

Applications of reactive molecular dynamics to the study of the thermal decomposition of polymers and nanoscale structures

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Abstract

The application of quantum mechanics and molecular simulation methods can yield new insights into the thermal reactivity of large molecules and nanoscale structures. One example of this approach is reactive molecular dynamics (RMD) as implemented in a computer program, called MD_REACT. This program was developed for simulating thermal decomposition reactions in polymer-based materials. In this investigation, we perform reactive molecular dynamics simulations on the homologous series of vinyl polymers: polyethylene (PE), polypropylene (PP), and poly(isobutylene) (PIB). A general mechanism for the thermal decomposition of vinyl polymers is formulated on the basis of the results of these simulations.

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1. Introduction

In principle, reactive molecular dynamics (RMD), or molecular dynamics with reactive force fields, can be used to simulate chemical reactions in large atomic and molecular systems. Using this technique, it is possible to reach nanometer length scales while accounting for the effects of inter-molecular interactions in condensed phases. It represents one possibility of how to span the power and limitations of static, zero-K, high-accuracy, few-atom solutions of the time-independent electronic Schrödinger equation (ab initio quantum chemistry) and dynamic, real-temperature, low-chemical accuracy, many-atom molecular simulations (molecular dynamics and ensemble Monte Carlo methods). Other investigators, particularly in materials science, have also begun to realize the potential advantages of this approach and have made significant advances in developing codes and reactive potentials [1–4].

We have applied RMD in previous investigations using a computer program referred to as MD_REACT [5–9] to simulate thermal decomposition reactions in polymers.

This program is based on a dynamic force field representation of the potential energy surfaces for a wide range of elementary chemical reactions. While classical molecular dynamics (MD) has been used extensively in the past to investigate phase transitions, molecular transport, and other properties that depend on conformational structure, MD_REACT represents the first systematic effort to extend this approach to model thermally-induced chemical transformations in large molecules in condensed phases.

There are serious questions about the accuracy of force fields traditionally used in MD simulations and how they should be modified to describe thermal decomposition reactions. In this paper, we report the results obtained using a modified version of the consistent valence force field (CVFF) [10], in which the bond-dissociation energies were computed by performing high-level (complete basis set) [11–14] electronic structure calculations on model compounds and radicals. Another deficiency of MD is its inability to capture the quantum nature of vibrational motion [15]. As a first attempt at the inclusion of these effects, we have modified the bond-dissociation energies used in the force field to reflect differences in the zero point energies of the products and reactants. While this does nothing to

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compensate for errors due to representing discrete vibrational energy levels by a continuum, we assume that this is less of a problem for scissions of the C–C bonds that comprise the polymer backbone than it is for hydrogen transfer and abstraction reactions. For this reason, the focus of our attention in this investigation is on homolytic dissociation and β -scission reactions, which are responsible for initiating and propagating the thermal decomposition process.

In what follows, we report results from RMD simulations on the homologous series of vinyl polymers: polyethylene (PE), polypropylene (PP), and poly(isobutylene) (PIB). Despite similarities in their structures, there are dramatic differences in the experimental product distributions, which result from the thermal decomposition of these polymers. The purpose of this investigation is, therefore, to gain insights into the factors, which determine the pre-dominant decomposition pathways.

2. Description of the method

2.1. Molecular dynamics

In its conventional formulation, molecular dynamics consists of solving the classical equations of motion for the time dependent positions (and velocities) of the atoms that comprise the system under investigation. The objective is usually to determine the time evolution of the molecular structure after it is subjected to a perturbation due to thermal motion and/or external forces. The perturbation is introduced in the form of a velocity distribution for the constituent atoms. The initial structures may be obtained from diffraction and spectroscopic data, from molecular calculations, or some combination of these sources of information.

The classical equations of motion are given by:

$$\frac{\partial H}{\partial p_i} = \frac{dq_i}{dt} \quad \frac{\partial H}{\partial q_i} = -\frac{dp_i}{dt} \quad (1)$$

In Eq. (1), q_i and p_i denote the coordinates and momenta of atoms and

$$H = \sum_i^N \frac{p_i^2}{2m_i} + V(q_1, q_2, \dots, q_{3N}) \quad (2)$$

is the Hamiltonian corresponding to the sum of the kinetic and potential energies associated with the molecular motion.

