

# Studies on thermal decomposition behaviors of polypropylene using molecular dynamics simulation

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**Abstract:** Polypropylene (PP) is one of the main components of waste plastics. In order to understand the mechanism of PP thermal decomposition, the pyrolysis behaviour of PP has been simulated from 300 to 1000 K in periodic boundary conditions by molecular dynamic method, based on AMBER force field. The simulation results show that the pyrolysis process of PP can mostly be divided into three stages: low temperature pyrolysis stage, intermediate temperature stage and high temperature pyrolysis stage. PP pyrolysis is typical of random main-chain scission, and the possible formation mechanism of major pyrolysis products was analyzed.

## 1. Introduction

Technological advances made in the plastics industry over the past several decades have steadily increased the volume of plastics used in various fields. However, the applications of these plastic goods have continuously given rise to plastic waste pollution problems around the world. At present, most of these plastic wastes are disposed of through dumping into landfills or burning in incinerators along with other solid wastes [1]. But these conventional method will be phased out in the near future due to the serious environmental problems they lead to. There is a dire need to develop and deploy new environmentally friendly and cost-effective plastic waste management technologies as currently used disposal options become less viable. Among these, thermo-chemical conversion to energy resources has been a significant way to use such waste plastics effectively and to meet with the growing demand from the energy sector [2].

Extensive researches were performed worldwide for the production of alternative fuels from waste plastics through the pyrolysis [3~5]. The previous studies on mechanism of plastics pyrolysis mainly focused on experimental studies to explore the distribution of products in different conditions. However, there are few researches about chemical reactions, formation mechanisms of the main products and evolutionary processes of intermediates during plastics pyrolysis. In this study, polypropylene (PP) has been chosen as a research object due to its wide occurrence in waste plastics. The pyrolysis processes of polypropylene (shown in Fig.1), of which polymerization degree is 20, have been simulated by molecular dynamics method and the possible formation pathways of major products were analyzed.



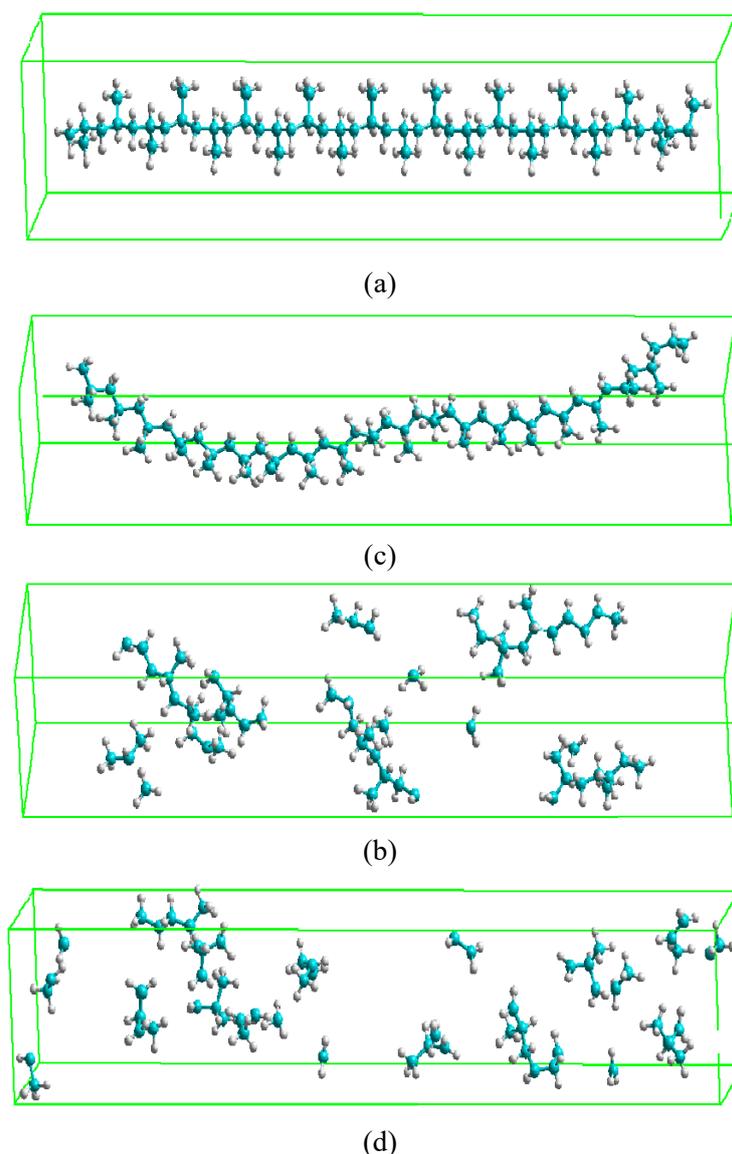


Fig. 1 (a) Optimized structure of polypropylene model compound; (b) A still frame of polypropylene simulated at low temperature stage; (c) A still frame of polypropylene simulated at intermediate temperature stage; (d) A still frame of polypropylene simulated at high temperature stage

