

Quantum chemical calculation of imidization mechanism of polyamic acid

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Abstract. In this paper, the imidization mechanism of polyamic acid to prepare polyimide has been studied by the density functional theory (DFT) method. Our results have shown that the imidization would proceed via two different reaction paths. The activation barrier via hydrogen transfer to closer carboxylate oxygen in the COOH is 220.35 kJ/mol while the activation barrier via hydrogen transfer to hydroxyl oxygen in the COOH is 220.70 kJ/mol. Both reaction paths would run in the actual thermal imidization process with closer high activation barriers. The high energy barrier interpreted the fact that additional energy or catalyst is usually needed during imidization. Moreover, the intrinsic imidization mechanism indicated is critical to further improve the imidization process.

1. Introduction

Polyimides (PIs), a kind of successfully commercialized polymer, have been used extensively in a wide variety of applications such as in aerospace and microelectronics due to their unique physical and chemical properties such as excellent thermal stability, high strength, good dielectric and chemical resistance [1-3]. Since high molecular weight polyimide were firstly synthesized by a two-stage polycondensation of pyromellitic dianhydride with diamines in 1955, the interest in this class of polymers has grown steadily [4-6].

The typical synthesis to prepare polyimides consists of a two-step scheme in which the first step involves polymerization of a processable polyamic acid (PAA) intermediate, followed by a second cyclization or imidization step of polyamic acid to yield the final polyimide. This preparative pathway is representative of most of the early aromatic polyimide work and remains the most practical and widely utilized method of polyimide preparation to date. Imidization is commonly completed through conventional thermal treatment or chemical imidization. Imidization process is critical to the production and performance of polyimide. At present, extensive experimental data on different aspects of the thermal and chemical imidization of polyamide acid have been accumulated [7]. However, the experimental data alone are insufficient to lay down the unambiguous mechanism of the imidization. There are different assumptions about the intrinsic mechanism of the direct imide ring formation. Quantum chemical calculation was confirmed to be useful to interpret the experimental data by semi-empirical quantum chemical methods (MNDO) [7]. Quantum chemical calculation should become more fruitful on investigating the reaction mechanism with the increase of calculation precision and velocity [8-9].

Herein, the reaction mechanism of imidization in PAA has been studied by the usage of density functional theory (DFT). Reaction kinetics is explored within the framework of transition state theory.



In detail, we calculate the minimum energy reaction paths (MERPs) during imidization in polyamic acid using the B3LYP exchange and correlation functionals.

2. Theory

In transition state theory, a reaction is a movement from the valley or minimum representing the reactants to the valley of the products on the potential energy surface. The path across the landscape, including any intermediates and transition states, describing the reaction mechanism. The highest point along the lowest energy reaction path connecting reactants and products is the transition states, while the transition structure refers to the geometric structure of the first-order saddle point.

2.1. Computational methods

To determine the minimum energy reaction paths and the transition states (TSs), we used the GEDIIS method as implemented in Gaussian 09 version. The geometry optimization and vibrational frequency calculations were done using the B3LYP exchange and correlation functionals with the B3LYP/6-31G(d,p) basis set. Vibrational frequencies are computed by determining the second derivatives of the energy with respect to the Cartesian nuclear coordinates and then transforming to mass-weighted coordinates. Frequency values represent the property of the stable point. Local minima have all positive frequencies while transition states have one imaginary frequency. Zero-point energy corrections on the potential energy surfaces is also obtained during the frequency calculation. Dynamic reaction path (DRP) based on an intrinsic reaction coordinate (IRC) or minimum energy path is followed in one or both directions from the transition state at the same level.

2.2. Quantum chemical model

Reactant configuration was simplified as the computational model considering both the calculation precision and calculation time. The available evidence shows that it is sufficient to consider model polyamic acid as the type shown in figure 1 [7].

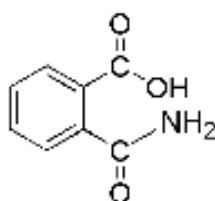


Figure 1. The computational model of polyamic acid.