Typically, the potential energy, V , is represented by an analytical function of the form:

$$V = \sum_{n\text{-bonds}} V_{\text{bond}}(r_i) + \sum_{n\text{-angles}} V_{\text{angle}}(\theta_i) + \sum_{n\text{-torsions}} V_{\text{torsion}}(\phi_i) + \sum_{n\text{-pairs}} V_{\text{non-bond}}(r_{ij}), \quad (3)$$

where the sums are over the covalent bonds, bond angles, torsion angles, and non-bonded pairs of atoms. The compo-

nent terms, which are described in more detail below, correspond to the energies involved in distorting the structure from the equilibrium values of the internal coordinates by stretching, bending and twisting the bonds. These functions are collectively referred to as the “force field,” even though the forces are actually obtained from the gradients of V . One of the most important characteristics of a force field is that it provides a mechanism for describing the potential energy surface for a large molecular system from components that can be parameterized on the basis of experimental information and/or the results of quantum mechanical calculations on smaller, model compounds. This makes it possible, at least in principle, to obtain accurate representations of potential energy surfaces for nanoscale molecular structures, which might otherwise be outside of the realm of computational chemistry.

In the past several years, we have made substantial progress in the development of force field-based reactive molecular dynamics. The feature that distinguishes reactive molecular dynamics from other conventional implementations of molecular dynamics is that covalent bonds between atoms are allowed to break and form during the course of the simulation. This method has been implemented in the MD.REACT algorithm [5–9]. One advantage of this approach over alternative methods, such as ab initio MD, is that the parameterization can be done independently of dynamics and so can be based on results obtained from very accurate calculations.

Components of the MD.REACT force field are described here, including how it is altered dynamically to account for chemical reactivity. Covalent-bond stretching potentials are represented by Morse functions,

$$V_{\text{bond}} = D[1 - \exp(-\alpha(r - r_e))]^2 \quad \alpha = \sqrt{k_b/(2D)}, \quad (4)$$

where D is the bond-dissociation energy, r the distance between the bonded atoms, r_e the equilibrium bond length, and k_b is the force constant. The potential energy term associated with the bond angle, θ , between adjacent bonds is given by:

$$V_{\text{angle}} = S(ab)S(bc)k_\theta(\theta - \theta_e)^2, \quad (5)$$

where θ_e is the equilibrium value, k_θ the angular force constant, and $S(ab)$ and $S(bc)$ are the switching functions, which are defined below. Rotations about covalent bonds are restricted by torsional potentials of the form:

$$V_{\text{torsion}} = S(ab)S(bc)S(cd)k_\phi[1 + \cos(n\phi - \phi_e)]. \quad (6)$$

The dihedral angle, ϕ , is defined by the three bonds between four adjacent atoms: a , b , c , and d . The parameters, k_ϕ , n , and ϕ_e determine the height, multiplicity, and position of the barrier to internal rotation. The switching functions, S , are fractional bond orders determined from the following expression:

$$S = \begin{cases} 1 & r \leq r_e \\ 1 - \frac{V_{\text{bond}}}{D} & r > r_e \end{cases} \quad (7)$$

In the context of Eqs. (5) and (6), these functions are used to account for the attenuation of bending and twisting forces as the covalent bonds stretch. The non-bond interactions ($V_{\text{non-bond}}$) are represented by sums of the Lennard–Jones 6–12 and Coulomb potentials.

