Theoretical study of the vibrational spectra of polyethylenimine and polypropylenimine

S. Lakard*, G. Herlem, B. Lakard, B. Fahys

LCMI, University of Franche-Comté, UFR Sciences and Techniques, 16 route de Gray, 25030 Besançon cedex, France

Received 19 October 2003; accepted 2 June 2004
Available online 12 September 2004

Abstract

This study concentrates on two polymers: linear polyethylenimine, L-PEI, and linear polypropylenimine, L-PPI. Detailed atomistic molecular models have been developed with the help of ab initio and quantum-mechanical calculations. The vibrational spectra of ethylenediamine, EDA, and 1,3-diaminopropane, DAP, which are the monomers leading to L-PEI and L-PPI, respectively, have been computed using different ab initio basis sets, from 3-21G to 6-31\(C^*\). The results obtained with the different basis sets are compared to determine which basis set is the most efficient to compute data about oligomers from \(n = 1–5\), where \(n\) is the number of repeat units used. The trends in the computed vibrational frequencies and intensities are monitored as a function of the chain length. The data are analysed in conjunction with the trends in computed equilibrium geometries.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Polymers; Ab initio calculations; Hartree–Fock; IR spectrum

1. Introduction

Linear polyethylenimine was first synthesized by chemical route in 1970 by Dick [1]. This polymer was obtained by cationic polymerization of 2-substituted-2-oxazolines [2] or by aqueous polymerization of aziridine [3]. However, we have recently developed an original electrochemical way to deposit L-PEI and L-PPI films on metallic or semiconducting surfaces [4,5]. These polymers films were identified using different spectroscopic methods, such as infrared ATR, Raman and X-ray photoelectron spectroscopy [6]. This electrochemical synthesis is far less complicated than the organic one and it allows to coat different surfaces with a thin and very adhesive film. Thanks to ab initio quantum-chemical calculations at the Hartree–Fock level, we have also established the electropolymerization mechanism leading to L-PEI or L-PPI films [7,8]. More, since these polymers are biocompatible and contain numerous amino groups we used them to develop (bio)chemical sensors [9,10].

Nevertheless, the conformation and packing of L-PEI and L-PPI have not been previously studied despite the fact that such characteristics dictate their most important physical and mechanical properties. To increase the processability of these polymers, for example to optimize the responses of the (bio)chemical sensors using these polymers, it is important to predict accurately their structure and chemical properties.

So, the aim of this work is to establish the theoretical vibrational spectra of a L-PEI or a L-PPI backbone, composed from \(n = 1–5\) monomer units, using Hartree–Fock method with different basis sets from 3-21G to 6-31\(+G^*\) since vibrational spectroscopy is an important tool for the characterization of organic polymers in the undoped state, as well as in the doped state [11].

2. Methodology

Ab initio calculations were performed with GAUSSIAN 98W [12] at the Hartree–Fock level of theory using
polarization and diffuse functions [13]. We used Hartree–Fock method rather than DFT methods since we have already proved that Hartree–Fock frequencies calculations, applied to diamines, are more appropriate than DFT methods in our case [14]. The geometry optimization calculations were obtained with a Self-Consistent Field (SCF) optimization. Thus these quantum-chemical calculations allowed us to access the energy, the molecular structure and the vibrational frequencies of each molecule by solving the SCF equations [15,16]. Thermodynamic properties were obtained, under standard conditions (T = 298.15 K and P = 1 atm.), after harmonic frequency calculations were done by diagonalizing the mass-weighted matrix of second derivatives of the energy with respect to nuclear displacements [17]. All calculations were computed on an IBM Supercomputer from the CINES Supercomputing Center (Montpellier France).

