

Environmentally Friendly Synthesis of Polypyrrole within Polymeric Nanotemplates-mechanism of polypyrrole synthesis

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ABSTRACT

This paper describes an innovative way to synthesize polypyrrole using self-assembly nano-templates poly (isobutylene-alt-maleic anhydride) (IMA) or poly (styrene-alt-maleic anhydride) (SMA). The reaction occurs in neutral pH water solution, requires no further electrochemical induction or chemical oxidizers as opposed to currently used methods. To understand the reaction mechanism, the reaction path was investigated theoretically by *ab initio* Density Functional Theory (DFT) simulations. It was found that water has a crucial role in the activation and elongation steps of the polymerization. This study is expected to have an important impact on a novel environmental friendly synthesis of conducting polymers.

Keywords: polypyrrole, amphiphilic alternating copolymer, confinement effect, computational chemistry

1 INTRODUCTION

In recent years, polypyrrole has been intensively studied due to its conducting property and its applications in organic light-emitting diodes (LED) [1], display [2], to charge dissipating films [3] and volatile organic light sensors [4][5]. To the best of our knowledge, up to now all the syntheses reported in literature involve electrochemical oxidation or chemical oxidation [6-8]. Lately, our group discovered an innovative way to synthesize polypyrrole using self-assembly nano- templates poly (isobutylene-alt-maleic anhydride) (IMA) [9] or poly (styrene-alt-maleic anhydride) (SMA) [10]. The templates are amphiphilic copolymers with hydrophobic core and hydrophilic outer layer in water solution. When immersed in the template system, pyrrole molecules polymerize in the hydrophobic cavity, with no external inductions. The reaction only takes place in a confined environment where the cavity is 2nm. This phenomenon, the confinement effect, has been widely reported in biological systems. Recent works [11,12] show that confined environment results in different dynamic and thermodynamic properties of fluids inside of the small cavities and therefore one could apply it to induce synthesis that would not happen in bulk environment. With that in mind, it is therefore important to investigate the reaction mechanism to provide insight information on synthesis within nanotubes. The aim of this paper is to use theoretical calculations to follow the reaction pathway. We

performed a thorough *ab initio* quantum chemical study over the reaction potential energy surface corresponding to different structures. The detailed reaction pathway is described including the transition states (TS), intermediate products and the energies will be calculated accordingly.

2 METHODS

All results have been found using the Gaussian 03 software package. All ground states and transition state calculations are done at the DFT level using the hybrid functional B3LYP and basis set 6-31+G. The imaginary frequencies of each TS were animated to ensure that the transition state corresponded to the correct reaction path.

2.1 Activation of Pyrrole

To determine the role of water on the activation step, two simulations were performed. The first simulation involved the increase of the N-H bond of pyrrole to obtain the activated form with protonations of either on alpha or on beta carbon. The second simulation was performed in the presence of water close to the N-H group of pyrrole. Water was aligned linearly with pyrrole through N-H. A relaxed scan was performed increasing N-H bond distance at 0.05Å increment 30 steps. The scan was done and compared at three levels: B3LYP/6-31+G (d), B3LYP/6-31+G and B3LYP/6-31G. Transition state was calculated through QST3 method at B3LYP/6-31+G level. Products and reactants were optimized at B3LYP/6-31+G.

2.2 Dimerization

Five conformations were proposed for dimerization with different binding arrangements (table 1). The most stable structure was chosen for further calculations. The binding of two activated monomers was performed in relaxed scan where C_{α} - C_{α} distance was decreased at 0.1Å increments 30 steps at B3LYP/6-31+G level. Further geometry rearrangement and proton shuffling were completed through 2D scans at HF/3-31G. All transition states were searched through QST3 method at B3LYP/6-31+G level. The stable intermediates were all optimized at the level of B3LYP/6-31+G.