The feature that distinguishes MD.REACT from other implementations of molecular dynamics is that covalent bonds are allowed to break and form during the simulations. This provides the capability to simulate chemical reactions, which are modeled by the following algorithm. After every time step of molecular dynamics, a fractional bond order (S) is computed for every covalent bond in the system. These bond orders are compared to a pre-defined criterion for bond-dissociation (BDC). If the bond order is less than or equal to BDC, the bond is eliminated and the information about the covalent connection is erased from the database. The atoms that were connected by the former bond are considered to be chemically active and are labeled accordingly. At the next stage, a new set of potential bonds is generated, consisting of all possible covalent interactions between the chemically active atoms. The bonds of the lowest energy are retained. The maximum number of bonds for each atom is determined by the rules of atomic valence. If the total number of bonds to an atom is equal to its valence and the fractional bond order of each of its bonds is higher than BDC, then the chemically active label is removed from the atom. Otherwise, if an atom retains its chemically active status, it is allowed to form one additional bond; provided that the sum of the bond orders associated with the valence +1 bonds to that atom does not exceed its valence. Thus, for example, a chemically active carbon atom can participate in five bonds as long as the sum of the bond orders associated with these bonds does not exceed four. In other words, the four valence electrons are distributed over five bonds. This feature is introduced to describe chemical reactions that occur via so-called hypervalent transition states, such as atom transfer reactions. Once the bond analysis is complete and the structural information is updated, the next time step of molecular dynamics is executed.

It should be noted that, as the result of the bond breaking–making routine, the bonds between atoms are not removed unless replaced by the new bonds that have lower energies. The bond-dissociation criterion determines whether covalently bonded atoms are eligible to participate in chemical reactions. In the simulations reported in this paper, BDC has been set to 0.7, which means that an atom is considered to be chemically active when the energy of at least one of its bonds is greater than or equal to $0.3D$, where D is the bond-dissociation energy. Since bonds are not replaced unless there is the possibility of making a new bond with a lower energy (and the sum of the bond orders is fixed), the simulations should be insensitive to the value of

BDC as long as the activation energies for all reactions are greater than $(1 - \text{BDC})D$. On the other hand, if BDC is too large, then the computational effort involved in examining all of the bonding possibilities may become excessive. The value of 0.7 was based on the assumption that none of the important elementary reactions have activation energies less than $0.3D$, which is about 100 kJ/mol for the C–C bonds and about 125 kJ/mol for the C–H bonds in these polymers.

The reactive molecular dynamics algorithm is implemented as a Fortran/C computer code (MD.REACT program) interfaced with Discover 95 (a commercially available molecular dynamics software offered by Accelrys Inc.¹). The function of the MD.REACT program is to compute the reactive force field, while Discover 95 updates the molecular geometry on the basis of the solution of the equations of motion. A separate computer program, called Molecview, has been developed to visualize the results of the MD.REACT simulations in 3D.

The set of the force field parameters used in the present work was based on the version 2.3 of the CVFF provided by Accelrys Inc. As an attempt to improve the parametric description of reactive potential energy surfaces, the dissociation energies and the equilibrium bond lengths (r_e) used in the force field were calibrated against the results of high-level quantum chemical calculations performed on model compounds selected to represent chemical transformations potentially important in the thermal decomposition of poly(methyl methacrylate). Details of the methods, procedures, and results of these calculations are reported elsewhere [6].

2.2. Simulation procedures

The simulations were performed on molecular models of the polymers consisting of a single chain (terminated with H atoms) consisting of 20 monomers. Non-bond interactions were calculated using an atom-based summation method [16] with a cut-off distance of 1.65 nm. Interactions between atoms in the active chain(s) and those in the bulk polymer were accounted for by imposing periodic boundary conditions.

The initial structures for the simulations were obtained via simulated annealing. The procedure we followed was to perform a molecular dynamics calculation at 600 K followed by an energy minimization (terminated when the maximum derivative was less than 42 J/(mol nm)). The process was repeated, decrementing the temperature by 10° at every iteration, until the specified temperature for the dynamics was reduced to 0 K. The resulting structures are displayed in Figs. 1–3. The densities at typical simulation temperatures

¹ Certain commercial equipment, instruments, materials or companies are identified in this paper in order to adequately specify the experimental procedure. This in no way implies endorsement or recommendation by NIST.

