans* to *gauche*. Several attempts have been made to describe PEO using rotational isomeric state (RIS) models parameterized on the basis of molecular mechanics predictions of the conformational energies and geometries of small model molecules. In an effort to account for discrepancies between RIS model, electron diffraction and *ab initio* results of PEO model compound (dimethyl ethane, DME), we have undertaken a detailed *ab intio* analysis of the conformational energies of DME. As we plan to study PEO/Salt complexes using both experimental (Extended X-Ray Absorption Spectroscopy, EXAFS) and computational (*ab initio* calculation) approaches, some preliminary results concerning structures and energetics of PEO/Li^+ were investigated based on a first principle calculation. It is expected that the outcome of this work will lead to a more understanding about the relationship between their atomistic nanostructures and material properties

COMPUTATION: RIS Model:

Geometries and conformational energies of model segments of PEO are determined at HF-SCF and MP2 level. The basis set used in this study, 6-311G and D95, are split valence (with three functions for the valence orbitals) and double-x, respectively. The basis sets can be further augmented by including a set of diffuse sp function [+ and ++] and polarization function [* and **]. Conformational geometries are determined by fully optimizing the original molecule geometries. Vibrational frequencies are calculated to verify the stationary points. Semi-empirical calculation of 3 model units of PEO is also performed at the PM3 level to determine the overall shape of the conformational energy map. Parameters for RIS model are obtained via multiple linear least square regression, RIS calculation is performed using an in-house Fortran program. **PEO/Li^+ Complexes:** Initial calculations on the starting geometries were made with the semi-empirical PM3 method, The subsequent final geometry optimizations at HF level used the standard 3-21G* basis set. Vibrational frequency calculations were performed at this level of theory to confirm that the structures obtained were true minima. Because of the size of the systems, the energies were finally evaluated using DFT methods at the B3LYP/6-31G* level of theory (B3LYP/6-31G*//HF/321G*). The bonding energies are defined as $E_{bond}=\{E(Li^+\text{-glyme complex})-[E(\text{glyme (in the complex geometry)}) + E(Li^+)]\}$. Suitable starting geometries were selected on the basis of two different stable complexes/structures with the conformations **aG⁻a aG⁺a** and **aG⁺a g⁺G⁺a,** referred to as structure **1** and **2**. Next, a sequence of three ether oxygen atoms is suitably arranged for coordination to a metal ion. All calculation are performed with the quantum chemistry package GAUSSIAN 98w which is installed on Pentium 4 CPU 3.2 GHz with 1 GB RAM.

RESULTS AND DISCUSSIONS:

Conformational Characteristics of PEO: The geometries and energies of the low-energy conformers of DME employing quantum chemistry methods (HF, MP2 and DFT) at various basis sets were obtained. The energy of *gauche* conformation of the O—C—C—O bond relative to the *trans* conformation depends strongly not only on the basis set size but also on electron correlation effects. The effect of basis set and electron correlation on the energy of the *tgt* conformer of DME relative to the *ttt* conformer were investigated as followed. First, molecular geometry of the *tgt* and *ttt* confomers of DME were optimized at the MP2 level using D95** basis set. Then, these optimized geometry was used in single-point energy calculation at both SCF and MP2 levels for various basis sets. These data are given in Table 1. Electron correlation effects were founds to be quite important. The MP2 energy differences are all at least 0.5 kcal/mol lower than SCF values for the same basis set. The electron correlation effects increase as the size of basis set increases. Geometries and conformational energies of nine rotamers of DME were optimized at the HF/6-311+G* and D95** level. Calculated dihedral angles of the skeleton bonds and conformational energies of the nine rotamers are also summarized in Table 2. Next, we develop a simple three state second-order RIS model for PEO and have establishes all parameter values based upon the *ab initio* conformational energies of model compound. The RIS model for poly(A-A-B) chains, in which all bonds are subject to a symmetric 3-fold torsion potential with the nearest neighbor interdependence, is given by the following three statistical weight matrices for three successive bonds of type A-A, A-B, and B-A.

$$U_{AA}=\begin{bmatrix}1 & \sigma_{BB} & \sigma_{BB}\\ 1 & \sigma_{BB} & \sigma_{BB}\omega_{AB}\\ 1 & \sigma_{BB}\omega_{AB} & \sigma_{BB}\end{bmatrix}\qquad U_{AB}=\begin{bmatrix}1 & \sigma_{AA} & \sigma_{AA}\\ 1 & \sigma_{AA} & \sigma_{AA}\omega_{AB}\\ 1 & \sigma_{AA}\omega_{AB} & \sigma_{AA}\end{bmatrix}\qquad U_{BA}=\begin{bmatrix}1 & \sigma_{AA} & \sigma_{AA}\\ 1 & \sigma_{AA} & \sigma_{AA}\omega_{AA}\\ 1 & \sigma_{AA}\omega_{AA} & \sigma_{AA}\end{bmatrix}$$

