



Study of high density polyethylene (HDPE) pyrolysis with reactive molecular dynamics



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ABSTRACT

PE pyrolysis is considered as an important process for converting plastic solid waste into fuel or other valuable chemicals to alleviate the environmental burdens. A computational approach can be of help for fully understanding the mechanisms and reaction pathways during PE pyrolysis in various industrial applications. In this paper, ReaxFF molecular dynamics was for the first time applied in simulating the pyrolysis of a High Density Polyethylene (HDPE) model system with 7216 atoms. Detailed reaction mechanisms and generation pathways of primary gas molecules were obtained by further analysis of the trajectories within a total of 250 ps simulation in NVT ensemble at 2000–3000 K using a newly created program, VARMD. The product profile and primary gas products evolution tendencies with temperature agree reasonably with the observations in Py-GC/MS experiments and literature data. The overall kinetics of \sim C31 were analyzed and used to predict the reaction time for 90% weight loss of HDPE thermolysis that falls in around the reported time observed experimentally in the literatures. The reaction mechanisms based on the detailed reactions from the simulation trajectories are in broad agreement with what reported in literatures. The work presented here validates that ReaxFF MD is a promising method to help building a systematic understanding of the detailed chemical reactions in pyrolytic process for polymers.

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1. Introduction

In recent years, pyrolysis of plastic solid waste is considered as an environment-friendly method for converting and upgrading plastic solid waste into fuel or valuable chemicals [1] to achieve efficient recovery of raw materials and energy in order to reduce usage of landfill and incineration. Pyrolysis of polyethylene (PE) is frequently employed to demonstrate the potential application of pyrolysis in plastic recycling by exploring the effective operating conditions and the liquid products generated in experiments [1–11]. However, most of the previous works were carried out under very different conditions and the results were condition-related closely, which is disadvantageous in investigations of reaction paths for PE thermolysis [1]. Particularly, experimental approaches could hardly capture the changes at the atomic level directly.

Computational investigations on PE pyrolysis is believed to be able to provide a deeper insight into the mechanisms of PE pyrolysis process [12] because chemical reactions can be observed directly at the atomic level. However, PE pyrolysis involves complex chemical reactions. The quantum chemistry (QM) method is often used only for simulation of reactive molecular systems that contain less than or around 100 atoms. The molecular systems in such small scale can hardly describe the behavior of a polymer, even for the simplest one. Classical molecular dynamic (classical MD or MD) can simulate large molecular systems but it's not suitable for chemical reactions due to its lack of description of bond formation and dissociation.

Reactive molecular dynamics is an atomic level simulation approach that allows investigation of large molecular systems involving chemical reactions by combining classical MD and empirical reactive force field. Nyden et al. [13] performed reactive molecular dynamics simulations of polyethylene and other homologous vinyl polymers in order to study the mechanism of thermal decomposition of vinyl polymers. The homolytic

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dissociation and scission reactions of the polymer backbone in a single PE chain, which are responsible for initiating and propagating the thermal decomposition process, were investigated using a modified CVFF force field [14] so that covalent bonds are allowed to break and form during the simulations. A similar approach was used by Knyazev [12] in investigating the influence of chain length to the kinetic feature of C–C bond dissociation for a series of linear alkanes and polyethylene macromolecules with a thousand constituent monomers. The reactive molecular dynamics simulations were carried out via the all atom OPLS-AA force field with C–C stretch terms replaced by the Morse function. Smith [15] performed a simulation to study C–C bond scission in single-chain ($n = 25–200$) PE system and bulk PE system ($n = 1–5$) with a periodic boundary with RMDff method, which enabled reaction simulations via replacing the bond stretch item with switch functions. The reactive molecular dynamics studied by Nyden, Smith and Knyazev were based on modifications of conventional force fields simply by replacing the covalent-bond stretching potentials with Morse functions or switch functions. These modifications may be not sufficient to describe the bond forming and breaking in the chemical reactions in PE pyrolysis. The C–H bond related reactions were not considered in Smith's and Knyazev's work. Moreover, only single PE chain models or very small scale bulk PE models were employed in these earlier researches, probably due to the limitation of computational power. These models may be not large enough to characterize the complexity of a bulk PE system, and consequently, some of the reactions may be not accessible due to the limited conformations sampled in relatively small models.

