

Theoretical study of the transesterification reaction of polyethylene terephthalate under basic conditions

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ABSTRACT

The depolymerization reaction of polyethylene terephthalate (PET) was analyzed using a computational chemistry approach. The reaction is a type of transesterification reaction using alkoxide. In this study we employed the calculated optimum structure, electrostatic potential distribution, activation energy, electric charges and pathway to investigate the mechanism. We found that the tetrahedral intermediate produced by ring formation with alkoxide is an essential feature of the depolymerization process. Moreover, there is a possibility that a PET molecule is depolymerized by multiple alkoxides at the same time. However, the effects of degree of polymerization and the position of attack by the alkoxides do not strongly influence the reactivity.

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1. Introduction

Polyethylene terephthalate (PET) is used extensively in the manufacture of fibers, photographic films and bottles for soft drinks. However, the amount of PET waste is increasing drastically and so a recycling process must be established for the preservation of resources and the protection of the global environment. There are three methods available to reduce the usage of natural resources by recycling plastic waste: physical, thermal and chemical recycling. Chemical recycling (feedstock recycling) chemically decomposes the PET waste into the original feedstock monomers and is of great interest for preventing hygiene and smell problems. When pure monomers are obtained, a PET resin with excellent performance can be resynthesized. In recent years, several processes of PET depolymerization by hydrolysis and alcoholysis have been reported with different depolymerizing agents and operating conditions [1–4]. The most studied chemical recycling reaction is that between PET and a mono alcohol, diol or other solvents under acidic or basic conditions [5–7]. However, a comprehensive understanding of the molecular interactions between PET and alcohol (alkoxide) is necessary for unraveling the details of the depolymerization mechanism.

In this study, a theoretical analysis was conducted to further study the PET depolymerization. Experimentally, PET is depolymerized to ethylene glycol (EG) and disodium terephthalate ($\text{Na}_2\text{-TPA}$) in boiling EG with sodium hydroxide under atmospheric

pressure. The Gaussian software package was selected from several available computational chemistry programs to simulate the EG alkoxide and the periodic structure of PET because it provides comprehensive molecular information such as optimized structures and electrostatic potentials (ESP) [8,9]. Computational chemistry has been never applied to PET depolymerization and this investigation is the first such quantum chemistry attempt. Various data obtained from these calculations, such as the optimum structure, ESP, electric charge and reaction path were useful for the analysis of the depolymerization mechanism. A comparison of such simulation data with conventional experimental kinetic data will assist in the general understanding of the fundamental behavior of polymer degradation.

2. Computation method

The depolymerization reaction of PET illustrated in Fig. 1 is a kind of transesterification reaction involving the addition of alcohol under basic conditions. The reaction proceeds via the exchange of the alkoxyl group of an ester compound with that of another alcohol. The attachment of the alkoxide breaks the single bond between the carbon and oxygen atom of the carboxyl group as shown by arrows in Fig. 1, and the PET is gradually decomposed into smaller components. Eventually, disodium terephthalate ($\text{Na}_2\text{-TPA}$) and EG are produced. Experience suggests that the transesterification reaction should proceed via a tetrahedral intermediate, or transition state, formed when the carbonyl carbon is attacked by alkoxide [10,11]. The characteristics of

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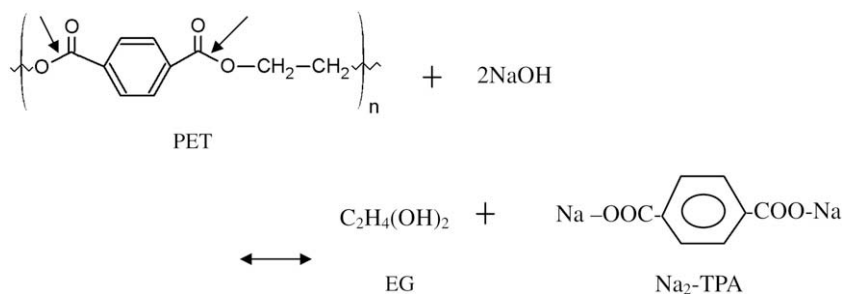


Fig. 1. Depolymerization reaction of PET.

transesterification have been previously considered in terms of activation energy considerations [12,13]. In this study, quantum data concerning the transition state is derived from calculations using the Gaussian software (Gaussian R 03W Ver. 6, Gaussian, Inc.) [12,13]. To simulate the mechanism of the transesterification reaction of PET, a two-stage procedure was adopted as follows.

