Ab initio study of the polymerization mechanism of poly(p-phenylenediamine)

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Abstract

The electrochemical oxidation of paraphenylenediamine (1,4-diaminobenzene, PPD) leads to the passivation of the electrode surface by a thin film as shown by using Cyclic Voltammetry technique. This film can be identified by InfraRed-Attenuated Total Reflectance as a polymeric film of poly(p-phenylenediamine), polyPPD. To establish the mechanism leading from PPD to polyPPD, we performed computations of energy and thermochemical values with the quantum-chemical Self-Consistent Field method at the Hartree–Fock level of theory. Then we compared this mechanism to the ones, previously established with similar ab initio calculations, leading to polyethyleneimine and polypropyleneimine in an attempt to generalize the mechanism of electropolymerization of diamines.

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1. Introduction

In this work we want to support, using both electrochemical experiments and computational data, the growth mechanism of polymeric films obtained by anodic oxidation of paraphenylenediamine, PPD. These polymeric films can be observed using classical Cyclic Voltammetry (CV) but the anodic oxidation of this aromatic diamine gives a broad peak that cannot be developed in an electrochemical mechanism study. Consequently, we performed InfraRed-Attenuated Total Reflectance (IR-ATR) spectra to characterize the different bonds of the polymer deposited on the electrode surfaces and we found that the electrochemical oxidation of PPD leads to poly(p-phenylenediamine), polyPPD.

Our attempt to establish the mechanisms of formation of these polymeric films must take into account other results dealing with the study of the electrochemical oxidation of aliphatic amines in some solvents [1–3]. It has been shown that the electrochemical oxidation of simple aliphatic amines is quite complex and may lead to several different products. Indeed Mann, Barnes, and Smith [4–7] showed that the amine is oxidized, in the first step, to the cation radical, which may either decompose by C–N bond cleavage to produce a carbocation (which may polymerize) or give an iminium ion which can hydrolyze to give an aldehyde in presence of moisture. These are the reasons why it is imperative...
to synthesize the electrolytes and to perform the electrochemical measurements in a glove box under an argon atmosphere. Moreover, we proved using electrochemical experiments and ab initio calculations that some diamines can lead to polyalkyleneimines [8,9].

So our idea is to carry out ab initio quantum-chemical calculations at the Hartree–Fock level of theory to prove that the oxidation of PPD leads to polyPPD. Indeed, the computational chemistry allows us to study chemical phenomena by running calculations on computers rather than by examining reactions and compounds experimentally [9–11]. This is of prime interest if one wants to establish a reaction mechanism since computational chemistry can be used to model short-lived or unstable intermediates and even transition states. So they can provide information about molecules or reactions which are difficult, and even impossible, to render evident through experiments. Computational chemistry is therefore both an independent research tool which allows us to confirm experimental results, and a crucial adjunct to experimental studies which allows us to obtain additional information.

Thus, thanks to quantum-chemical calculations of the energy of each intermediate and of their thermochemical properties, we succeeded in establishing the successive steps of the polymerization of PPD. To determine if the mechanism established can be generalized to aliphatic and aromatic non-substituted diamines, we compared this electropolymerization mechanism to the mechanisms of formation of polyethyleneimine (PEI) and polypropyleneimine (PPI) from ethylenediamine (EDA) and 1,3-diaminopropane (DAP), respectively.

2. Materials

All solutions were obtained from Aldrich (analytical grade). PPD was used at the concentration of 0.1 M in a phosphate buffer solution, pH 7.0. 2.1. Apparatus and methods

The electrochemical apparatus was a classical three-electrode setup using an Autolab PGSTAT 20, from Ecochemie, potentiostat–galvanostat. The working electrode was a platinum wire protruded from glass sheath. The reference electrode was a silver reference electrode (SRE), and the counter-electrode was a platinum wire. All experiments were carried out at room temperature (293 K). The solutions were purged by ultrahigh purity argon. We used a NEXUS 470 spectrophotometer coupled to an Omnic software from Nicolet to perform IR-ATR spectra.