## 2. Calculation method

Before the thermal decomposition simulation, the molecular structure must be optimized. First, the polypropylene model compound was heated to a high temperature in order to make the structure of molecules stretch and relax fully at high temperature, and then it was cooled down to obtain optimal molecular structure by molecular dynamics method. After that, we could get the original molecular size:  $4.93(\text{\AA}) \times 4.13(\text{\AA}) \times 52.28(\text{\AA})$ , and set simulation box size as  $10(\text{\AA}) \times 10(\text{\AA}) \times 55(\text{\AA})$ . The pyrolysis processes were simulated in periodic boundary conditions by using AMBER force field. During the course of simulation the bond breakages were only considered, and simulating temperature range was set from initial temperature 300 K to final temperature 1000 K. The heating time was 20ps with time step of 0.001ps. The value of energy (E) and temperature (T) was extracted once every 50 time steps. All simulation and computation were completed by using Hyperchem suite of programs.

### 3. Results and discussion

Thermogravimetric experimental analysis results showed that the thermal decomposition temperature range of PP is 300~500 °C, and the temperature corresponding to the maximum rate of weight loss is 726 K at heating rate of 20 K/min [6,7]. In the simulation, the temperature range was set from 300K to 1000K. The optimized molecular structure of PP is shown in Fig. 1-(a), and the temporal evolution of temperature and total energy (including kinetic energy and potential energy) is shown in Fig. 2. During the process of heating, the temperature and total energy of simulating PP model compound rise along with time.

The simulation process of pyrolysis of PP model compound can be divided into three stages: the low temperature stage, the intermediate temperature stage and the high temperature decomposition stage. In the low temperature stage (below 550K), some physical changes occur in the PP molecule which absorbs heat energy in heating process. As a result, atomic bonds lengthen, bond angles and dihedral angles change, and the molecular chain bends (shown in 1-(b)). In the intermediate temperature stage (550K-750K), as the temperature increases, molecule group moves intensely and a large number of C-C bonds of main chain break down randomly (shown in Fig. 1-(c)). Thus the whole PP molecule depolymerizes and the various fragments with different polymerization degree are formed. In the high temperature stage (above 750K), a large number of smaller molecular fragments are formed (shown in Fig. 1-(d)). In the simulation, due to the molecular fragments are not discharged and still remain in the simulation box, these molecular groups continue to decompose with the temperature increase. From the above simulation results we can know that it is important to control thermal decomposition temperature to obtain different products.

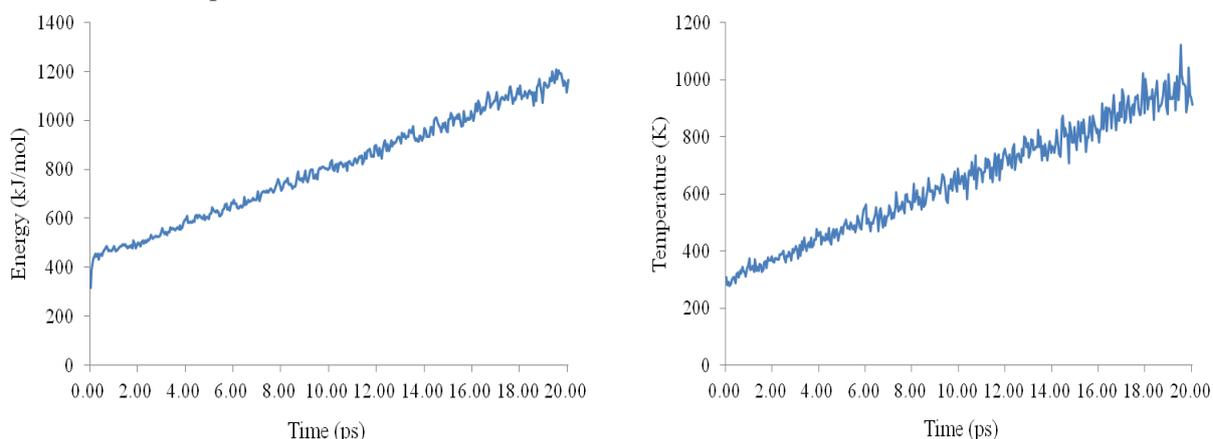


Fig. 2 The energy and the temperature histories of simulating polypropylene model compound

The PP pyrolysis reaction mechanism is random main-chain scission, namely macromolecular main-chain cracks randomly to generate various free radicals. These free radicals further decompose into various products through intramolecular or intermolecular hydrogen transfer reaction. The experimental results of PP thermal decomposition indicated that the main gaseous products were propylene, methane, ethylene, propane, butane and so on [8~10]. Fig. 3 shows the formation mechanism of various kinds pyrolysis products. PP model compound **1** can decompose into the radicals **2** and **3** through the homolytic cleavage of the C-C bond (shown in Fig. 3-(1)). The radical **2** can further decompose into the radical **4** and propylene **5** through the C-C homolytic cleavage (shown in Fig. 3-(2)). The radical **2** can also be converted into the radical **6** through a intramolecular hydrogen transfer, and the radical **6** further decompose into the radical **7** and butane **8** through the C-C homolytic cleavage (shown in Fig. 3-(3)). Methane can be formed through the  $\beta$ -scission (shown in Fig. 3-(4)). The radical **3** can be transformed into the radical **10** through a intramolecular hydrogen transfer, and the radical **11** and propane **12** are formed through the C-C homolytic cleavage of the radical **10** (shown in Fig. 3-(5)). The radical **3** can also be transformed into the radical **13** through a intramolecular hydrogen transfer, and the radical **13** further decompose into the radical **14** and ethylene **15** (shown in Fig. 3-(6)).