3. Results and discussion

3.1. Molecular structures of polyamic acid

We have done an energy minimization for all reactants and products. Reaction process is based on the characteristics of the reactants. Thus, structural optimization of the polyamic acid was analyzed first.

The different optimized geometries of polyamic acid are shown in figure 2. The mirror conformation is ignored on account of the same energy. Based on the position of the carbonyl, hydroxyl and amino groups, there are four different conformations. Namely, the carbonyl groups are both inside the loop (figure 2a), the carbonyl groups are both outside of the ring (figure 2b), the carbonyl group attached to the -NH₂ group is inside the ring while the carbonyl group attached to OH is outside of the ring (figure 2c) and the opposite (figure 2d).

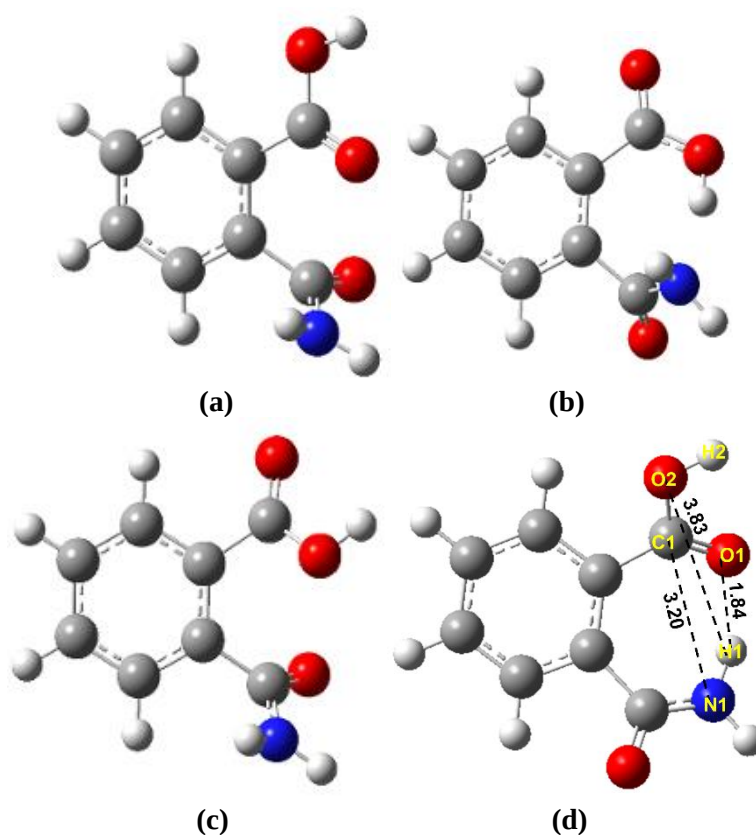


Figure 2. Typical conformations of polyamic acid (unit: Angstrom).

The absolute energy value of the different conformations from (a) to (d) in figure 2 are -1547518.7 kJ/mol, -1547494.5 kJ/mol, -1547517.8 kJ/mol and -1547524.1 kJ/mol, respectively. The conformation in (d) possesses the lowest energy, 5.4-29.6 kJ/mol lower than several other conformations. Hence, it is the most likely stable conformation of the polyamic acid. The minimum energy reaction paths would be calculated based this stable quantification model.

3.2. Minimum energy reaction paths

The cyclization of neutral polyamic acid should be expected to run via the bonding of C-N and the transfer of hydrogen in the NH₂ to oxygens in the COOH. The hydrogen could transfer to carboxylate oxygen or hydroxyl oxygen in the COOH, which results in two different reaction paths. The carboxylate oxygen is closer to the hydrogen. Figure 3 is the calculated structures of transition state and intermediate product via the transfer of hydrogen to the closer carboxylate oxygen (O1). The imidization proceeds via the tetrahedral intermediate (INT) and four-membered transition states TS1 and TS2 in the stepwise mechanism. Relative energy of stationary points on the potential energy surface in the reaction of PAA → PI + H₂O without any catalysis are shown in figure 4. The imidization energy barrier (TS1) via this path is 220.35 kJ/mol. The activation barrier in the second step is 147.32 kJ/mol, which is 73.02 kJ/mol lower than that in the first step.