First stage: calculation of the optimum structure of the ground and transition states. The molecular structures of the ground state (PET and alkoxide of EG) and the transition state during PET transesterification were simulated. The activation energy of the depolymerization reaction was obtained from the optimized structures calculated as the minimum energy configuration from an initial appropriate coordination of the atoms. The basis set used in this calculation is HF/STO-3G* [14,15].

Second stage: calculation of the ESP distribution of PET and alkoxide using the output data from the first stage.

Although a more complex atomic orbital basis set is more accurate for simulating large molecules [16], a simple basis set (HF/STO-3G*) was used because of excessive computation times required by the more complex basis set. The difference of the averaged ESP between the simple and complex basis set is within 6% and the same trends were obtained from both basis sets.

Each electron density has different values of the ESP distribution, therefore, the distribution must be compared at the same isosurface value [17]. In this case, the ESP distribution is visualized for an isosurface value of electron density = 0.001 [electron/au³].

3. Results and discussion

3.1. Electrostatic properties of PET and alkoxide

The ESP distribution of EG alkoxide is shown in Fig. 2. Here $q(\text{O})$ is the Mulliken charge of the oxygen atom, which has the highest value in the molecule. In the case of EG alkoxide, there are two *cis* and *trans* conformations. When the oxygen atoms are oriented on the same side of the carbon–carbon bond, the compound is referred to as *cis*-EG, whereas, when the oxygen atoms are arranged on opposite sides, it is referred to as *trans*-EG. The ESP distribution and the Mulliken charge both indicate that negative charge concentrates on the oxygen atom due to its high electronegativity. However, in the case of *cis*-EG, the charge is reduced because the two oxygen atoms share one hydrogen atom. The ESP distribution is closely related to the charge, and so the negative charge distribution, shown in red and orange¹, indicates stronger nucleophilicity. In the calculations described below, only results of the depolymerization reaction by *trans*-EG alkoxide are shown because the

trans conformation is more stable in the solution than is the *cis* conformation.

The results of calculations of the Mulliken charge and ESP distribution of PET are shown in Fig. 3. Here, the Mulliken charge of the carbonyl carbon becomes the most positive value of all the atoms in PET. This occurs because the two oxygen atoms of the carboxyl group induce an electron shift from the carbon atom due to their higher electronegativities. Therefore, the ESP distribution of PET provides a quantitative indication of the electrophilicity of the carbonyl carbon atom. Therefore, the depolymerization reaction occurs via the nucleophilic attack of the EG alkoxide oxygen at the electrophilic carbonyl carbon of PET. Moreover, the formation of a hydrogen bond between the hydrogen atom of the alkoxide and the carbonyl oxygen can become the driving force for a stable transition state of the transesterification reaction. Such a transition state, as shown in Fig. 4, appeared for every calculation and was stable in the optimized structure. It is a tetrahedral intermediate with a pentagonal ring. The energy difference between the ground and transition states equates to the activation energy for the reaction.

3.2. Effect of degree of polymerization on activation energy

Normally, the degree of polymerization of PET is 100–200 and it is impossible to calculate the optimum structure of such a large molecule. To gain insight into the role of the length of the polymer chain, we performed calculations for the depolymerization reaction for PET molecules ranging from a dimer to a decamer (2–10 structural units) and the results are shown in Fig. 5. The values of the activation energy remain very constant regardless of the degree of polymerization as long as the depolymerization is of a PET of more than three structural units (trimer). We expect that this tendency will be quantitatively maintained for PET with more structural units and therefore we can use the activation energy result for a short chain.