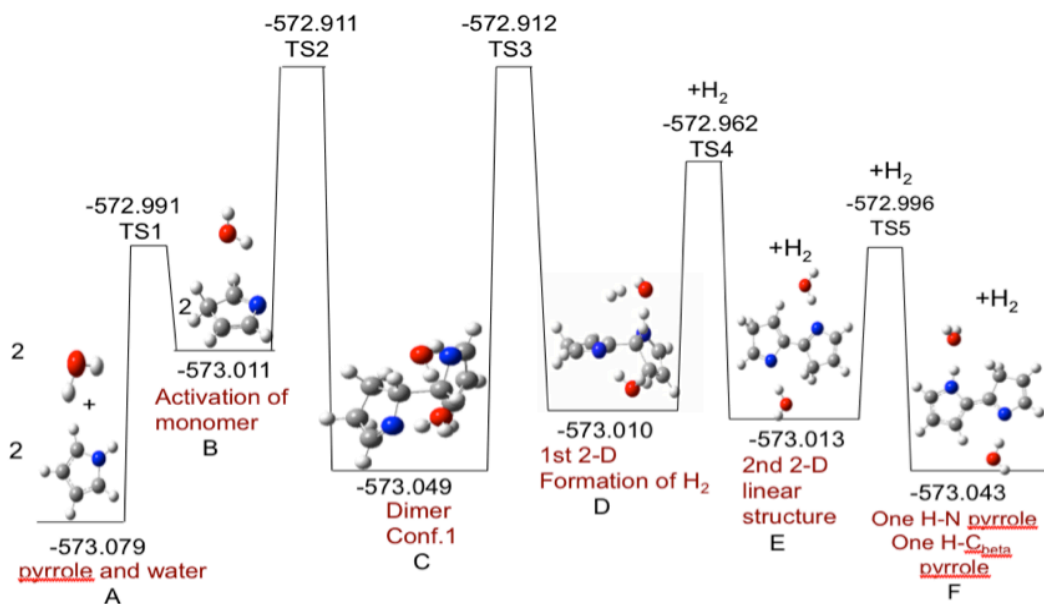


Figure 1: reaction pathway. All intermediates are marked from A-F. The transition states are labeled from TS1-TS5. The energies are in Hartree.

2.3 Rearrangement

The final structural rearrangement of the pyrrole dimer was performed so that one pyrrole is reprotonated on its nitrogen while the other pyrrole stays activated at beta-carbon. The ground state and transition state calculations were done at B3LYP/6-31+G level.

3.1 Activation of Pyrrole

3. RESULTS

The complete reaction pathway is mapped out through computation simulations (Figure 1). The reaction is mediated by water and the final product is linear and conjugated.

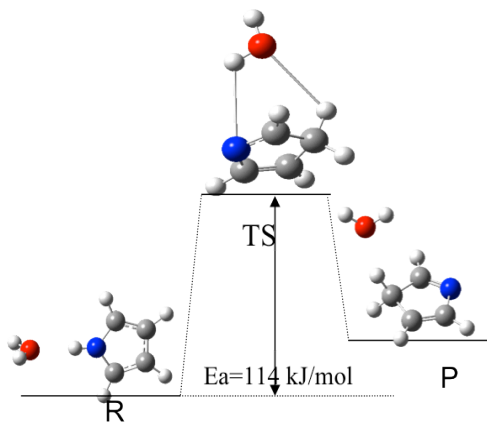


Figure 3: reaction pathway of water-pyrrole activation. In this step, water facilitates proton transfer from nitrogen to beta carbon. B3LYP/6-31+G basis set was used here.

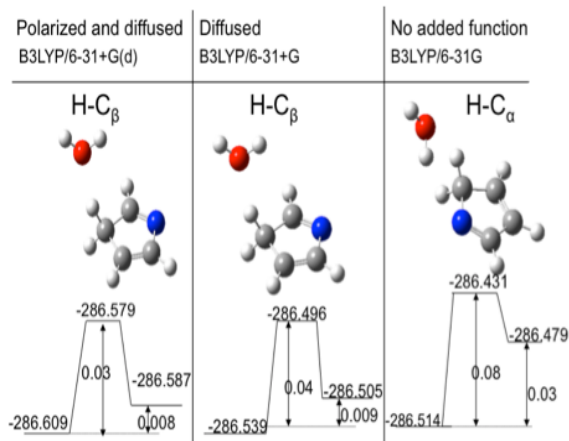


Figure 2: Water-pyrrole scan by three different basis sets

When water is present during the reaction, pyrrole can act both as a proton donor (the proton attached to the nitrogen) to water and as a proton acceptor (to the pi-electron cloud). A study on water-pyrrole complex indicated that the proton donor form is energetically favored by 6.72 kcal/mol [13]. Therefore in the initial step water was linearly linked to N-H of pyrrole.

A relax scan was performed where N-H bond increases at 0.05Å increment. Three different levels of basis sets were used to calculate for comparison: B3LYP/6-31+G (d), B3LYP/6-31+G and B3LYP/6-31G. Both B3LYP/6-31+G (d) and B3LYP/6-31+G basis sets result in

protonation at beta-carbon, where the lower basis set B3LYP/6-31G protonates the alpha-carbon instead which gave energetically less favored reaction path (Figure 2). The structures from B3LYP/6-31+G (d) and B3LYP/6-31+G are similar and are close in energy. For simplicity only B3LYP/6-31+G was chosen as the level of theory in this study.