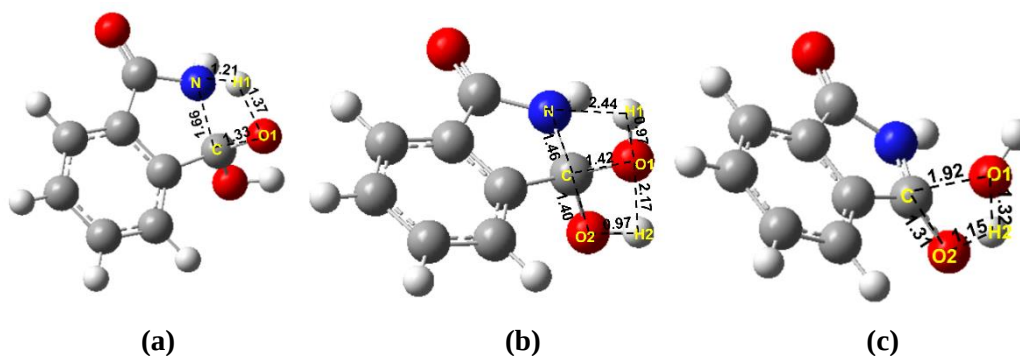


Figure 3. Molecular structures of the transition states and the intermediate via the transfer of H to O1 (unit: Angstrom); (a) Transition states TS1; (b) Intermediate; (c) Transition states TS2.

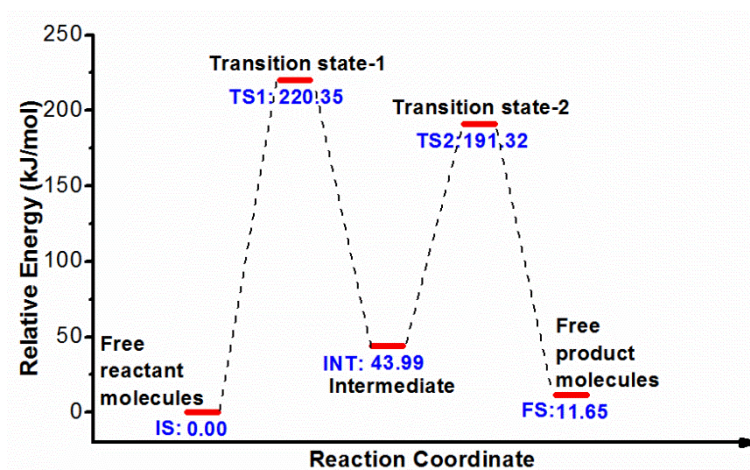


Figure 4. Calculated relative energy of stationary points on the potential energy surface in the reaction of $\text{PAA} \rightarrow \text{PI} + \text{H}_2\text{O}$ via the transfer of H to O1 reaction coordinate.

Figure 5 shows the calculated structure of the transition state via the transfer of hydrogen to the hydroxyl oxygen (O2). The imidization proceeds via the transition states TS3 in the $\text{S}_{\text{N}}2$ mechanism. Relative energy of stationary points on the potential energy surface in the reaction of $\text{PAA} \rightarrow \text{PI} + \text{H}_2\text{O}$ without any catalysis are shown in figure 6. The imidization energy barrier via this path is 220.70 kJ/mol.

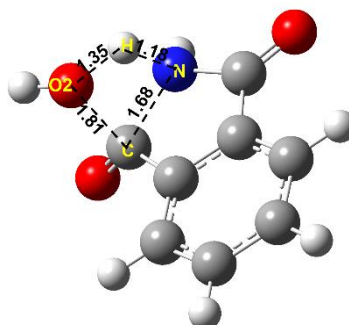


Figure 5. Molecular structure of the transition states TS3 via the transfer of H to O2 (unit: Angstrom).