### 3. Results and discussion

#### 3.1. Modelling the monomers

In order to test the ability of Hartree–Fock method to calculate accurately IR vibration bands of L-PEI and L-PPI, we have computed the IR vibration bands of ethylenediamine, EDA, and 1,3-diaminopropane, DAP. In fact, these diamines contain the same types of groups (amino and –CH₂ groups) and their electrochemical oxidation lead to L-PEI and L-PPI, respectively. We used different basis sets from 3-21G to 6-31G* taking into account their Scale Factor SF (SF = 0.9085 for 3-21G basis sets and SF = 0.8929 for 6-31G* basis set) [18]. After the optimization of each molecule, frequency calculations were performed. These calculations allow to predict the theoretical gas phase infrared spectra [19]. Then we compared computed vibrational frequencies with Gas Phase IR experimental vibration bands (see Table 1 for EDA and Table 2 for DAP) [20] since all calculations were made in the gas phase. All basis sets seem efficients to obtain the infrared vibrational spectrum of EDA since they gave computed vibrational frequencies not far from the experimental Gas Phase IR spectrum frequencies (Table 1). Indeed, in the case of EDA, we obtain an average difference between the computed frequencies and the experimental ones of less than 2%. However, the most accurate basis set seems to be 6-31G* basis set associated with Hartree–Fock method since the differences between the Hartree–Fock frequencies and the experimental spectrum frequencies are lower than the differences between experimental frequencies and calculated frequencies obtained with any other basis set.

#### 3.2. Modelling the polymers

Despite the fact that 3-21G or 6-31G basis sets, for example, are simpler and cheaper in computation time than 6-31G* basis set, the results obtained with these basis sets are nearly as good as those obtained with 6-31+G* basis set.
thanks to the frequencies scale factor. Consequently, they can also be used to model EDA, DAP and molecules of similar structures.

3.2. Modelling the oligomers

Then theoretical vibrational frequencies of L-PEI and L-PPI were obtained by building oligomers of L-PEI (H-(NH–CH₂–CH₂)ₙ–NH₂) and oligomers of L-PPI (H-(NH–CH₂–CH₂–CH₂)ₙ–NH₂) composed of n = 2–5 monomer units and to compute their vibrational frequencies using Hartree–Fock method with 6-31G basis set since this latter basis set was both efficient to model the monomers of these oligomers and cheaper than 6-31+G* basis set. Fig. 1 represents the structure of L-PEI and L-PPI after geometry optimization using 6-31G basis set. One can observe in this figure that L-PEI keeps a linear polymeric chain contrary to L-PPI which is bended. This can be explained by the presence of a third –CH₂ group between the amino groups in L-PPI. We can also notice that after the optimization of each oligomer, frequency jobs were performed using a frequency scale factor SF = 0.8929.

Computed vibrational frequencies and correspondent IR spectra of L-PEI and L-PPI are given in Tables 3 and 4 in Fig. 2. These values are concordant with the polymer structures since they are characteristic from N–H, C–H and C–N groups. They are also concordant with the experimental spectra previously made of these polymers [21]. Indeed the main experimental characteristic bands of

![Fig. 1. Oligomers of L-PEI (a) and L-PPI (b) containing 5 monomer units after geometry optimization (HF/6-31G).](image)