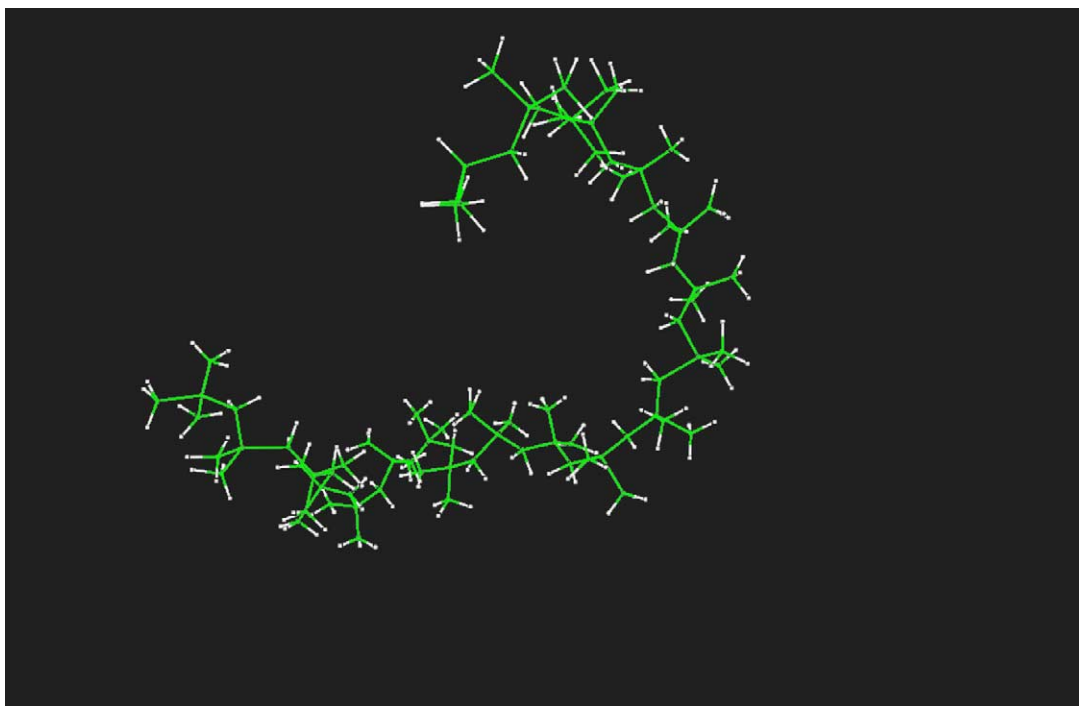


Fig. 1. Initial annealed structure for PIB.

were approximately 0.7, 0.8, and 0.9 g/cm³ for PIB, PP, and PE, respectively.

Simulations were performed at a series of temperatures between 1200 and 2700 K. The temperature was controlled by velocity scaling with a variance of ± 10 K [16]. Temper-

ature dependent rate constants ($k(T)$) were computed as the average number of reactions per unit time from three independent simulations at each temperature. The activation energies and pre-exponential factors were obtained by fitting the $\ln k(T)$ to T^{-1} in accordance with the Arrhenius