In the matrices, the rows and columns define the states of bonds i - 1 and i, respectively. The three accessible rotational isomeric states for each bond are t, g^+, and g^-, used in this order in the matrices. The σ_{AA} and σ_{AB} are the statistical weights for the A-A and A-B type first-order interactions, and ω_{AA} and ω_{AB} represent the second-order interactions. They are calculated as Boltzmann factors using the energies calculated from an *ab initio* QM calculation. The short-range interactions determine the local chain conformation for an unperturbed chain. Our RIS model of PEO includes low-energy $g^{\pm}g^{\mp}$ C-O-C-C-O conformations and the energy of the O-C-C-O *gauche* conformation is considered to be slightly higher than that of the *trans* conformation. Some sets of the *ab initio* and representative RIS conformational energies are summarized in Table 3. All statistical weight parameters were calculated from these results. Next, standard matrix multiplication methods were utilized to determine mean-square chain dimensions and dipole moments from statistical weights and matrices estimated from conformational average of *ab initio* optimized conformational energies of DME. Calculated and experimental values of polymer properties are also given in Table 4. The local bond property i.e. NMR vicinal coupling constant was also found in close agreement with experiment.

Structures and Energetics of PEO/Alkali Salt Complexes: Several stable structures of the 1:1 complexes of a lithium ion with tetra-, penta- and hexaglyme [$CH_3O(CH_2CH_2O)_nCH_3$, n=4–6] have been obtained with ab initio calculations at the Hartree–Fock level of theory employing the 3-21G* basis set. Twenty-three different stable complexes were found with coordination numbers of lithium ranging from four to six. The total energies and the binding energies were evaluated by using density functional theory (DFT) calculations (B3LYP/6-31G*//HF/3-21G*) and showed the total binding energy to increase with the glyme length. The average binding energy for the different glymes reaches a maximum of 620 kJ mol^{-1} for the hexaglyme complexes, with an absolute maximum of 631 kJ mol^{-1} obtained for a hexacoordinated Li^+–hexaglyme complex. The average binding energy per bond for a specific coordination number for lithium shows only minor changes when extending the oligomer (<5 kJ mol^{-1} bond^{-1}). The large number of complexes obtained with clearly different geometry within a small energy range — six different complexes within 15 kJ mol^{-1} for lithium–tetraglyme — clearly reflects the flexibility of the oligomer chains. To compare all the Li^+-oxygen distance qualitatively for all complexes obtained, a histogram is shown in Figure 1(b) from which an estimate give us a peak at 2.03 Å. This value will be later compared with the RDF obtained the EXAFS experimental results. The large number of complexes obtained with clearly different geometry within a small energy range clearly reflects the flexibility of the oligomer chains.

CONCLUSION:

On the basis of high-level quantum chemistry calculations (HF-SCF, MP2, DFT), we have shown that the conformer populations of PEO determined from *ab initio* electronic structure calculations of the low-energy conformation of model compounds using a large basis set and including electron correlation effects agree with those estimated from experimental electron diffraction data and reproduce NMR coupling constants, characteristic ratio and dipole moment reasonably well. The structures and energetics of PEO/Li^+ complexes showed the total binding energy to increase with the chain length. Distribution of Li-O distance are found in the range of 1.9 to 2.4 Å with the highest peak at 2.0 Å.

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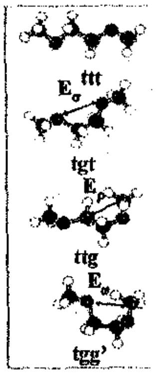
Table 1 The difference in Energy between the *ttt* and *tgt* Conformer of DME

Basis set	ΔHF	ΔMP2	ΔB3LYP
6-31G*	1.40	0.60	0.52
6-31+G*	1.40	0.41	0.64
6-311+G*	1.26	0.28	0.71
6-311++G*	1.24	0.23	0.54
D95**	1.30	NA	NA
D95+(2df,p)	0.96	NA	NA

ıble 2 DME Geometries and Energies (calculates at HF/6-311+G* and D95**)

Conformation (degeneracy)	Φ_1	Φ_2	Φ_3	Δ 6-311+G*		Δ D95**	
				HF	MP2	HF	MP2
TTT	179.94	-179.92	-179.99	0.00	0.00	0.00	0.00
TGT	-174.78	-174.75	73.42	1.26	0.29	1.30	0.83
TTG	-178.21	89.72	179.52	2.08	1.67	3.85	1.40
GTG	90.12	90.08	178.19	4.30	3.48	3.52	3.01
GTG'	88.95	-88.96	178.00	4.09	3.37	3.10	2.69
TGG	-178.34	79.96	65.95	3.34	1.96	1.65	1.90
TGG'	-177.86	-91.13	71.46	1.78	0.28	3.96	0.44
GGG	63.83	63.84	48.22	4.26	1.68	3.85	1.69
GGG'	85.24	-82.45	72.68	1.26	2.10	3.52	1.77

