Ab initio and DFT Study of Aliphatic Diamines and of their Electropolymerization Mechanism

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The anodic oxidation of ethylenediamine (EDA), 1,3-diaminopropane (1,3-DAP) or diethylenetriamine (DETA) leads to the passivation of many different electrode surfaces by an insulating thin film as shown by using an Electrochemical Quartz Crystal Microbalance coupled with Cyclic Voltammetry technique [1].

These films were characterized as polyethyleneimine (PEI) and polypropyleneimine (PPI) films using both spectroscopic methods such as Infra Red-Attenuated Total Reflection or InfraRed Absorption Spectroscopy and *ab initio* calculations [2]. These former were obtained using either Hartree-Fock (HF) theory or Density Functional Theory (DFT) with the SVWN, BLYP and B3LYP functionals. The computed vibrational frequencies of EDA were compared to the Gas Phase infrared spectrum of EDA. All methods gave computed vibrational frequencies not far from the Gas Phase IR spectrum frequencies but the most accurate method seems to be the HF method. Consequently, we have chosen to use this method to modelize EDA and to study, for example, the electropolymerization mechanism of EDA that leads to PEI. More, to have an additional evidence that PEI is the product of EDA oxidation, we computed the vibrational frequencies of $H\text{-}(NH\text{-}CH_2\text{-}CH_2)_{10}\text{-}NH_2$, an intermediate of the polymerization reaction, and compared them to the vibrational frequencies obtained from the IR-ATR spectrum previously studied. As the results of the HF vibrational frequencies calculations are concordant with the IR experiments, we can conclude that our vibrational calculations confirm that the oxidation of EDA leads to PEI.

To establish the mechanism of this polymerization (Figure 1), we performed HF quantum-chemical calculations since they allow us to modelize short-lived or unstable intermediates and even transition states. So they can provide information about some intermediates which are difficult, and even impossible, to render evident through experiments. Thus thanks to quantum-chemical calculations of the energy in gas phase or in solution (Figure 2) and of some thermochemical properties of the different intermediates, we established the successive steps of the polymerization of ω–diamines [3,4].

In order to understand why ω–diamines lead to the growth of a polymer when other diamines could not, we computed optimized minimum-energy geometries of different aliphatic diamines and of their protonated forms using HF and DFT calculations [5].

The molecular structures, vibrational frequencies and charge distributions of these diamines were also determined. More, we explored and compared the ability for HF and DFT methods to predict structure, thermodynamic properties and vibration modes of these diamines. The computed gas phase acidities as measured by the proton affinities of the diamines were obtained. This reaction, the energy change of which defines the proton affinity, is a fundamental property of compounds and is used as a basis for predicting other kinds of chemical reactivity. Most methods used predicted it well, typically to within 10 kcal/mol. Moreover, the molecular energetics calculations showed the less stable diamine is the non substituted one (EDA). That is why EDA is easier to oxidize than the substituted diamines and so why EDA polymerizes in PEI when other diamines do not. Finally, charge distribution calculations highlighted EDA is easier to protonate than the other diamines. That is why PEI, obtained by oxidation of EDA, is very sensitive to pH changes and can be used to modify surfaces so as to elaborate pH sensors [6].

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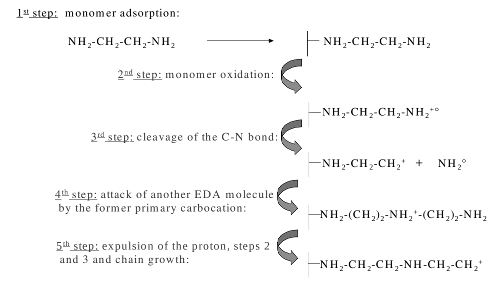

Figure 1 : Mechanism of Electropolymerization established using *ab initio* Calculations

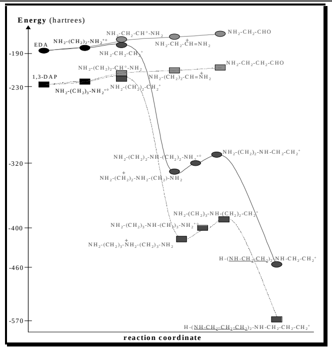

Figure 2 : Potential Energy Surface