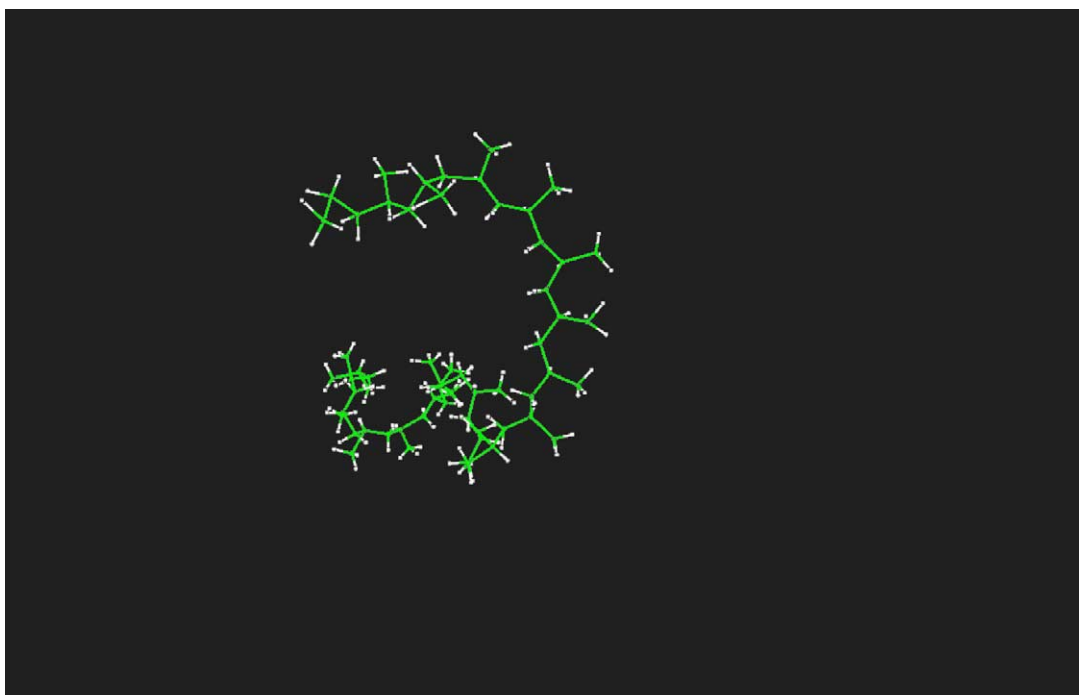


Fig. 2. Initial annealed structure for PP.

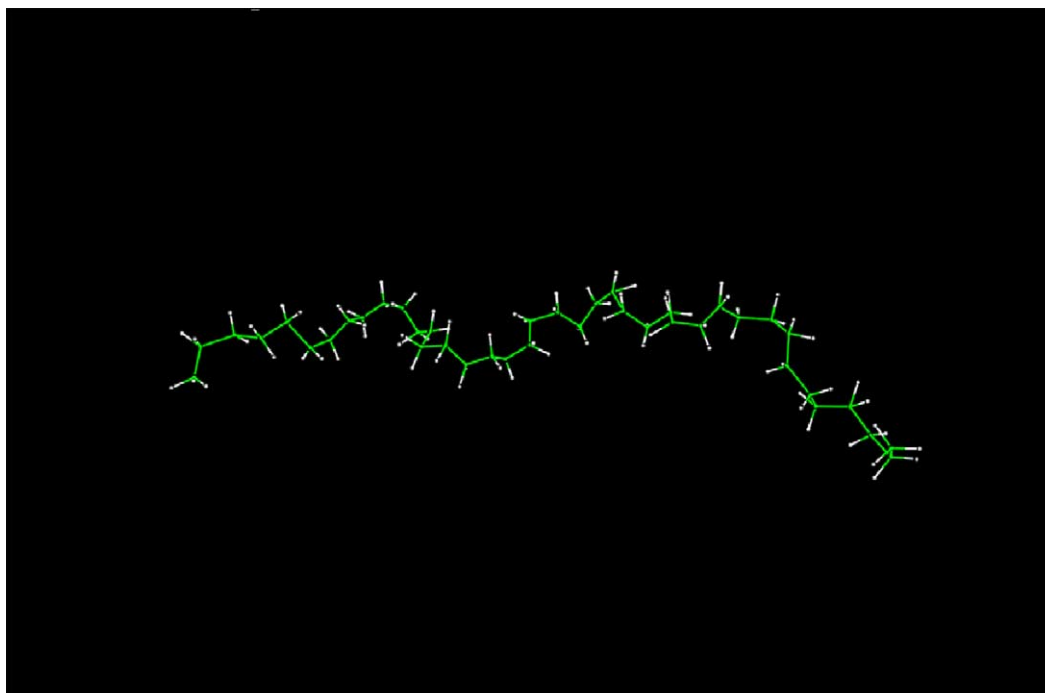


Fig. 3. Initial annealed structure for PE.

expression, $k(T) = A \exp(-E_a/RT)$. The average uncertainties, based on the standard deviations of the least squares fits, are approximately $\pm 5\%$ for the pre-exponential factors and $\pm 10\%$ for the activation energies.