To compare two conformations, H-C_β and H-C_α, both transition states were searched by QTS3 method [14]. The result shows that the protonated beta conformation is kinetically (100kJ/mol lower) and thermodynamically (54.6kJ/mole lower) favored. Furthermore, a control group was done with no water molecule presented. It shows that only protonated-alpha conformation was obtained. Water was the only agent present in reaction system, so that it is reasonable to believe water directs proton transferring during the reaction. We can then calculate the stabilization energy by water using equation (1)

$$\Delta E(\text{stabilization}) = E(\text{water-pyrrole}) - E(\text{water}) - E(\text{pyrrole}) \quad (1)$$

The stabilization energy -40 kJ/mol shows that the presence of water molecules not only facilitates proton transfer, but also was needed to obtain an activated pyrrole molecule in a beta-carbon conformation.

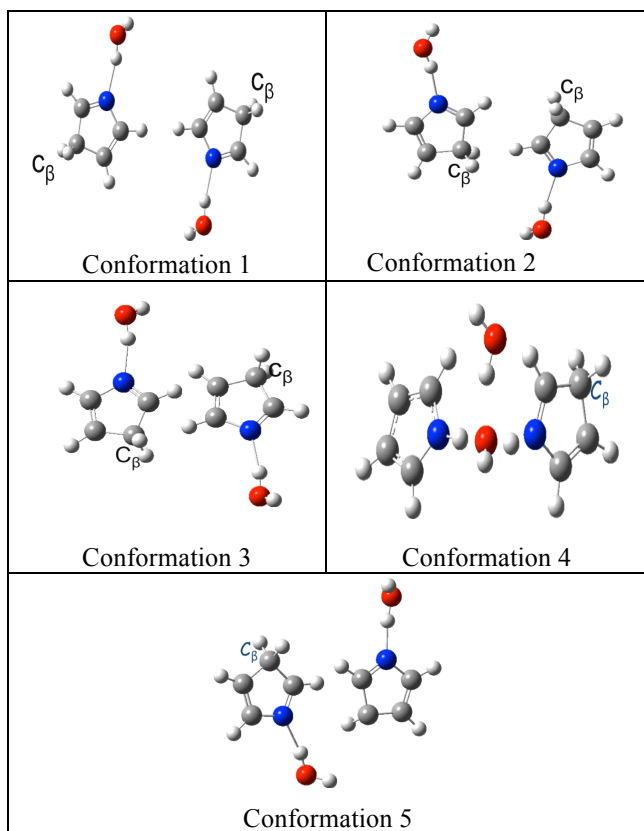


Table 1: Five conformations proposed for dimerization. 1 gave the lowest activation energy and the most stable product.

Previous studies [15, 16] have indicated that pyrrole could reversibly convert to H-C_β and H-C_α through tautomerization in the absence of water with the alpha pyrrole (H-C_α) tautomer being more stable kinetically and thermodynamically. In contrast, our work shows the H-C_β conformation is to be more favorable (Figure 2).

3.2 Dimerization of Pyrrole

The dimerization of activated pyrrole monomers was studied subsequently and the reaction is shown in figure 1, step B-C. Five possible conformations were proposed based on possible binding arrangements (Table 1). In all structures, C_α's are the polymerization sites, given that the reaction occurs between C_α-C_α. Conformations 1, 2 and 3 include two H-C_β pyrrole monomers with different geometry arrangements. Specifically, conformation 1 and 2 align two monomers show an inversion point: 1 has both H-C_β facing outward and 2 positions both H-C_β inward. Conformation 3 lines two pyrrole monomers in the same direction so that one H-C_β faces outward and another one faces inward. Conformations 4 and 5 also included two pyrroles, however one is activated and the other one is not.

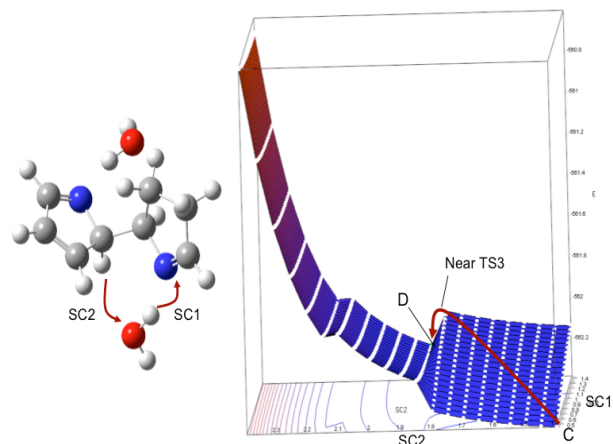


Figure 4: first 2-D scan. The two dimensions of scan are shown in red arrows on the left. The reaction pathway is marked on the right in red arrow. The reaction goes from structure C to D, with the pre-transition state of TS3.