3. Methodology

Ab initio calculations were performed with GAUSSIAN 98W [12] at the Hartree–Fock level of theory using the split valence, incorporating polarization and diffuse functions [13], 6-31 + G* basis set internally stored in the program for 298.15 K at 1 atm. The geometry optimization calculations were obtained with a Self-Consistent Field (SCF) optimization. Thus, these quantum-chemical calculations allowed us to access the energy of each molecule by solving the SCF equations [14,15]. Standard reaction free enthalpies $\Delta_rG^\circ$ were also computed using Freq keyword in GAUSSIAN 98W. Thermodynamic properties were obtained after the calculation of harmonic frequencies by diagonalizing the mass-weighted matrix of second derivatives of the energy with respect to nuclear displacements [16]. All calculations were computed on an IBM Supercomputer from the CINES Supercomputing Center (Montpellier, France).

4. Results and discussion

4.1. Growth of polymeric films on electrode surfaces

We have already shown, using CV experiments, that surface electrode passivation can occur under anodic oxidation of an electrolyte composed with one salt dissolved in one pure non-substituted and aliphatic diamine, for instance EDA (NH$_2$–CH$_2$–CH$_2$–NH$_2$) [8,17,18] or DAP (NH$_2$–CH$_2$–CH$_2$–CH$_2$–NH$_2$) [8,18]. This phenomenon can be characterized by CV since the cyclic voltammograms
exhibit a drop of current between the first scan and the following ones.

Fig. 1 shows the cyclic voltammogram of PPD swept at 20 mV s\(^{-1}\) in pH 7.0 phosphate buffer solution containing 0.1 M PPD at a platinum electrode (similar curves can be obtained with gold, Si p (100) or Fluorine doped Tin Oxide electrode surfaces). It can easily be observed that the electrochemical process of PPD was completely irreversible, and the oxidation peak with a potential of \(+1.6\) V/SRE appeared only during the first scan. Oxidation currents of PPD dropped significantly with successive steps, and almost no oxidation current is observed in the second scan. This behavior is indicative of the quick formation of a non-conductive polymeric film on the electrode surface and is very similar to the behavior of EDA and DAP on platinum electrodes. More, the peak broadness is characteristic of amines and renders the experimental study of the electrochemical mechanism impossible. That is why we will try in Section 4.3.2 to determine the electropolymerization mechanism using ab initio calculations at the Hartree–Fock level of theory.

As a conclusion to this electrochemical experiment, we can assume that the anodic oxidation of PPD leads to a thin and insulating polymeric film and we can think that since PPD contains two amino groups in its molecular structure, it can be easily oxidized at a positive potential to produce cationic radicals of PPD and further react with PPD monomers to form the corresponding polyPPD film as we will see in the next part.

4.2. Characterization of the polymer films synthesized

4.2.1. Infrared spectroscopy

Before we try to establish the polymerization mechanism by using ab initio quantum-chemical calculations at the Hartree–Fock level, we have to briefly prove that polyPPD is obtained by oxidation of PPD. To determine the nature of the film deposited we performed, with a NEXUS 470 spectrophotometer coupled to an Omnic software from Nicolet, IR-ATR spectra, which allowed us to identify this film as polyPPD. Indeed, all characteristic vibration bands of polyPPD can be observed on the spectrum of oxidized PPD on a platinum surface (see Fig. 2): N–H stretching of primary amine (3387 and 3200 cm\(^{-1}\)), N–H stretching (3334 cm\(^{-1}\)) and N–H deformation (1678 cm\(^{-1}\)) of secondary amine, C–N aromatic stretching (1283 cm\(^{-1}\)), C–H aromatic stretching (3040 cm\(^{-1}\)), C–C aromatic stretching (1499 cm\(^{-1}\)) and C–H aromatic deformation (827 cm\(^{-1}\)). Thus, this spectrum confirms that the oxidation of PPD leads to polyPPD.

