

Simulation of Thermal Decomposition for Polymer Molecules

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The thermal decomposition of typical polymer (PE, PP, PVC, PTFE, LB) model molecules has been simulated by quantum molecular dynamics (QMD). In the calculations, we controlled the N ose-Hoover thermostats in the thermal energy range of 14 ~ 20 kcal/mol, and the sampling position data with a time step of 0.5 fs were carried out up to 5000 steps. We obtained the distribution of thermal decomposed fragment products with positive, neutral and negative charges to the main chain carbon number, or the atomic mass unit from the output data at the 5000 step in 20 runs. The calculated distribution of the decomposition products enables us to be compared with the experimental results of gas mass spectrometry and secondary ion mass spectrometry (SIMS) under the main assumption of thermal decomposition process for the cleavage of polymer bonds.

INTRODUCTION

Molecular dynamics (MD) and quantum molecular dynamics (QMD (MD with MO or DFT method)) computer simulations will become powerful tools to study a wide variety of events to obtain quantities that can be directly compared with experimental results as well as yield microscopic pictures about the mechanisms and reaction pathways unavailable from experimental data. The MD approach without MO method has also been quite successful in providing quantitative agreement with experimental energy and angular distributions of solid [1], the high-energy particle bombardment of organic film adsorbed on a metal substrate [2-5], and the bombardment of a polyethylene crystal [6]. They need to use the empirical potential functions [7-11] to solve the motion equations in MD approach, since the approach does not involve the MO or DFT method. On the other hand, we are able to obtain the resolution of motion equations automatically by QMD method, because the potential functions can be determined from the MO or DFT calculations. In order to obtain the quantities and microscopic pictures by the QMD with *ab initio* MO method, we need enormous computational time even with the supercomputer in the present time. Then, in this work,

we propose to simulate the chemical decomposition reaction of large molecules in the reasonable computational time by a QMD with semiempirical MO method. (The computational time is much shorter in the time of 10^{-2} order than that by QMD with *ab initio* MO method).

We already described in previous works [12, 13] that the cleavage sites of representative polymers in static and time-of-flight secondary ion mass spectrometry (SIMS) can be estimated from the two-center bond energies for the electric neutral model oligomers using semiempirical AM1 MO method [14] under the main assumption of the thermal decomposition process for the cleavage of polymer bonds on the utmost surface of solid polymer sample. In the present study, we will simulate the thermal decomposition of typical polymer (PE, PP, PVC, PTFE, LB) using the model molecules by QMD with semi-empirical AM1 method, in order to yield microscopic pictures in the decomposition process unavailable from experimental data.

COMPUTATIONAL DETAILS

In the NTV (the number of particles, temperature, volume) ensemble, we used the

following Nöse-Hoover Hamiltonian in the hypothetical system [15, 16],

$$\hat{H} = \sum_i \frac{P_i^2}{2m_i} + V_N(r^N) + \frac{P_\eta^2}{2Q} + NkT_0\eta \quad (1)$$

The thermal decomposition of typical polymers (PE, PP, PVC, PTFE, LB) has been simulated using the model molecules by QMD with semi-empirical AM1 method. The thermal energy was controlled with the Nöse-Hoover thermostats and sampling position data carried out up to 2.5 ps (5000 steps). The equations of nuclear motions were integrated using 5-values Gear method [17] as a predictor-corrector algorithm with a time step of 0.5 fs. We can obtain the distribution of thermal decomposed fragment products with positive, neutral and negative charges to the main chain carbon number, or the atomic mass unit from the output data of 5000 step in 20 runs due to the changes of 20 random initial states for the motion of nuclear particles. Thus, the calculated distribution of the decomposition products to the number of main chain carbon may be compared with the experimental

results due to the thermal decomposition gas mass spectrometry. On the other hand, we may compare the calculated positive- or negative- ion fragment spectra of the polymer model molecules with the experimental ion mass spectra in static SIMS, or time-of-flight (TOF)-SIMS.

RESULTS AND DISCUSSIONS

As indicated in previous works [12, 13], the cleavage sites of representative polymers in TOF- and static-SIMS can be estimated from the two-center bond energies of the electric neutral model oligomers by semiempirical MO calculations using the AM1 method. The cleavage of the intermolecular bonds may be classified into three cases; a) the scission can occur in any bonds (PE, PP, PVA), b) the cleavage of the main chain occur in any bonds, after pendant groups break first (PVC), c) the main chain carbons with the pendant groups break in any bonds of main chain (PVF, PTFE (Teflon)). Thus, we will, here, simulate the thermal decomposition of typical polymer (PE, PP, PVC, PTFE, LB) molecules by QMD method in the decomposition process not available from experimental data.