The thermal decomposition simulations were carried out in two stages. First, the structures were equilibrated by constant-pressure and -temperature (NPT) molecular dynamics. The thermal motion was initiated by giving each atom a three-dimensional velocity chosen at random from the Maxwell–Boltzmann distribution. In order to avoid dissociation of covalent bonds during equilibration, the Morse term in the CVFF was substituted for by a harmonic potential with $r_e^{\text{harmonic}} = r_e^{\text{Morse}}$ and $k_b^{\text{harmonic}} = k_b^{\text{Morse}}$. The duration of the equilibration dynamics was 1 ps. The reactive molecular dynamics, which comprised the second stage of the simulations, were carried out at constant volume and temperature (NVT) starting with the structure and velocity distribution obtained from the corresponding equilibration stage. The duration of the reactive molecular dynamics was 5 ps.

3. Results and discussion

The final frames from representative simulations for each polymer are compared in Figs. 4–6. The mechanism derived from analysis of the results obtained for PIB is almost identical to what we found in a previous investigation of the thermal decomposition of PMMA [6]. The decomposition process is initiated by scissions of the polymer backbone, which occur with surprisingly low activation energies (Table 1).

Monomers, which are the major volatile product, are formed by β -scission of the primary and tertiary macroradicals. At some temperatures, the initiation reaction appeared to occur simultaneously with the evolution of a monomer. The depolymerization of the primary radicals is terminated by β -scission of the pendant methyl groups. The tertiary macroradicals are considerably more stable, but we did observe first order termination by β -scissions of hydrogen atoms in some of the higher temperature simulations. This difference in the reactivities of the primary and tertiary macroradicals is consistent with the hypothesis advanced by Kashiwagi et al. [17] to explain experimental molecular weight distributions obtained from gel permeation chromatography of partially degraded PMMA.

The simulations indicate that isobutylene (monomer) is the dominant volatile (low molecular weight) product of the thermal decomposition of PIB. In the lowest temperature (1200 K) simulations, however, the chains fragmented without depolymerizing. Given sufficient time, the resulting macroradicals will presumably either volatilize without

Table 1

| Molecule | Arrhenius parameters | | | |
|----------|----------------------|----------------|----------------------|----------------|
| | Chain scission | | Depolymerization | |
| | A (s^{-1}) | E_a (kJ/mol) | A (s^{-1}) | E_a (kJ/mol) |
| PIB | 8.8×10^{12} | 42 | 1.5×10^{14} | 68 |
| PP | 1.3×10^{14} | 99 | 2.5×10^{14} | 101 |
| PE | 2.5×10^{15} | 181 | 1.0×10^{18} | 307 |

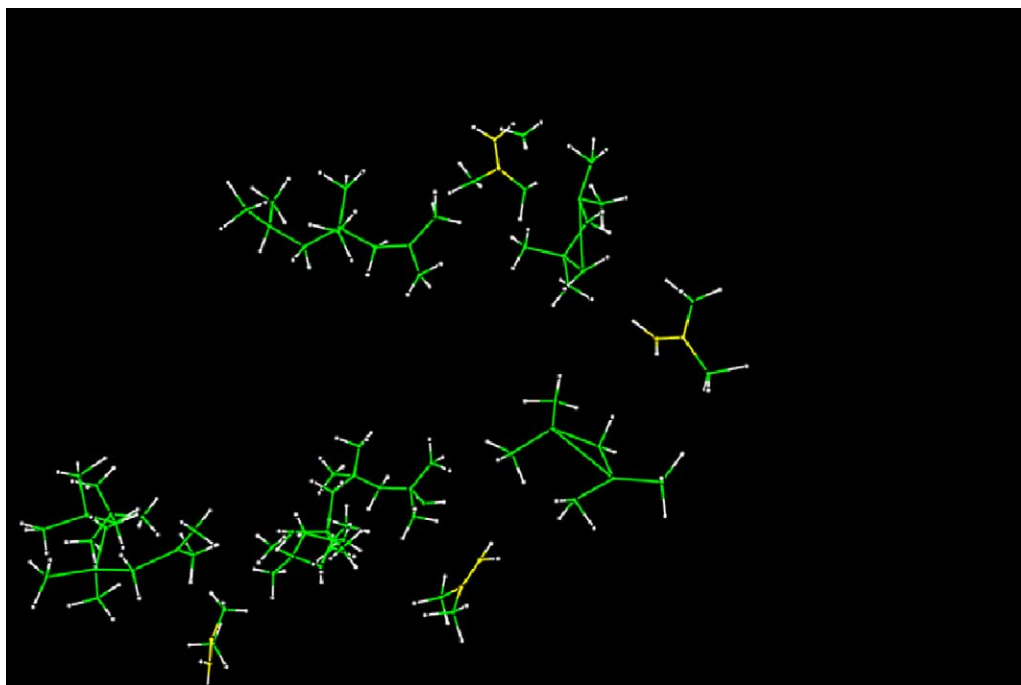


Fig. 4. Final frame from simulations of the thermal decomposition of PIB at 1750 K.