4.2.2. Ab initio calculations

To test the ability of Hartree–Fock method to compute accurately IR vibration bands, we have computed the IR vibration bands of PPD using 6-31 + G* and STO-3G basis sets taking into account their Scale Factor [17] (SF = 0.8929 for 6-31 + G* basis set and SF = 0.8329 for STO-3G basis set) and then we compared them to IR experimental vibration bands previously published [18]. One can observe in Table 1 that experimental and computed IR vibrational frequencies of PPD are concordant. More, despite the fact that STO-3G is simpler and less expensive in computation time than 6-31 + G*, the results obtained with this basis set are as good as those obtained with 6-31 + G*, thanks to the frequencies scale factors.

Then to obtain the theoretical vibrational frequencies of polyPPD, we decided to draw an oligomer of polyPPD composed of five monomer units: H–(NH–C\(_6\)H\(_4\))\(_5\)–NH\(_2\) (Fig. 3) and to compute its vibrational frequencies using Hartree–Fock method with STO-3G basis set. Indeed the computation time
would be far more important with the 6-31 + G* basis set and the accuracy of the computed frequencies not far better than for STO-3G basis set since this latter basis set was efficient for modeling the monomer of this oligomer. More it would be difficult to compute the frequencies of a longer oligomer since the computation time is important for such a molecule. The results of these calculations are given in Table 2 and one can observe that computed vibrational frequencies of the oligomer are concordant with experimental vibrational frequencies of polyPPD. Consequently, these ab initio calculations confirm the experimental IR spectrum of oxidized PPD and prove that it is possible to compute accurately the IR vibrational frequencies of oligomers composed of several monomer units.

4.3. Reaction mechanism leading to poly(p-phenylenediamine)

4.3.1. Description of the proposed mechanism

From the studies by Mann, Barnes and Smith [4–7] on the electrochemical oxidation of primary amines and from previous studies we made on the electrochemical oxidation of aliphatic diamines [19,20], we took the anodic oxidation of PPD
the mechanism described in Fig. 4. The first step is the adsorption of PPD on the surface electrode. Then this monomer is oxidized with the loss of an electron and the formation of a cation radical. This step is followed by the cleavage of the C–N bond with formation of a primary carbocation, which attacks another molecule of PPD. After the expulsion of the proton from the protonated amine, an additional loss of an electron and C–N bond cleavage take place. Therefore polyPPD, \((C_6H_4 – NH)_n\), grows progressively on the electrode surface.

4.3.2. Results of ab initio calculations

To test the mechanism we proposed for the formation of polyPPD from PPD we have now to perform quantum-chemical calculations to obtain the energies of the successive intermediates involved in this mechanism. Then we can compare their stability and confirm the suggested reaction mechanism. From the methods of calculation previously described, we computed the energies (in arbitrary units, 1 a.u. = 1 hartree = 627.509 kcal mol\(^{-1}\) = 27.2116 eV) of the successive intermediates involved in the electropolymerization mechanism (Tables 3 and 4) and then we represented the potential energy surface of the reaction (Fig. 5).

First of all, when PPD is electrochemically oxidized, we impose a potential on PPD sufficient to oxidize it in a cation radical form. This cation radical is unstable compared to the monomer and rapidly leads to primary carboxation. These two steps form the chain initiation of the polymerization process. Then the carboxation attacks another

![Fig. 3. Oligomer of polyPPD (composed of five monomer units). Dots represent the Van Der Waals radius of each element.](image)

<table>
<thead>
<tr>
<th>Vibration bands</th>
<th>Experimental (cm(^{-1}))</th>
<th>HF/STO-3G (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>N–H asymmetric stretching of primary amine</td>
<td>3387</td>
<td>3439</td>
</tr>
<tr>
<td>N–H stretching of secondary amine</td>
<td>3334</td>
<td>3366</td>
</tr>
<tr>
<td>N–H symmetric stretching of primary amine</td>
<td>3200</td>
<td>3278</td>
</tr>
<tr>
<td>C–H aromatic stretching</td>
<td>3040</td>
<td>3107</td>
</tr>
<tr>
<td>N–H deformation of secondary amine</td>
<td>1678</td>
<td>1635</td>
</tr>
<tr>
<td>C–C aromatic stretching</td>
<td>1499</td>
<td>1516</td>
</tr>
<tr>
<td>C–N aromatic stretching</td>
<td>1283</td>
<td>1234</td>
</tr>
<tr>
<td>C–H aromatic deformation</td>
<td>827</td>
<td>848</td>
</tr>
</tbody>
</table>
Step 1: monomer adsorption

