Development of Molecular Dynamics Method to Simulate Polymerization Process with Metallocene Catalyst

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Abstract: A new molecular dynamics simulation program has been developed to treat the chemical reaction process such as polymerization, with changing potential parameters during calculation. It was applied to the ethylene polymerization process with the metallocene catalyst and the dynamic behavior and temperature dependency of polymerization process were observed.

Keywords: Molecular Dynamics Simulation, Metallocene Catalyst, Ethylene Polymerization.

1. Introduction

The metallocene molecule is a remarkable catalyst to produce polyolefin because of its high polymerization activity and molecular weight selectivity. For further application, theoretical investigations are required for polymerization process by the metallocene molecule. In this study, a new molecular dynamics simulation method has been developed to treat the chemical reaction process in ethylene polymerization and applied on the zirconocene(methyl) molecule.

2. Theoretical

Our original 'RYUDO-CR[1]' program had been used to execute classical Molecular Dynamics (MD) simulation with chemical reaction phenomena. In this simulation, the following functions are used to express the interatomic potential energy.

$$E_{ij} = \frac{q_i \cdot q_j}{r_{ij}} + D_{ij}\{\exp[-2\beta_{ij}(r_0 - r_{ij})] - 2\exp[-\beta_{ij}(r_0 - r_{ij})]\} + H(\theta_0 - \theta_{ijk}) + H[1 + s \cdot \cos(n \cdot \varphi - \varphi_0)] + \left(\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}}\right) \quad (1)$$

Here, first term means the coulombic interaction, second term means the Morse potential for covalent bond, third term means the 3-body angle potential, fourth term means 4-body torsion potential, last term means Lennard-Jones (LJ) potential for Van der Waals interactions.

To apply RYUDO-CR to ethylene polymerization process on zirconocene catalyst, a new function has been developed to express the chemical reaction mechanism as shown in Figure 1. During MD simulation, this bond and potential parameter change will occur when the ethylene molecule is close to Zr atom and the judgement inequality shown as below is vailed.

$$\mathrm{N} < \mathrm{P} * \left(\frac{R_{max} - R}{R_{max}}\right)^{C} \quad (2)$$

Here, N is random number, P is a probability, C is a distance dependency, R_{max} is a maximum distance of reaction. By using random number, this method expresses the reaction based on the probability theory.

The simulation model which has one zirconocene catalyst molecule as shown in Figure 2 which constructed from a $[(CH_3)^2C(Cp)(Flu)]ZrCl_2$ molecule[2] and 70

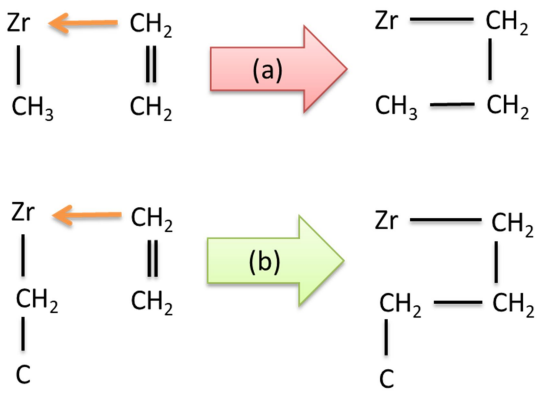

Figure 1. Reaction Mechanism of Ethylene Polymerization (a) at start, (b) continues.

ethylene molecules in 55Å cubic simulation box has been used to the polymerization simulation with this method for confirming. During the MD simulation, the three-dimensional periodic boundary condition has been applied to simulation box and the temperature has been controlled to 373K with velocity scaling method. The time step of this simulation is 0.1[fs/step].