reacting or terminate by inter-molecular hydrogen abstraction reactions as they are transported through the polymer melt. Unfortunately, at the present time, we cannot run the simulations long enough to capture these events and, thereby verify this hypothesis. Methane and methyl radicals are released as a result of the termination of the primary macro-

radicals. The relative number of these compounds, with respect to the number of monomers, was observed to increase with increasing temperature. We also observed the formation of ring structures, especially C_6H_{10} , in some of the highest temperature simulations (2300 K). These observations are consistent with the experimental analysis of the volatile

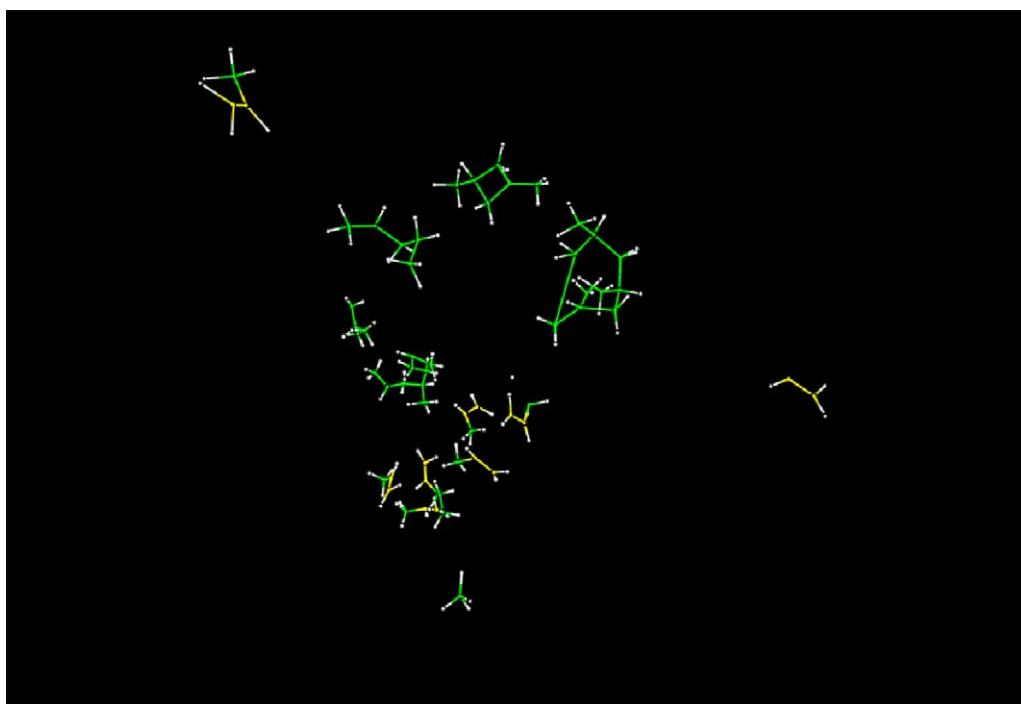


Fig. 5. Final frame from simulations of the thermal decomposition of PP at 2300 K.