\[ \text{NH}_2 - \text{phen} - \text{NH}_2 \rightarrow \text{adsorption} \rightarrow \text{H}_2\text{N} - \text{phen}_2 - \text{NH}_2 \]

surface

Step 2: monomer oxidation

\[ \text{H}_2\text{N} - \text{phen}_2 - \text{NH}_2 \xrightarrow{-e^-} \text{H}_2\text{N} - \text{phen}_2^+ - \text{NH}_2 \]

Step 3: cleavage of the C-N bond

\[ \text{H}_2\text{N} - \text{phen}_2^+ - \text{NH}_2 \rightarrow \text{H}_2\text{N} - \text{phen} + + \text{NH}_2^- \]

Step 4: attack of another \( \alpha \)-diamine by the former primary carbocation

\[ \text{H}_2\text{N} - \text{phen} + + \text{PPD} \rightarrow \text{H}_2\text{N} - \text{phen}_2 + \text{phen}_2 - \text{NH}_2 \]

Step 5: expulsion of the proton, steps 2 and 3 and chain growth

\[ \text{NH}_2 - \text{phen}_2 - \text{NH}_2 \xrightarrow{1.-H^+} \text{NH}_2 - \text{phen}_2 - \text{NH}_2 \xrightarrow{2.-e^-} \text{NH}_2 - \text{phen}_2^- - \text{NH}_2 \xrightarrow{3.-NH}_2^+ \]

Fig. 4. Anodic electropolymerization of paraphenylenediamine.
Table 3
Energies of the first intermediates involved in the mechanism of formation of polyPPD

<table>
<thead>
<tr>
<th>Step</th>
<th>Reactants</th>
<th>$E$ (a.u.)</th>
<th>Products</th>
<th>$E$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 2:</td>
<td>$\text{NH}_2\text{NH}_2$</td>
<td>$-340.7665308$</td>
<td>$\text{NH}_2\text{NH}^+\text{NH}_2$</td>
<td>$-340.5606831$</td>
</tr>
<tr>
<td>Step 3:</td>
<td>$\text{NH}_2\text{NH}^+\text{NH}_2$</td>
<td>$-340.5606831$</td>
<td>$\text{NH}_2\text{NH}_2^+$ $\text{NH}_2$</td>
<td>$-339.9256202$</td>
</tr>
<tr>
<td>Step 4:</td>
<td>$\text{NH}_2$ $\text{NH}_2^+$ $\text{NH}_2$</td>
<td>$-339.9256202$</td>
<td>$\text{NH}_2\text{NH}_2^+$ $\text{NH}_2\text{NH}_2$</td>
<td>$-625.7205714$</td>
</tr>
<tr>
<td>Step 5:</td>
<td>$\text{NH}_2\text{NH}_2^+$ $\text{NH}_2\text{NH}_2$</td>
<td>$-625.7205714$</td>
<td>$\text{NH}_2\text{NH}_2^+$ $\text{NH}_2\text{NH}_2$</td>
<td>$-625.1535484$</td>
</tr>
</tbody>
</table>
molecule of PPD in order to reduce its energy and to lead to a more stable molecule. Thereafter the expulsion of a proton takes place and a new oxidation step occurs. In brief, in the case of PPD, for example, we had H–(NH–C6H4)1–NH2 and we have now H–(NH–C6H4)2–NH2. So, we can assume there is a polymeric propagation chain sequence, which leads to (NH–C6H4)x+1 from (NH–C6H4)x. Thus, the polymerization reaction can be described as:

**Chain initiation:** the oxidation of PPD produces primary carbocations:

\[
\text{NH}_2\text{C}_6\text{H}_4\text{NH}_2 \rightarrow \text{NH}_2\text{C}_6\text{H}_4\text{NH}_2^+ \rightarrow \text{NH}_2\text{C}_6\text{H}_4\text{NH}_2
\]

\[\text{C}_6\text{H}_4^+ + \text{NH}_2\]

