

Different dynamic behaviors of the dissociation and recombination reactions in a model calculation of polyethylene by first-principles steered molecular dynamics simulation



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ABSTRACT

We investigate the different dynamics of the stress-induced dissociation and recombination reactions in a model of polyethylene by a first-principles molecular dynamics simulation at the B3LYP/6-31g(d) level. The dissociation under external forces acting on the chemical reaction site at 300 K follows the same pathway as the one calculated by the static first-principles method because it has a similar activation barrier to that of the static first-principles calculation. On the other hand, in the recombination process, thermal fluctuations causes collisions between hydrogen atoms at the chain ends. Furthermore, when external forces do not directly act on the chemical reaction site, two different dissociation processes are observed. On the other hand, recombination process is not observed due to rarely contact of the radical carbon. These results indicate that dissociation and recombination dynamics are very different, showing the importance of the dynamic calculation.

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1. Introduction

Polyethylene is used in many industrial materials, such as cables, paints, and plastics. However, degradation of polymers decreases the toughness of the polymeric materials against the stress. One of the main causes of degradation is the scission of polymers through oxidation [1,2]. In the first step, a radical polymer generated by heat, ultraviolet light, or gamma irradiation reacts with an oxygen molecule. To reduce the degradation, it is essential to understand the mechanisms of the chemical reactions. The scission process of polyethylene by oxidation [3–7] can be summarized as follows. (1) $P^{\cdot} + O_2 \rightarrow POO^{\cdot}$, where P represents the polymer backbone and \cdot indicates a radical. (2) $POO^{\cdot} + PH \rightarrow POOH + P^{\cdot}$. (3) $POOH + P^{\cdot} \rightarrow PO^{\cdot} + POH$. (4) $PO^{\cdot} \rightarrow P=O + P^{\cdot}$ (scission). The evolution of scission events affects the structural changes in polymers and their strength [8]. Therefore, both the statics and the dynamics at finite temperatures are important for the evolution of scission events.

A first-principles calculation is one of the most powerful tools to reveal the atomic-scale phenomena. It was applied to the model

calculations of polyethylene. Cysewski et al. [9] calculated the spin density of polyethylene with an alkyl, oxyl, and a peroxy radical. Ignatyev et al. [10] examined the oxidation of the alkane C_2H_5 . Kysel et al. [11] revealed the H abstraction process of polyethylene by an alkoxy, alkyl, and a peroxy radical at the chain ends. However, both the static first-principles calculation and the first-principles molecular dynamics method are required to reveal the evolution of the scission events, which is important for the strength of the materials. Recently, a first-principles molecular dynamics simulation showed various atomic behaviors in chemical reactions [12–17]. To reveal the dynamics of polymers on an atomic scale, the dissociation processes were studied under external forces by using a first-principles molecular dynamics method [18–21]. However, the recombination process has not been investigated. When the recombination reaction does not occur after chain scission, a radical generated at the chain end abstracts a hydrogen atom from another polymer. The radicals generated in other polymers lead to more chain scission reactions. The evolution of scission reactions affects the strength of polymers [8,22], thus the rate of recombination is very important for materials. Therefore, to clarify the relevance of the evolution of stress-induced scission reactions, we have studied the dynamics of both the dissociation and recombination reactions. The processes are

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difficult to be revealed by larger scale tight-binding and empirical molecular dynamics simulations because there is a radical in the system. In the experiment, the degradation process by oxidation is very complicated. Then, it is very difficult to observe an elementary reaction. Thus, we use first-principles molecular dynamics simulation in this study.

We report the β scission reaction in a model of polyethylene using a static first-principles calculation. Furthermore, we discuss the difference between the dissociation and recombination processes under external forces at 300 K using our own first-principles molecular dynamics program, Violet.

2. Methods

To investigate the scission mechanism of polyethylene, we perform the first-principles calculation. Becke's three-parameter hybrid density functional B3LYP method [23–25] is used. Optimized geometries, reactant complexes, transition state structures, product complexes, and their energies are computed in Gaussian 03 [26] with the 6-31g(d) basis set. Frequencies are calculated in the transition state to characterize the stationary point. We verify that the transition state connects the reactant and product complexes by intrinsic reaction coordinate (IRC) calculations.

To reveal the dynamics of the dissociation and recombination processes, we use our first-principles molecular dynamics program, Violet [27,28], based on unrestricted density functional theory at the B3LYP/6-31g(d) level. The forces are calculated by Hellmann–Feynman theorem with Pulay corrections [29]. The leapfrog algorithm is used for atomic motion with a time step of 0.2 fs. Their temperature is set at 300 K with all atoms, and is controlled by the Berendsen thermostat [30]. Because the computational time is limited and chemical reactions are rare events, we apply external forces to the atoms. This method has frequently been used in previous first-principles molecular dynamics calculations [18–21]. Davis et al. [18] showed that deforming polymers produces forces on the atomic scale and that it stimulates chemical reactions. Here, we assume that the external forces are caused by the deformation of polymers. Atoms under external forces, called attachment points (APs), are pulled or pushed towards the pulling/pushing points (PPs). Therefore, external forces are added to the first-principles internal forces only at the APs. In both of dissociation and recombination processes, the initial structure is optimized by Gaussian 03 at B3LYP/6-31G(d) level. Then, the relaxation calculation is performed for 200 fs before external forces are applied. The external forces are set at 2, 3, and 4 nano Newton (nN) for the dissociation and recombination processes, respectively. To reveal the dissociation and recombination reactions, the two carbon atoms should be pulled toward opposite direction and pushed toward the same position, respectively. Then, in the dissociation process, PPs are set on the extended line of pulled carbon–carbon bond at the initial state. Under external forces, two forced atoms are finally pulled to opposite directions. To prevent the excessive supply of energy by external forces, the external forces are set at 0 N when the distance between carbon atoms is $1.534 \text{ \AA} \times 1.5$ in the dissociation process, where 1.534 \AA is the length of single carbon–carbon bond of C_9H_{20} calculated by Gaussian 03 at B3LYP/6-31G(d) level. In the recombination process, PP is set on the middle position between pushed carbon atoms at the initial state. The external forces are stopped when the distance between carbon atoms is $1.534 \text{ \AA} \times 1.23$. These values are enough to cross over the activation barrier and prevent extra supply of energy. We confirm that the values do not influence the results in this article by changing the length from $1.533 \text{ \AA} \times 1.6 = 2.453 \text{ \AA}$ to $1.533 \text{ \AA} \times 1.7 = 2.453 \text{ \AA}$ and from $1.533 \text{ \AA} \times 1.1 = 1.687$ to