All five structures underwent relaxed scans where C_α-C_α distance was decreased at 0.1Å increments 30 steps at B3LYP/6-31+G level. The most stable product, conformation 1, with the lowest activation energy was selected for further characterization. Following the C_α-C_α bond formation of the dipyrrole, a second proton transfer occurs from H-C_β to adjacent pyrrole resulting in two H-C_β's on one pyrrole, with the second pyrrole remaining unprotonated (Figure 1, step B-C). This calculated dimer C is structurally different from stand-alone polypyrrole where its nitrogen atoms are unprotonated and the C_α centers are protonated. With that in mind, further proton transfer was studied.

Using dimer C as a starting structure, a two-dimensional relax scan was performed. The N-H distance was decreased along the first dimension (0.2 Å increments, 20 scans) and C-H distance was increased along the second as shown in figure 4 (0.2 Å, 20 scans). Due to the complexity of the calculation, the 2-D scan was performed at HF/3-31G level. The potential energy surface obtained during the scan is illustrated in figure 4. The formation of H₂ gas was indicated and the structure is further stabilized in energy. The lowest energy path from reactant C to product D was chosen as the reaction pathway (Figure 4). The saddle point was searched by QST3 method at B3LYP/6-31+G level. The second 2-D scan was done in the same fashion with omission of the H₂ molecule, but on the C-H and N-H bonds on the opposite side of dimer (figure 1, step D-E). During the second 2-D scan, proton shuffled again resulted a completely linear structure where both pyrroles are protonated at beta-carbon. The reaction pathway was also selected based on the lowest energy sequence, and the saddle point was chosen as the near transition state. Which was then optimized using QST3 at the B3LYP/6-31+G level (Figure 5).

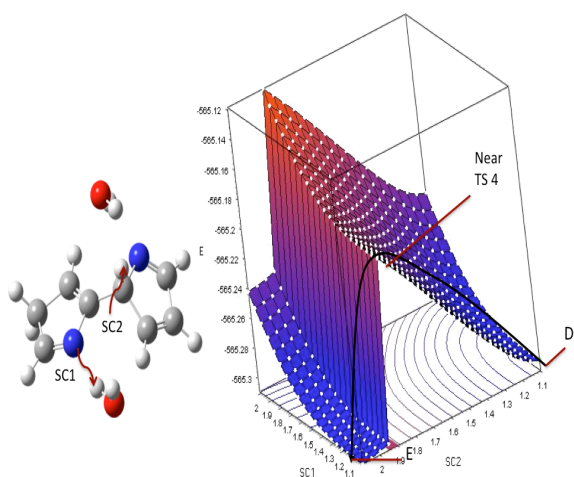


Figure 5: second 2-D scan. The two dimensions of scan are shown in red arrows on the left. The reaction pathways marked on the right in black arrow from D-E.

3.3 Rearrangement of Pyrrole Dimers

Comparison between structure E and the polypyrrole indicated that there is further proton shuffling since both nitrogen atoms remained unprotonated in structure E (Figure 1). The final product was achieved by protonating one nitrogen and keeping the other pyrrole activated at the beta carbon (Figure 1. Step E-F). The final structure is further stabilized in energy and the dimerization is complete. As a result, polymerization will proceed in the fashion that the incoming monomers will add to the activated beta-carbon pyrrole at C_α centers and the proton will transfer back to the nitrogen from C_β after dimerization.

CONCLUSION

This paper described a detailed study of the polymerization of pyrrole in aqueous environment. Understanding the details of the novel synthesis in great details would provide us profound insight to control the structure at the nanoscale. It is our interests, from both theoretical and practical point of view, to understand the reaction pathway, intermediate reactivity and calculate the energies accordingly. The theoretical characterization of the synthesis and the number steps involved showed the essential role of water in this confined polymer template for the activation as well as polymerization of pyrrole. The synthesis is template-directed and the soft templates used here provide a confined space. Future work will study the confinement effect with larger cavity spacing to help determine the role of space restriction in directing the synthesis. This study is expected to have an important impact on a novel environmentally friendly synthesis of nanostructures. It will contribute to knowledge in utilizing nanotemplates to synthesize novel materials.

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