Such carbocations react with PPD monomers to initiate the polymerization process:

\[
\text{NH}_2\text{C}_6\text{H}_4^+ + \text{NH}_2\text{C}_6\text{H}_4\text{NH}_2 \rightarrow \text{NH}_2\text{C}_6\text{H}_4
\]

\[\text{NH}_2\text{C}_6\text{H}_4\text{NH}_2\]

**Table 4**

Energies of the intermediates of the first steps of the polyPPD growth (SCF optimization)

<table>
<thead>
<tr>
<th></th>
<th>X = 0</th>
<th>X = 1</th>
<th>X = 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>H–</td>
<td>–</td>
<td>– 625.7205714</td>
<td>– 910.3013421</td>
</tr>
<tr>
<td>X</td>
<td>– 340.5606831</td>
<td>– 625.1535484</td>
<td>– 910.2893675</td>
</tr>
<tr>
<td>H–</td>
<td>– 339.9256202</td>
<td>– 624.5145285</td>
<td>– 909.0936092</td>
</tr>
</tbody>
</table>

**Fig. 5.** Potential energy surface of the reaction path versus the reaction coordinate.
Chain propagation:
H-(NH-C₂H₄)₅-NH₂⁺ - C₆H₄-NH₂
↓Expulsion of a proton followed by oxidation
H-(NH-C₂H₄)₅⁺ - NH₂⁺
↓Cleavage of the C-N bond
H-(NH-C₂H₄)₅⁺ - NH - C₆H₄⁺ + NH₂⁺
↓+PPD
H-(NH-C₂H₄)₅⁺ - NH₂⁺ - C₆H₄⁺ - NH₂

4.4. Comparison between the mechanism of electropolymerization of polyPPD and the mechanisms of electropolymerization of PEI and PPI

By comparing the mechanism of polymerization of polyPPD described here with the mechanisms of electropolymerization of PEI and PPI previously described [8], one can deduce that all these mechanisms are quite similar since they all begin with the chain initiation consisting in the oxidation of the monomer followed by the loss of an electron and the reaction of the resulting carbocation with another monomer. Then the chain propagation of the oligomer takes place in all the mechanisms.

Thus, this mechanism has been established for NH₂ – R – NH₂ molecules where R is either – CH₂–CH₂–, – CH₂–CH₂–CH₂– or – C₆H₄–.

Chain initiation: the oxidation of the monomer produces primary carbocations:

NH₂ – R – NH₂ → NH₂ – R – NH₂⁺ → NH₂ – R⁺ + NH₂

Such carbocations react with monomers to initiate the polymerization process:

NH₂ – R⁺ + NH₂ – R – NH₂ → NH₂ – R – NH₂⁺ – R – NH₂

Chain propagation:
H-(NH-R)₅⁺ - NH₂⁺ - C₆H₄-NH₂
↓Expulsion of a proton followed by oxidation
H-(NH-R)₅⁺ - NH₂⁺
↓Cleavage of the C-N bond
H-(NH-R)₅⁺ - NH - R⁺ + NH₂⁺
↓+monomer
H-(NH-R)₅⁺ - NH₂⁺ - R - NH₂

The results of the computed energies of the intermediates involved in these mechanisms are compiled Table 5 and the evolution of the energy

<table>
<thead>
<tr>
<th>EDA</th>
<th>DAP</th>
<th>PPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>R =</td>
<td>-CH₂-CH₂-</td>
<td>-CH₂-CH₂-CH₂-</td>
</tr>
<tr>
<td>H-(NH-R)₅⁻ - NH₂⁺ - Y - NH₂</td>
<td>-189.00</td>
<td>-227.99</td>
</tr>
<tr>
<td>H-(NH-R)₅⁻ - NH₂⁺</td>
<td>-188.84</td>
<td>-227.88</td>
</tr>
<tr>
<td>H-(NH-R)₅⁻ - NH - R⁺ + NH₂</td>
<td>-322.74</td>
<td>-400.81</td>
</tr>
<tr>
<td>H-(NH-R)₅⁻ - NH₂⁺</td>
<td>-322.11</td>
<td>-400.18</td>
</tr>
<tr>
<td>H-(NH-R)₅⁻ - NH - R⁺ + NH₂</td>
<td>-321.93</td>
<td>-400.00</td>
</tr>
<tr>
<td>H-(NH-R)₅⁻ - NH₂⁺ - R - NH₂</td>
<td>-455.14</td>
<td>-572.11</td>
</tr>
<tr>
<td>H-(NH-R)₅⁻ - NH₂⁺</td>
<td>-455.19</td>
<td>-572.30</td>
</tr>
</tbody>
</table>