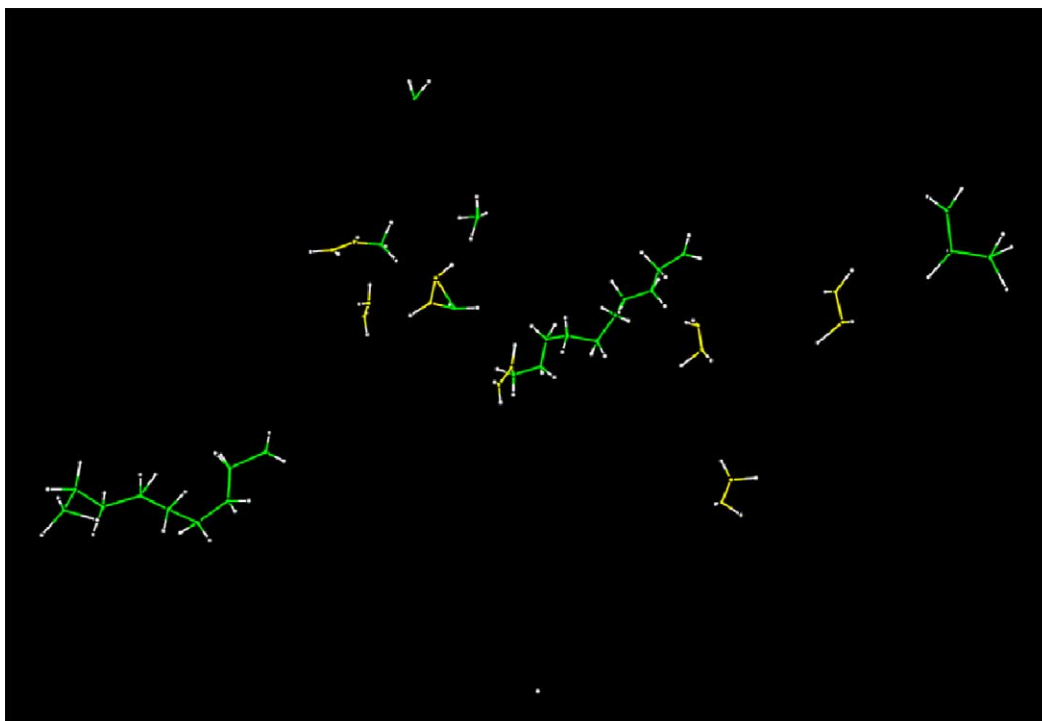


Fig. 6. Final frame from simulations of the thermal decomposition of PE at 2700 K.

products of the decomposition of PIB summarized in reference [18].

In contrast to PIB, the simulations on both PP and PE required much higher temperatures to initiate thermal decomposition. Furthermore, since the termination reactions (which presumably have higher activation energies) become more competitive with the propagation reactions with increasing temperature, the PP and PE simulations yielded a smaller percentage of monomers and a greater variety of cyclic and other low molecular weight hydrocarbons than was observed for PIB. The activation energies (Table 1) for both homolytic (initiation) and β -scissions of the chains (depolymerization) exhibit a clear trend increasing with successive substitutions of hydrogen atoms for the bulky methyl groups in going from PIB to PP and from PP to PE.

More calculations are needed before we can provide a definitive explanation for the observed trends in these activation energies. However, it seems clear that whatever is responsible for the anomalously low activation energies in PIB is related to the length of the polymer chain. Indeed, our simulations on the isobutylene dimer indicate that the activation energy for chain scission in this molecule is on the order of the bond-dissociation energy (~ 345 kJ/mol) obtained from the quantum mechanical calculations on model compounds. One aspect of the problem that we intend to investigate further is the variation of bond energies along the polymer backbone. More specifically, we think that the initiation reactions may be occurring at weak links resulting from steric interactions between the bulky pendant groups. In this regard, it is interesting to note that both PIB and PP adopt

highly coiled conformations, whereas PE, which is much more stable with respect to both homolytic and β -scission reactions, is much more extended. We think that the asymmetries introduced by the coiling may result in steric strain at random positions along the chain, which then dissociate at low temperatures.

4. Conclusions

On the basis of these simulations, we conclude that the differences in product distributions resulting from the thermal decompositions of PE, PP, and PIB are due to differences in the activation energies for the initiation and propagation reactions, which increase dramatically with the substitution of pendant methyl groups for hydrogen atoms. As a consequence, the onset of thermal decomposition occurs at much higher temperatures in the less substituted (i.e. PP and PE) polymers. At these higher thermal decomposition temperatures, the termination reactions become more competitive with the propagation reactions so that a smaller fraction of monomers is formed in favor of cyclic and other low molecular weight hydrocarbon fragments.

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