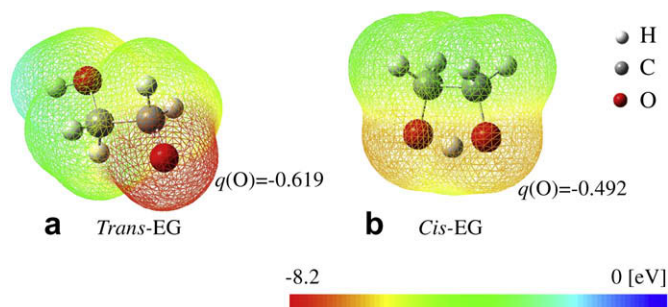


Fig. 2. Electrostatic potential distribution for alkoxide. (a) *Trans*-EG, (b) *cis*-EG.

¹ For interpretation of the references to color in this text, the reader is referred to the web version of this article.

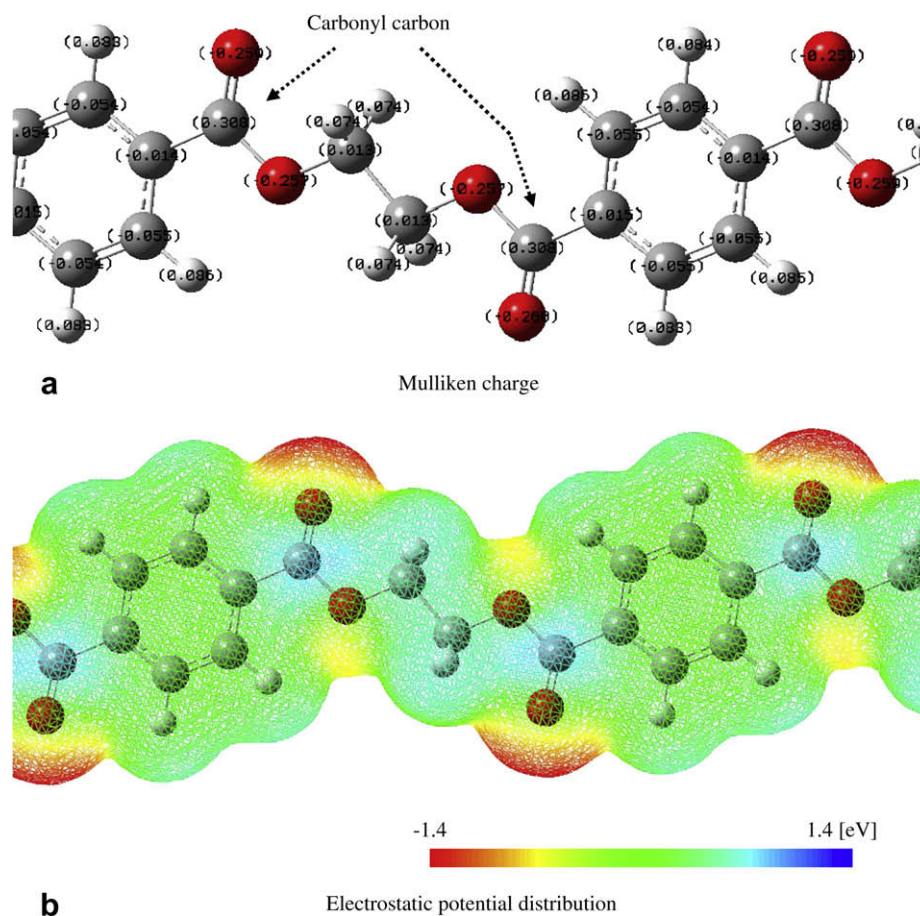


Fig. 3. Mulliken and electrostatic potential distribution of PET. (a) Mulliken charge, (b) electrostatic potential distribution.