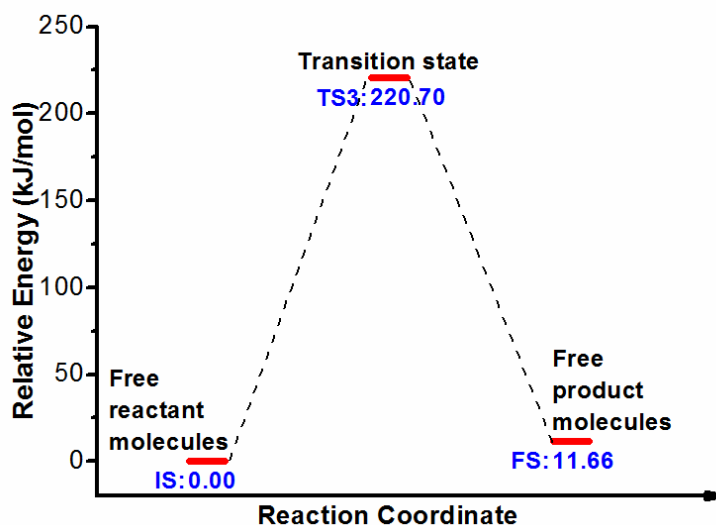


Figure 6. Calculated relative energy of stationary points on the potential energy surface in the reaction of $\text{PAA} \rightarrow \text{PI} + \text{H}_2\text{O}$ via the transfer of H to O₂ reaction coordinate.

After passing the transition states as shown in figure 3 and figure 5, the product polyimide and water (H_2O) was obtained by the formation of a more stable five-membered ring. We have confirmed that reactants (polyamic acid) and products (polyimide and water) can both be obtained from the transition states based on an intrinsic reaction coordinate (IRC) or minimum energy path.

As a result of B3LYP calculations of transition states, the energy barrier according to the $\text{S}_{\text{N}}2$ mechanism is a little higher. During the actual imidization process, both reaction paths above would run based on very close activation barrier. This is different from the results calculated by MNDO method [7], which indicated that the stepwise mechanism was more favorable than the concerted mechanism.

Generally, the imidization is characterized by high activation barriers. This is in agreement with the intense heating of polyamic acid to obtain imidization. The energy barrier of TS1 calculated by MNDO method is 283 kJ/mol [7]. It should be noted that experimental activation energies of the thermal imidization of polyamic acid are in the range of 80-130 kJ/mol [9], which is much lower than the calculated reaction barrier. Besides, the result of B3LYP calculations is closer to the experimental data than the MNDO calculations. The high values of the calculated energy barriers are accounted for not only by the shortcomings of the calculation method, but also by the absence of consideration of such medium effects as catalysis of the cyclization by the carboxyl groups of polyamic acid, the difference of electric susceptibility from unity, etc. [7]. The possibility of catalysis by carboxyl groups suggests that one of the reasons that the thermal process does not yield a completely cyclized final polyimide may be a depletion of catalytically active carboxyl groups in imidization. Based on the above results, additional energy or catalyst could be used to change the paths of C-N bonding and hydrogen transfer to lower the imidization temperature.

4. Conclusion

The minimum energy reaction paths during the imidization of polyamic acid have been studied in the current work. As a result of the calculations, the imidization would proceed via two different reaction paths. The activation barrier via hydrogen transfer to the closer carboxylate oxygen in the COOH is 220.35 kJ/mol while the activation barrier via hydrogen transfer to hydroxyl oxygen in the COOH is 220.70 kJ/mol. Both reaction paths would run in the actual imidization process based on very close activation barrier. In general, the imidization is characterized by high activation barriers. This is in agreement with the intense heating of polyamic acid to obtain imidization. Based on the above

conclusions, we could use the catalyst or additional energy to change the paths of C-N bonding and hydrogen transfer to lower the imidization temperature.

Acknowledgments

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