Table 5
Energies of the successive intermediates involved in the mechanism leading to PEI from EDA, PPI from DAP and polyPPD from PPD
during the polymerization process is represented in Fig. 6. We can observe in this latter figure that the intermediates involved in the mechanism of polymerization of PPD are the stablest ones since the benzene ring has a stabilizing effect. However, the evolution of the energy during the polymerization process is quite similar in all cases as proved by Fig. 6.

### 4.5. Thermochemistry

We have previously shown [8] that it is very important to evaluate the free enthalpy of the reaction between the primary carbocation and a monomer since the value of the free enthalpy allows us to prove that the reaction leading to a linear polymer is thermodynamically more favored than the reaction between a secondary carbocation and a monomer leading to a branched polymer. We can also observe that the more negative the free enthalpy of this reaction is, the easier the polymerization will be. That is why we computed the free enthalpy of this reaction (at \( T = 298 \text{ K}, \ P = 1 \text{ atm} \)) for each monomer using thermochemical calculations with SCF criteria:

**For EDA:**

\[
\text{NH}_2\text{–CH}_2\text{–CH}_2\text{–CH}_2\text{+NH}_2\text{–CH}_2\text{–CH}_2\text{–NH}_2 \rightarrow \text{NH}_2\text{–CH}_2\text{–CH}_2\text{–NH}_2 \]
\[
\Delta G(\text{EDA})^\circ = -65.1 \text{ kcal mol}^{-1}
\]

**For DAP:**

\[
\text{NH}_2\text{–CH}_2\text{–CH}_2\text{–CH}_2\text{+NH}_2\text{–CH}_2\text{–CH}_2\text{–CH}_2\text{–NH}_2 \rightarrow \text{NH}_2\text{–(CH}_2)_3\text{–NH}_2\text{–(CH}_2)_3\text{–NH}_2
\]
\[
\Delta G(\text{DAP})^\circ = -60.7 \text{ kcal mol}^{-1}
\]

**For PPD:**

\[
\text{NH}_2\text{–Ph}^\text{+} + \text{NH}_2\text{–Ph–NH}_2 \rightarrow \text{NH}_2\text{–Ph–NH}_2^\text{+}
\]
\[
\text{–Ph–NH}_2
\]
\[
\Delta G(\text{PPD})^\circ = -79.4 \text{ kcal mol}^{-1}
\]

It appears that these three free enthalpies are negative and consequently all these reactions are thermodynamically favored. It can also be noticed that the most favored reaction is the reaction involving PPD (other reactions have roughly the same free enthalpies). So we can deduce that the primary carbocations obtained by electrochemical oxidation of the initial monomers have an important affinity for the monomers and so they react easily with these monomers to evolve progressively in longer and longer linear oligomers and polymers.

### 5. Conclusion

First of all, we showed that the electrochemical oxidation of PPD leads to polymeric films, which were, identified by IR-ATR spectroscopy and ab initio calculations as polyPPD films. Then we established, using energy calculations with the SCF quantum-chemical methods at the Hartree–Fock level of theory, the polymerization mechanism leading from PPD to polyPPD and we generalized this mechanism to other non-substituted aliphatic or aromatic diamines leading to polyalkyleneimines. We have also compared these different mechanisms and we found they are quite similar even if the energies and thermochemical values of the intermediates involved in these mechanisms vary from one monomer to the other.

In addition, we showed that quantum computational chemistry is a very powerful method especially when it is associated to experimental techniques such as spectroscopic methods (here, IR-ATR spectroscopy) because it provides information about molecules, in particular unstable molecules.
which are impossible to observe through the experiment.

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References