3.3. Position attacked in the polymer by the alkoxide

Although, the EG alkoxide attacks the carbonyl carbon of PET, as shown in Fig. 4, an actual PET molecule includes as many carbonyl carbon atoms as the degree of polymerization. Hence, we considered the effect of which carbonyl position is attacked

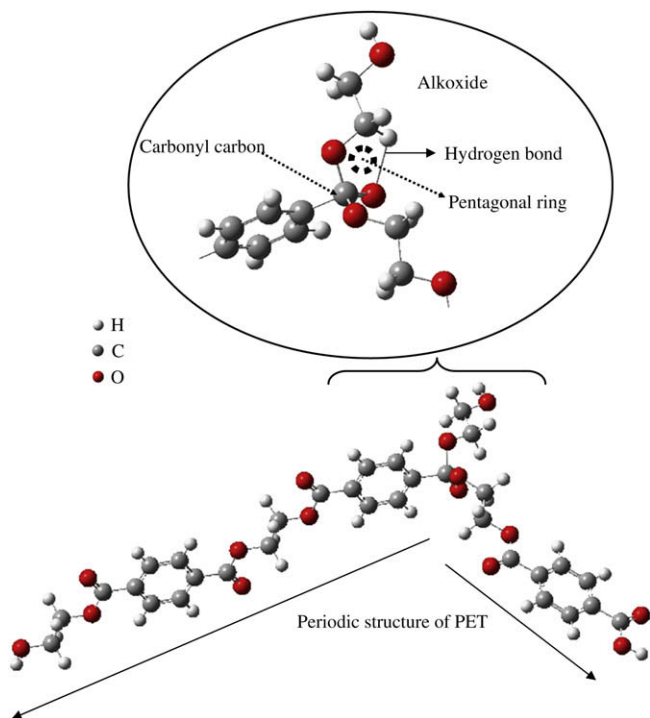


Fig. 4. Transition state of transesterification by alkoxide.

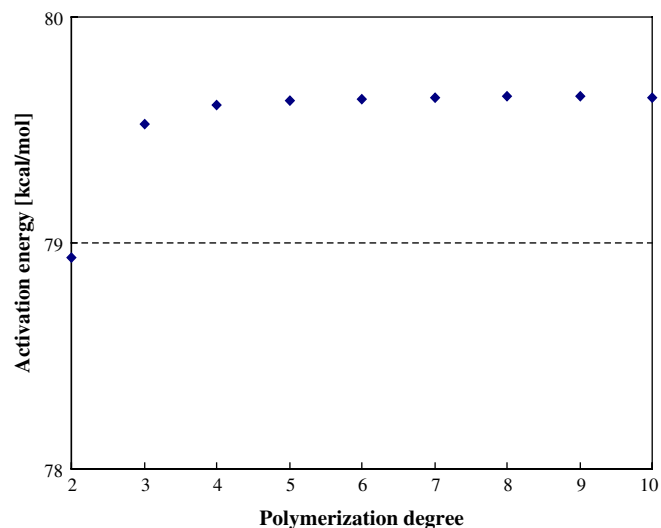


Fig. 5. Effect of degree of polymerization on activation energy.

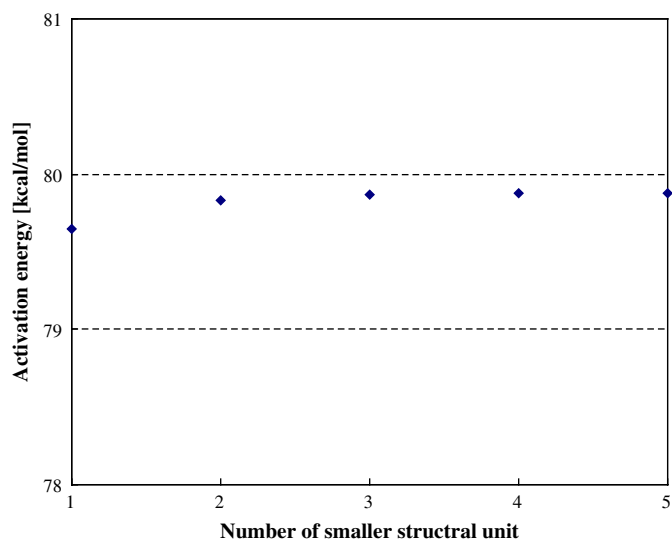


Fig. 6. Activation energy for different position of attack in the polymer.