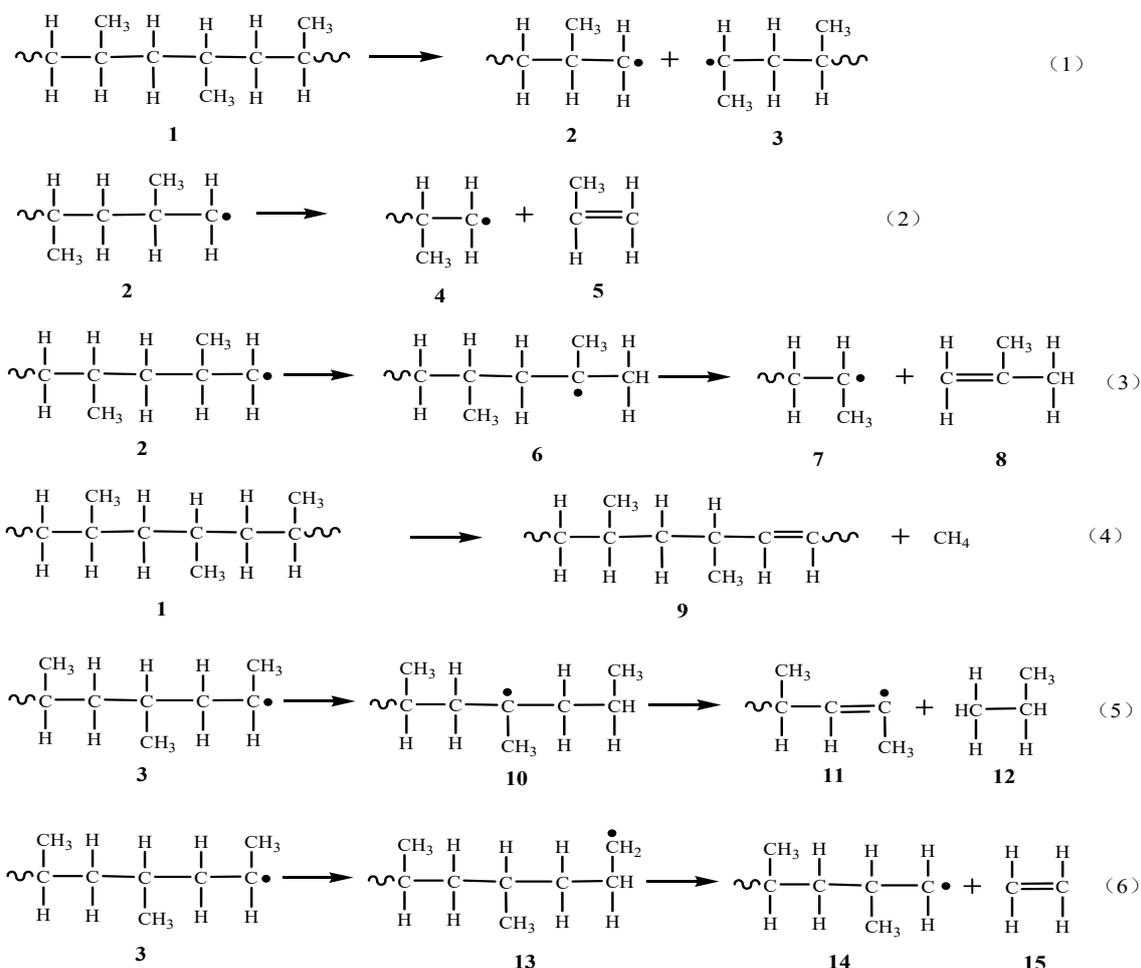


Fig. 3 Formation mechanism of various kinds of pyrolysis products

#### 4. Conclusions

The thermal decomposition processes of PP has been simulated from initial temperature 300 K to final temperature 1000 K in periodic boundary conditions by molecular dynamic method. The simulation process of pyrolysis of PP model compound can be divided into three stages: the low temperature stage (below 550 K), the intermediate temperature stage (550-750 K) and the high temperature decomposition stage (above 750 K). In the intermediate temperature stage, a large number of C-C bonds of main chain break down randomly, and the whole PP molecule depolymerizes and the various fragments with different polymerization degree are formed. The possible formation mechanism of major pyrolysis products was analyzed.

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