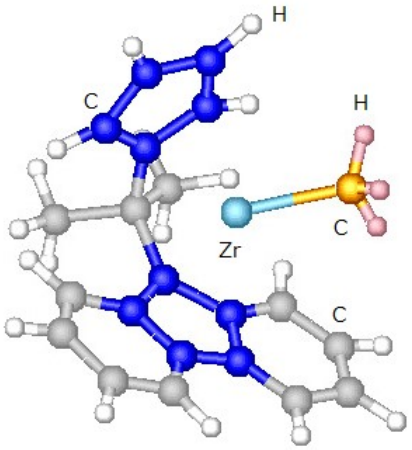

Figure 2. Simulation model of Zirconocene

3. Results and discussion

The ethylene polymerization simulation with new function in RYUDO-CR has been successfully completed and the snapshot of simulation model at the start and end of simulation are shown in Figure 3. 11 ethylene molecules have been reacted and formed a straight-chain polyethylene structure during 1,000,000 step (=0.1ns) MD simulation.

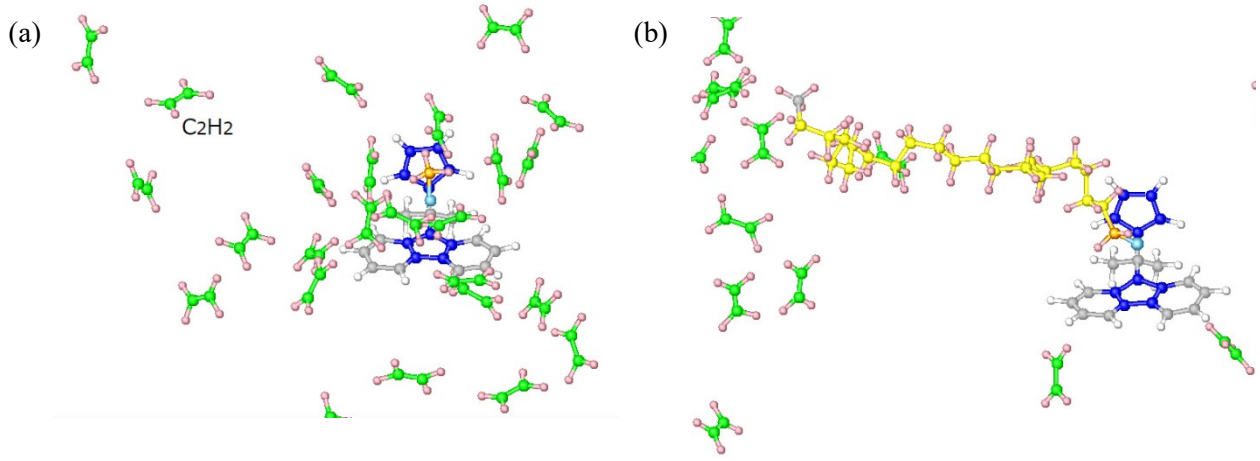

Figure 3. (a) Initial structure, (b) 1,000,000 step simulation result

Figure 4 shows the trajectory of C atoms in ethylene molecules around zirconocene during 1,000,000 step MD simulation. It is observed that some ethylene molecules adsorb to fluorenyl side opposite to Zr and move on fluorenyl structure toward Zr side.

At the other temperature simulation, different polymer length has been observed. These results will be shown during the presentation.

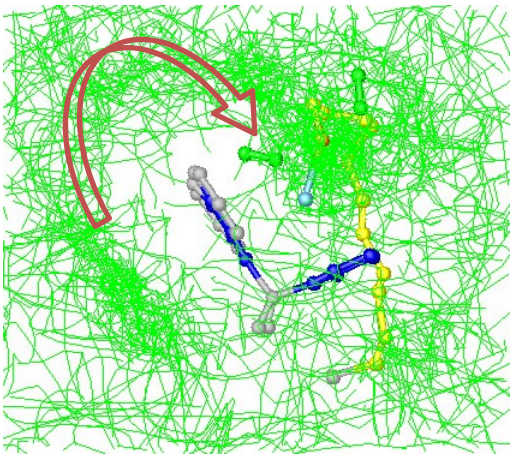

Figure 4. Trajectory of C_2H_2

4. Conclusions

The ethylene polymerization process on zirconocene catalyst can be simulated by classical molecular dynamics method using RYUDO-CR program with new developed function to express the chemical reaction mechanism. It will make easy to simulate whole structure of polymerization and compare various metallocene molecule, temperature, etc.

References

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