on the activation energy. Fig. 6 shows the activation energy in the case where a decamer (10 structural units) is split up into two components (1:9, 2:8, 3:7, 4:6 and 5:5) by attack at different carbonyl units; the x -axis values indicate the smaller of the components produced. The effect on the activation energy of the position of depolymerized is small. This reflects an evening-out of the Mulliken charge or ESP distributions on every carbonyl carbon of PET as the molecule grows larger due to the periodic structure.

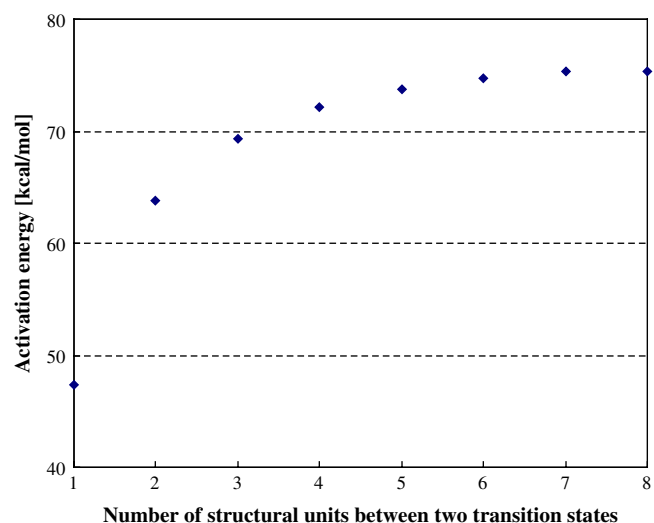


Fig. 8. Activation energy for consecutive transesterification.

3.4. Pathway of transesterification

To analyze the manner in which the EG alkoxide approaches the carbonyl carbon of PET, the pathway was calculated. These calculations employed a PET trimer as the results above suggest that this size oligomer provides a reasonable model for the behavior of a large polymer. Fig. 7 shows the ESP distribution at four positions along the reaction coordination, defined as the distance, d [nm] between the alkoxide oxygen atom at the side of the PET and the carbonyl carbon atom. First, for a separation of 0.41 nm (Fig. 7(a)),