The Reactive Force Field (ReaxFF) proposed by van Duin [16,17] is a bond order based potential, i.e. all connectivity dependent energy terms in the potential are bond order dependent, and this makes the energy transit smoothly during bond dissociation. These energy terms include bonded interactions that consist of energy of bond, lone-pairs, over-coordination, under-coordination, valence angle, energy penalty for handling atoms with two double bonds, coalition (three-body conjugation), conjugated bonds (four-body conjugation), torsion angles, and hydrogen bond. The non-bonded interactions between all atom pairs are calculated without exclusion of bonded pairs in conventional force field. The distance-corrected Morse-potential is used for van der Waals interactions, and similar corrections are employed in Coulomb potential. In addition, EEM (Electronegativity Equilibrium Method) is used to optimize and update atomic partial charges in every MD time step, thus it has a better consideration on polarization. As a result, the ReaxFF MD allows the simulation of larger molecular reactive systems with accuracy close to DFT in reproducing potentials of alkanes [17] and aromatic hydrocarbon [18]. ReaxFF MD has been applied in research of combustion, pyrolysis and explosion of relatively larger systems at high temperatures [16]. Castro-Marcano et al. [19] reported ReaxFF MD simulations of Illinois No. 6 coal char combustion, where the maximum scale of the molecular model simulated was around 35,000 atoms including a coal char model composed of 7458 atoms and 14,000 O₂ molecules. Large scale ReaxFF MD simulation was performed in investigation of coal pyrolysis by Zheng et al. recently, in which a Liulin coal model with 28,351 atoms was employed. Reasonable evolution tendency of product profiles with temperature and relevant reaction mechanisms were obtained [20]. These two large scale systems ever simulated with ReaxFF MD indicates its potential applicability in macromolecules with chemical reactions involved. Recent publications on simulation of macromolecules using ReaxFF MD such as carbonization in polyacrylonitrile (PAN) based carbon fibers [21] and pyrolysis of phenolic polymer [22] demonstrated its potential in the investigation of complex and detailed reaction mechanisms in PE pyrolysis. This paper presents the first attempt of using

ReaxFF MD to investigate the PE pyrolysis process in order to get depth understanding of its complex chemistry. More details about ReaxFF can be found in the work by van Duin et al. [16].

In this paper, a High Density Polyethylene (HDPE) model containing 8 PE chains with 7216 atoms was constructed. The ReaxFF molecular dynamics simulations of this model were performed to investigate the detailed chemical reactions in PE's thermal decomposition. Distribution of lumped pyrolysis products and gas products was reported and discussed. Overall weight loss kinetic features of $\sim C_{31}$ were analyzed and discussed. Based on the bond order of atoms and changes in species or radical fragments in the simulated molecular system, detailed reaction mechanisms and generation paths of main gas products were obtained by further analyzing the simulation trajectories using VARMD (Visualization and Analysis of Reactive Molecular Dynamics), a newly created program. VARMD was implemented using C++ and Qt [23] for examining the complexity of the chemical reaction network in ReaxFF MD simulation by chemical structure analysis. The interrelationships among the atoms, bonds, fragments, species and reactions are analyzed directly from the 3D coordinates and bond orders of atoms in a trajectory obtained in ReaxFF MD simulation, thus the detailed chemical reactions can be generated. VARMD has been used to reveal reactions and relevant mechanisms in ReaxFF MD simulation of coal pyrolysis in the authors' group [20,24]. The algorithms of VARMD will be described in a separate paper.

2. Methods

2.1. Computational

2.1.1. Model construction

To characterize a bulk HDPE system as much as possible, models consist of 8 PE chains ($n = 150$) were constructed in a cubic periodic box using the Amorphous Cell module of Accelrys Material Studio 5.5 [25]. Periodic boundary conditions were applied to remove possible surface effects. The geometry of the model was optimized with the density set to 1.0 g/cc. The DREIDING potential was used both in the system construction step and geometry optimization. The PE model containing 7216 atoms in the cubic cell with an edge length of 38.242 Å is shown in Fig. 1.

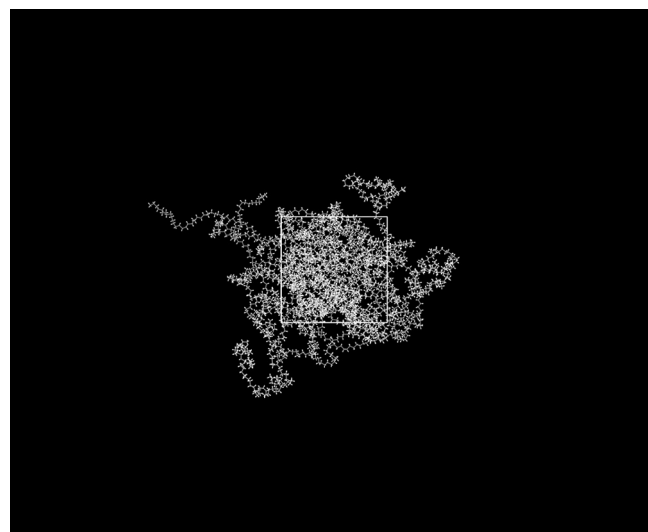


Fig. 1. The 1.0 g/cc PE model system with 8 PE chains ($n = 150$).

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