$1.533 \text{ \AA} \times 1.4 = 2.146 \text{ \AA}$, in dissociation and recombination processes, respectively.

3. Results and discussion

To reveal the evolution of chain scission, we first investigate the activation barrier of β scission ($\text{PO}^\cdot \rightarrow \text{P}=\text{O} + \text{P}^\cdot$) without external forces and stretching by first-principles calculations using Gaussian 03. During the scission of polyethylene by oxidation, intramolecular and intermolecular reactions occur. Here, we consider intramolecular reactions. PO^\cdot is generated as follows. A radical polymer (P^\cdot) is generated by heat, ultraviolet, or gamma irradiation. Then, an oxygen molecule reacts with the radical and POO^\cdot is formed. In the intramolecular reaction, POO^\cdot abstracts a second-neighbor hydrogen atom and generates a radical and a OOH termination. The P^\cdot radical abstracts the OH of the POOH and the OH group is formed at the second-neighbor position from PO^\cdot . Here, we consider C_9 as a polymer backbone (P) and place a radical in the center of the polymer. Then, we calculate the β scission of $\text{C}_4\text{H}_9\text{CHO}\cdot\text{CH}_2\text{CHOHC}_2\text{H}_5$. Fig. 1 shows the reactant, transition state, and product, and the potential energy profiles at the B3LYP/6-31g(d) level. The polyethylene dissociates into two polymers through the transition state: $\text{C}_4\text{H}_9\text{CHO}\cdot\text{CH}_2\text{CHOHC}_2\text{H}_5 \rightarrow \text{C}_3\text{H}_7\text{C}\cdot\text{H}_2 + \text{C}_2\text{H}_5\text{CHOHC}_2\text{H}_5$. The activation energy is 13.5 kcal/mol and the product is less stable than the reactant by 6.6 kcal/mol. In the reaction, the dissociated carbon–carbon distance is elongated from 1.541 Å at the reactant to 2.178 Å at the transition state. To verify the effect of the chain length, we also calculate the β scission of C_6 ($\text{C}_2\text{H}_5\text{CHO}\cdot\text{CH}_2\text{CHOHC}_2\text{H}_5$). The activation energy is 13.5 kcal/mol, and the product is less stable than the reactant by 6.7 kcal/mol. The activation energy and reaction energy do not change when the chain length is short. Therefore, we use a short chain (C_6) for modeling the β scission process in the first-principles molecular dynamics simulation.

We also calculate the intramolecular OH abstraction ($\text{C}_4\text{H}_9\text{CHOHC}_2\text{H}_5 + \text{C}_4\text{H}_9\text{CHO}\cdot\text{CH}_2\text{CHOHC}_2\text{H}_5 \rightarrow \text{C}_4\text{H}_9\text{CHOHC}_2\text{H}_5 + \text{C}_4\text{H}_9\text{CHO}\cdot\text{CH}_2\text{CHOHC}_2\text{H}_5$) by Gaussian 03 at B3LYP/6-31G(d) level. The product is more stable than the reactant by 52.8 kcal/mol and the activation barrier is 21.6 kcal/mol which is similar as that of 23.8 kcal/mol in PEO calculated at UB3P86/6-31++G(d,p) level [31]. Furthermore, we calculate the intermolecular OH abstraction ($\text{C}_4\text{H}_9\text{CHOHC}_4\text{H}_9 + \text{C}_4\text{H}_9\text{C}\cdot\text{H}_4\text{H}_9 \rightarrow \text{C}_4\text{H}_9\text{CHO}\cdot\text{C}_4\text{H}_9 + \text{C}_4\text{H}_9\text{CHOHC}_4\text{H}_9$). The product is more stable than the reactant by 53.0 kcal/mol and the activation barrier is 9.32 kcal/mol. This is lower than that in the intramolecular reaction. Adding to these reactions, additional oxygen atoms possibly react with P^\cdot with no barrier suggested in Ref. [32,33,31]. However, it is difficult to judge which reaction is favored. This is because the reaction with oxygen atoms strongly depends on diffusion of oxygen atom in polymers. If oxygen

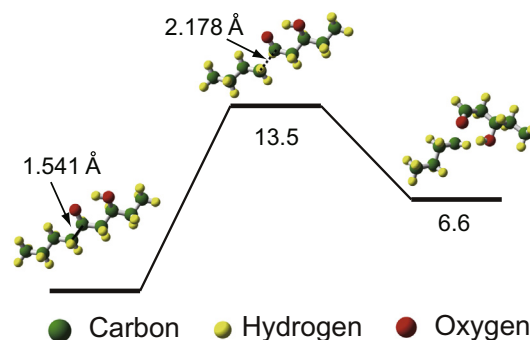


Fig. 1. Reaction profile for β scission of $\text{C}_4\text{H}_9\text{CHO}\cdot\text{CH}_2\text{CHOHC}_2\text{H}_5$. Energy differences are in kcal/mol.

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