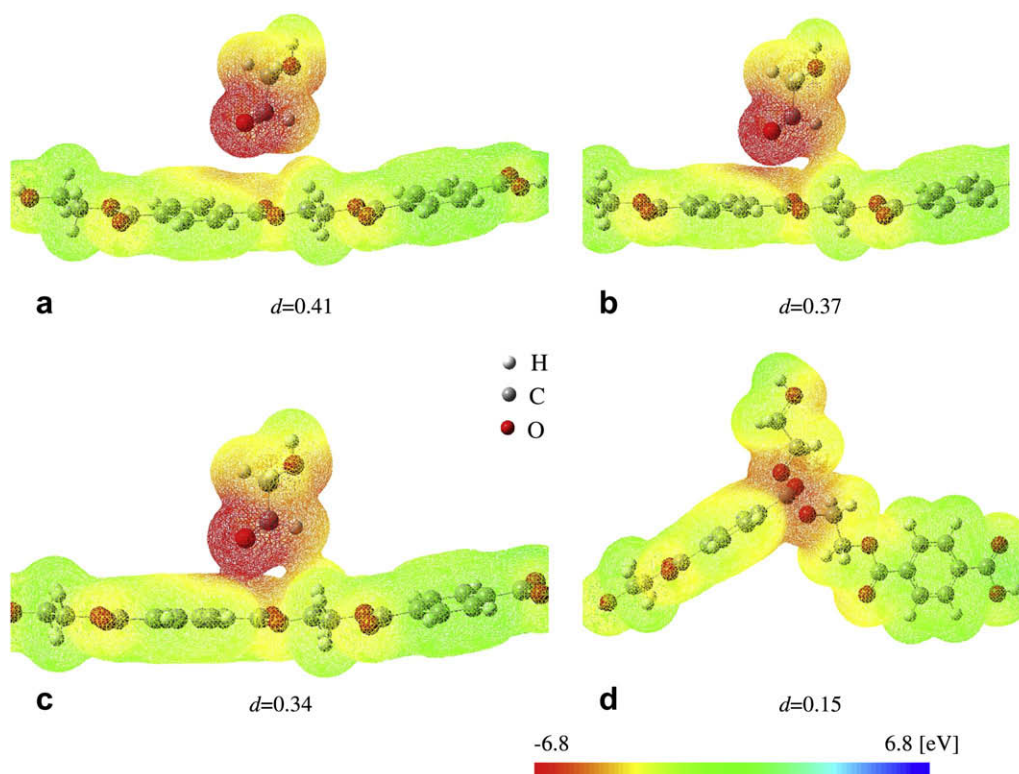


Fig. 7. Pathway and ESP for depolymerization reaction by alkoxide. (a) $d = 0.41$, (b) $d = 0.37$, (c) $d = 0.34$, (d) $d = 0.15$.

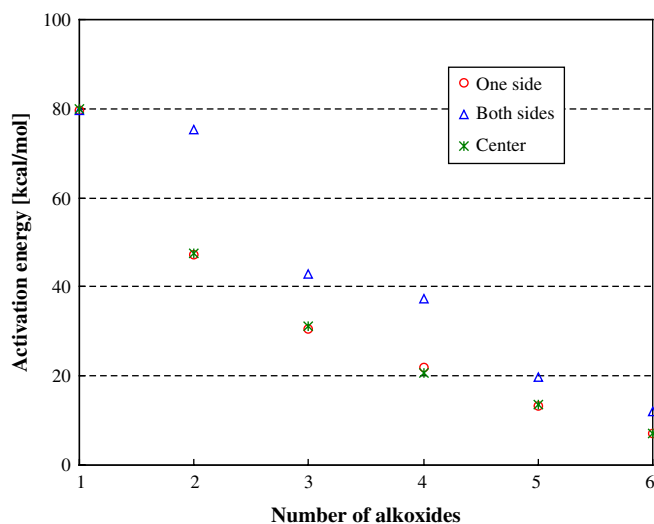


Fig. 9. Activation energy for multiple transition states.

the ESP distributions of PET and alkoxide are undisturbed. Then the EG alkoxide gradually gets closer to the carbonyl carbon (Fig. 7(b) and (c)). A pentagonal ring is formed thanks to the nucleophilicity of the alkoxide, the electrophilicity of the carbonyl carbon and the formation of a hydrogen bond. However, the ester bond is still planar just after the alkoxide is attached. Eventually, at $d = 0.11$ nm (Fig. 7(d)), the carbonyl carbon assumes a tetrahedral structure with the pentagonal ring. This point is defined as the transition state. The periodic structure of the PET becomes kinked around the carbonyl carbon in the transition state because of the need of the carbonyl carbon to be part of a tetrahedral intermediate for the transesterification to succeed.

3.5. Attack by alkoxide on PET already having a transition state

Generally, PET has a very long periodic structure. Therefore, there is a possibility that a PET molecule already in one transition

state could be attacked by a second alkoxide at another carbonyl location. To test this idea, we assumed that the second transesterification occurs by the attachment of alkoxide after the outer ester bond of PET decamer (10 structural units) became the first transition state. Fig. 8 shows the activation energy for such a consecutive transesterification. Here the x -axis is the number of structural units that separate the first and second transition states. When the two transition states are near, the activation energy becomes smaller than that for a single transesterification. On the other hand, when two carbonyl bonds that are distant are attacked sequentially, the activation energy approaches that of the individual transesterification reaction.