Table 3 RIS model of PEO from *ab initio* calculation of DME model compound



Conformer	RIS Representration	MP2 6-311+G*	MP2 D95**	RIS Energy[a]	RIS Energy[b]
ttt	0	0.00	0.00	0.00	0.00
tgt	Eσ	0.29	0.75	-0.20	0.23
ttg	Eρ	1.67	1.24	1.40	1.75
tgg	Eσ+ Eρ	1.96	1.77	1.20	1.98
tgg'	Eσ+ Er+Eω	0.28	0.24	0.38	0.30
gtg	2Eρ	3.48	2.90	2.80	3.50
gtg'	2Eρ	3.37	2.61	2.80	3.50
ggg'	Eσ+ 2Eρ+Eω	2.10	1.68	1.78	2.05
g'gg'	Eσ+ 2Eρ+2Eω	3.48	2.53	0.95	0.37
ggg	Eσ+ 2Eρ	1.68	1.69	2.60	3.73

[a]Parameter set 3 Es = -200, Er = 1400 and Ew = -825 cal/mol. [b]Parameter set 4 Eσ = 230, Eρ = 1750 and Eω = -1680 cal/mol. Disagreement for g'g'g and ggg conformational energy is due to third order interaction effect (not included in the present work)

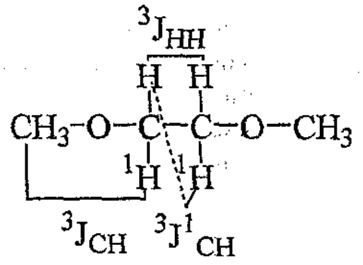
Table 4 Characteristic ratio and dipole moment ratio for PEO

	$<r>_0^2/nl^2$ (273 K)	$<\mu>_0^2/nm^2$ (273 K)	[d ln$<r>_0^2$/dT] ($10^{-3}K^{-1}$)	[d ln$<\mu>_0^2$/dT] ($10^{-3}K^{-1}$)
Observed*	5.2	0.53	0.23	2.6
PM3	2.08	0.54	0.17	0.27
Ab initio				
Parameter sets 3	5.2	0.24	0.26	1.98
Parameter sets 4	3.75	0.15	0.95	3.34

Observed: D. R. Beech and C. Booth, *J. Polym. Sci., Part A-2*, 1969, 7, 575.
Calculate: A, Abe *Polym. J.*, 1982, 14, 427.

Table 5 Bond conformations and NMR vicinal coupling constants of PEO

Case	f_t^{CC}	f_t^{CO}	**298 K**		
			J_{HH} (Hz)	J^1_{HH} (Hz)	J^1_{CH} (Hz)
PM3	0.19	0.63	6.17	4.51	4.41
Ab initio					
Parameter sets 3	0.22	0.81	6.03	4.72	3.03
Parameter sets 4	0.27	0.74	5.79	5.07	3.61
Electron diffractiona	0.21	0.64	-	-	-
RISa	0.21	0.79	-	-	-
Exptla,b	-	-	5.85	4.69	4.09
			5.81	4.78	4.23



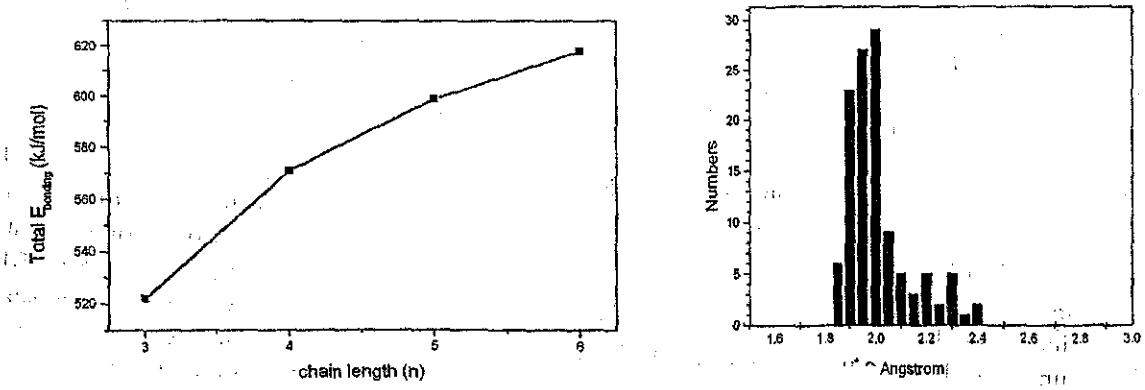


Figure 1 (a) Total bonding energy as a function of chain length (b) histograms of Li^+-oxygen distance.