<table>
<thead>
<tr>
<th>Vibration band</th>
<th>EDA</th>
<th>L-PEI (n = 2)</th>
<th>L-PEI (n = 3)</th>
<th>L-PEI (n = 4)</th>
<th>L-PEI (n = 5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH asym stretching (cm⁻¹)</td>
<td>3499</td>
<td>3500</td>
<td>3500</td>
<td>3500</td>
<td>3500</td>
</tr>
<tr>
<td>NH sym stretching (cm⁻¹)</td>
<td>3392</td>
<td>3391</td>
<td>3390</td>
<td>3391</td>
<td>3394</td>
</tr>
<tr>
<td>NH stretching II (cm⁻¹)</td>
<td>2919</td>
<td>2915</td>
<td>2915</td>
<td>2915</td>
<td>2915</td>
</tr>
<tr>
<td>CH asymmetric stretching (cm⁻¹)</td>
<td>2784</td>
<td>2881</td>
<td>2891</td>
<td>2899</td>
<td>2899</td>
</tr>
<tr>
<td>CH symmetric stretching (cm⁻¹)</td>
<td>1646</td>
<td>1647</td>
<td>1648</td>
<td>1647</td>
<td>1647</td>
</tr>
<tr>
<td>N–H deformation (cm⁻¹)</td>
<td>1489</td>
<td>1496</td>
<td>1505</td>
<td>1511</td>
<td>1513</td>
</tr>
<tr>
<td>C–N stretching (cm⁻¹)</td>
<td>1042</td>
<td>1043</td>
<td>1047</td>
<td>1041</td>
<td>1063</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vibration band</th>
<th>DAP</th>
<th>L-PPI (n = 2)</th>
<th>L-PPI (n = 3)</th>
<th>L-PPI (n = 4)</th>
<th>L-PPI (n = 5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH asym stretching (cm⁻¹)</td>
<td>3491</td>
<td>3492</td>
<td>3493</td>
<td>3493</td>
<td>3492</td>
</tr>
<tr>
<td>NH sym stretching (cm⁻¹)</td>
<td>3385</td>
<td>3385</td>
<td>3385</td>
<td>3386</td>
<td>3386</td>
</tr>
<tr>
<td>NH stretching II (cm⁻¹)</td>
<td>2898</td>
<td>2898</td>
<td>2898</td>
<td>2897</td>
<td>2897</td>
</tr>
<tr>
<td>CH asymmetric stretching (cm⁻¹)</td>
<td>2850</td>
<td>2861</td>
<td>2857</td>
<td>2856</td>
<td>2868</td>
</tr>
<tr>
<td>CH symmetric stretching (cm⁻¹)</td>
<td>1647</td>
<td>1646</td>
<td>1646</td>
<td>1647</td>
<td>1647</td>
</tr>
<tr>
<td>N–H deformation (cm⁻¹)</td>
<td>1484</td>
<td>1501</td>
<td>1500</td>
<td>1499</td>
<td>1499</td>
</tr>
<tr>
<td>C–N stretching (cm⁻¹)</td>
<td>1049</td>
<td>1058</td>
<td>1062</td>
<td>1052</td>
<td>1058</td>
</tr>
</tbody>
</table>
L-PEI appearing in the infrared spectrum of L-PEI are: N–H stretching (3310 cm⁻¹, too large to discriminate bands corresponding to –NH groups from bands corresponding to –NH₂ groups), N–H deformation (1601 cm⁻¹), C–N stretching (1162 cm⁻¹), C–H stretching (2939 and 2873 cm⁻¹) and C–H deformation (1484 cm⁻¹). And the main experimental characteristic bands of L-PPI appearing in the infrared spectrum of L-PPI are: N–H stretching (3363 cm⁻¹), N–H deformation (1633 cm⁻¹), C–N stretching (1179 cm⁻¹), C–H stretching (2951 and 2864 cm⁻¹) and C–H deformation (1489 cm⁻¹). Consequently, the computed infrared spectra confirm our experimental characterization of L-PEI and L-PPI. More, from these calculations, we can conclude that the calculation method we used is efficient.

We can also notice that computed vibrational frequencies of L-PEI and L-PPI are very similar despite the fact that L-PPI monomer contains an additional –CH₂ group. Indeed these two polymers contain the same type of groups at roughly the same wavenumbers. Consequently, the additional –CH₂ group has no significant effect on the vibrational spectra. On the contrary, L-PEI and L-PPI contain N–H stretching vibrational frequencies characteristic from a secondary amine which are not present in the theoretical spectra of their respective polymers (EDA and DAP). We have also tested the influence of the polymer chain length and we can observe that when the number of monomer units increases from n=2 to 5, the computed frequencies of the vibrational modes remain roughly constant.

4. Conclusion

In this study, we computed vibrational spectra of EDA and DAP using Hartree–Fock method with different basis sets. We showed that this method is appropriate to modelize EDA and DAP since the computed and experimental infrared spectra are concordant.

More computational techniques were used to estimate the theoretical spectra of polymers (L-PEI and L-PPI) since these polymers are obtained from electrochemical oxidation of EDA and DAP) and compare them with experimental spectra. The vibrational values of experimental spectra for these polymers were very close to the modelling ones. One explanation could be that ab initio parameters and force fields derived from them model these molecules well, and the amount of simulation time for these specific linear polymers was adequate. So the level of theory we have chosen can provide accurate data concerning the structure and properties of polymers at the atomic level. Future developments are likely to include the extension of electronic-structure techniques to larger and more complex systems unsing for example Bloch functions adapted to periodic systems such as L-PEI or L-PPI which are two crystalline solids.

Acknowledgements

The authors would like to thank CINES (Montpellier, France) calculation center for the computational facilities.

References