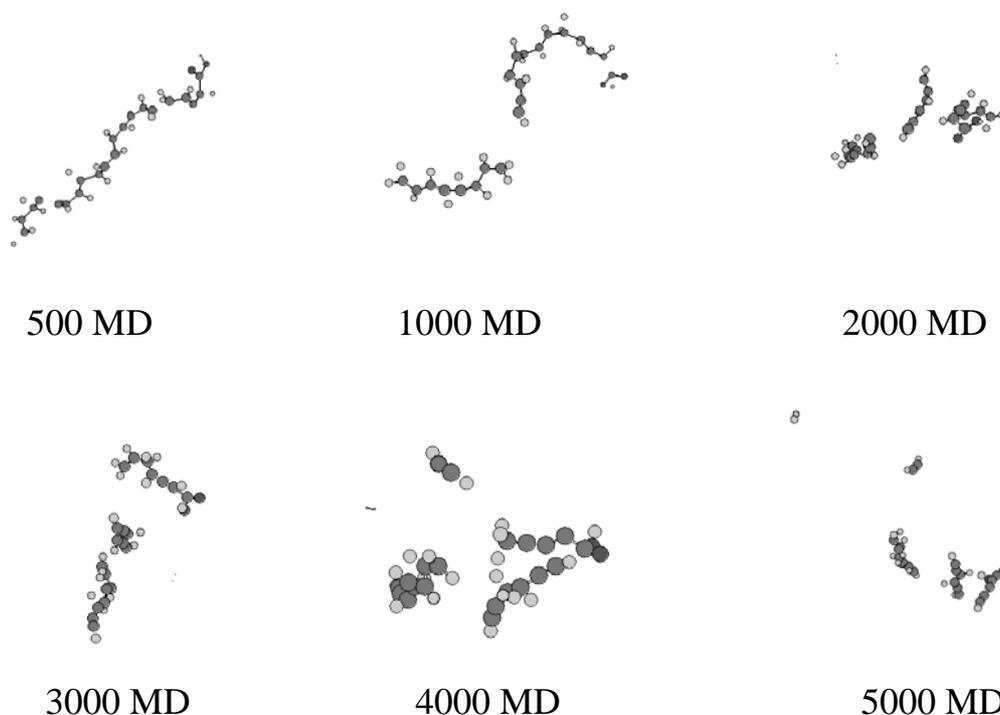


Fig. 1. Thermal decomposed data of LB model molecule at 500, 1000, 2000, 3000, 4000, and 5000 MD steps

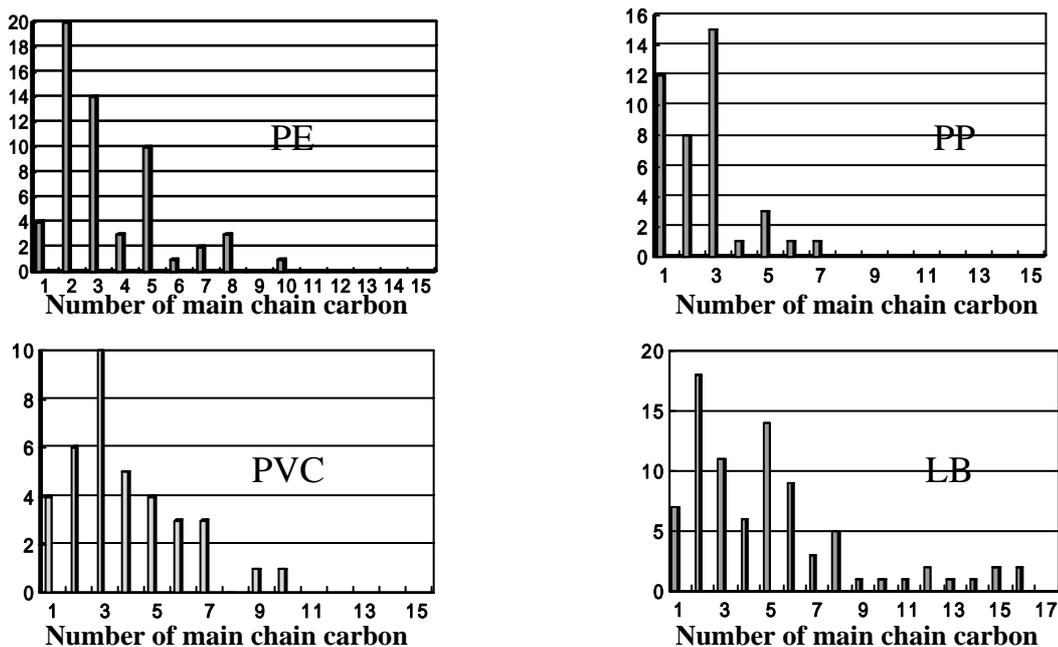


Fig. 2 Thermal decomposed products to the main chain carbon numbers of PE, PP, PVC, and LB model molecules