Fig. 9 shows the activation energy variation when multiple alkoxides attack one polymer at the same time. In this calculation, it is assumed that there are three manners of attachment of the multiple alkoxides. Alkoxides attach from either one side, both sides, or at the center of a PET decamer. In Fig. 9, the x -axis represents the number of attacking alkoxides. The activation energy decreases with the number of alkoxides, that is, when more transition states are formed more closely together. This means that multiple transesterification reactions can occur simultaneously on the periodic structure of PET. The activation energy of the transition state for reaction from both sides decreases in a staircase pattern. This can be understood by referring to Fig. 8, which shows a lowering of the activation energy when two transition states are closer together. As the number of multiple transition states increases, the likelihood that pairs of transition states are separated by small numbers of structural units goes up in a step fashion, and therefore the activation energy in Fig. 9 drops in a similar staircase manner.

Fig. 10 contrasts the molecular structure of the transition state of a PET decamer for the attack of one and nine alkoxides. Although the structure with one transition state consists of two straight structural units, the structure with multiple alkoxides twists like DNA. We confirmed that in every case the negative electric charge around the transition state has no effect on the neighboring ester bond. Accordingly, the activation energy for the attachment of multiple alkoxides decreases with the number of alkoxides as shown in Fig. 9 because the spiral structure becomes more stable than the straight structure.

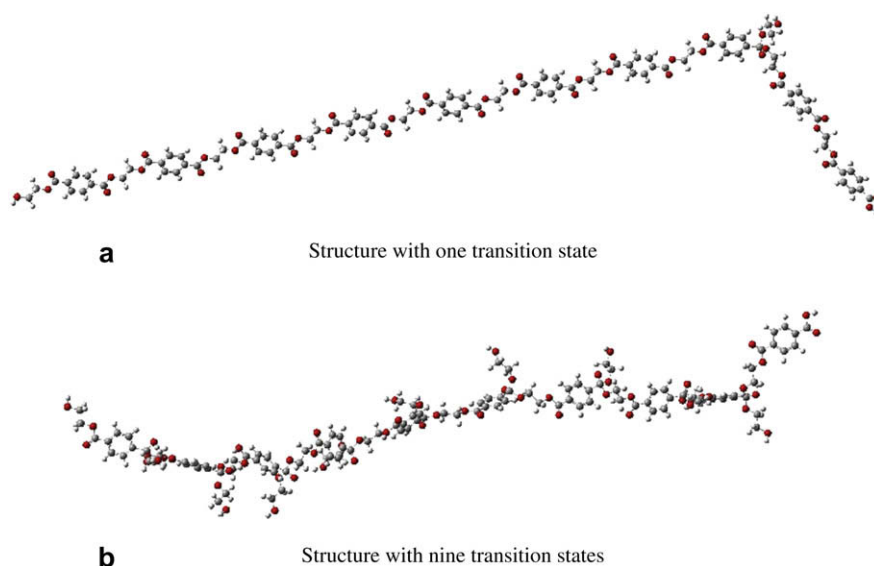


Fig. 10. Molecular structure of PET with multiple transition states.

4. Conclusions

The depolymerization mechanism of PET (polyethylene terephthalate) was investigated using data obtained from a computational chemistry approach. The attachment of alkoxide to the carbonyl bond is essential for the transesterification reaction, and the reaction occurs via a transition state that comprises a tetrahedral intermediate with a pentagonal ring. The activation energy, obtained as the difference between the ground and transition states at various conditions, shows that the effects of the degree of polymerization and the position of attack by the alkoxide do not strongly influence the reactivity. Moreover, there is a possibility that multiple alkoxides attack one polymer simultaneously. The activation energy of the transesterification appears to decrease for multiple transition states, for reasons we conjecture as being due to the stabilization caused by the formation of a spiral structure.

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