a) Thermal decomposition process

We simulated the thermal decomposition process of five polymers (PE, PP, PVC, PTFE, LB) using the model molecules by QMD program. The N6se-Hoover thermostats for the polymers were controlled in the thermal energy range of 14 ~ 20 kcal/mol, and the sampling position data with a time step of 0.5 fs were carried out up to 5000 steps. As an example of data for the polymers, Fig. 1 shows the thermal decomposed data of LB model molecule at 500, 1000, 2000, 3000, 4000, and 5000 steps with 20 kcal/mol thermal energy control. It can be seen from the figure that the smaller fragments exist with the increasing sampling data steps.

For the polymers, we obtained the distribution of thermal decomposed fragment products with positive, neutral and negative charges to the main chain carbon number from the output data of 5000 step in 20 runs due to the changes of 20 random initial states for the motion of nuclear particles. Thus, the calculated distribution of the decomposition products to the carbon numbers enables us to be compared with the experimental results due to the thermal decomposition gas mass spectrometry.

b) Secondary positive ion fragment spectra

In simplified emission process of a fragment ion from solid polymer surface, an impact cascade and excited area are created around the point of primary particle impact through energy and momentum transfer from bombarding particle to the solid polymer, when a polymer sample is bombarded by source ions of a few ten keV kinetic energy. The surface fragment ions are then formed by dissociation of sputtered neutral molecular species on the utmost surface layer. The surface fragment ions are thus emitted, if a sufficient amount of energy is transferred. Here we can consider that the results of the dissociation polymers correspond to the thermal decomposition in mass spectrometry. By considering the thermal decomposition, we are able to simulate the thermal decomposition of PE, and PTFE polymer molecules as examples by QMD method in order to compare the decomposed data at 5000 MD step in 20 runs with the experimental results in SIMS [18].

For the PE and PTFE polymers, we obtained the distribution of thermal decomposed fragments with positive, neutral and negative charges to the atomic mass unit from the output data of 5000 step in the 20 runs. In the total fragments at 5000 MD step in the 20 runs, we confirmed that there are 90 % neutral

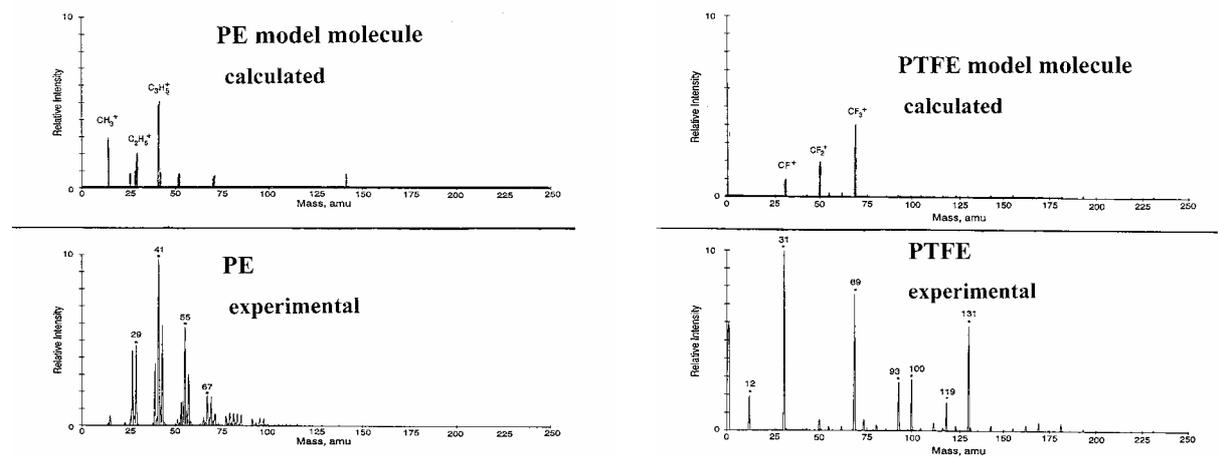


Fig. 3 calculated secondary positive-ion fragment spectra of the PE and PTFE polymer model molecules with the experimental results.

charged fragments, 5 % positive and 5% negative charged ion-fragments, respectively. Thus, we showed the calculated distribution of the positive ion charged fragments with the experimental results in static SIMS in Fig. 3. In order to obtain the good accordance of simulation results with experimental ones, we should use the larger polymer model molecules like the decamer model molecule.

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