

## REACTIVE MOLECULAR DYNAMICS MODEL OF THERMAL DECOMPOSITION IN POLYMERS

Stanislav I. Stoliarov<sup>a</sup>, Marc R. Nyden<sup>b</sup>, Richard E. Lyon<sup>c</sup>

<sup>a</sup>Galaxy Scientific Corporation, Egg Harbor Twp., NJ 08234

<sup>b</sup>Building and Fire Research Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899

<sup>c</sup>Federal Aviation Administration, Fire Safety Section, Atlantic City, NJ 08405

### ABSTRACT

The application of quantum chemical and molecular simulation methods can reveal new insights into the thermal degradation chemistries of materials. This work presents and employs an extension of classical force-field-based molecular dynamics to modeling chemical reactions. The method, which may be called Reactive Molecular Dynamics (RMD), is used to investigate the mechanism and kinetics of the thermal decomposition in a series of structurally related polymers including polyethylene, polypropylene, and polyisobutylene. Preliminary results of the RMD simulations indicate that changes in the conformational entropy of decomposing macromolecules have a profound effect on the rate of the decomposition process.

KEY WORDS: Reactive Molecular Dynamics, Thermal Decomposition, Polyolefins

### 1. INTRODUCTION

The use of organic polymers in constructed facilities and clothing is now ubiquitous throughout the world. Despite having many useful properties, these materials must be considered to present a significant risk to public safety because of their inherent flammability. While research in materials flammability has a long and successful history, it is only recently that scientists have begun to recognize the importance of obtaining a clear understanding of the mechanisms and kinetics of thermal decomposition and molecular transport in the polymer melt (1).

Progress in obtaining mechanistic information has been hampered by an absence of direct experimental techniques for monitoring chemical transformations in the condensed phase at elevated temperatures. Indeed, thermal decomposition mechanisms are described in the literature only for the simplest polymers (2-3) and these studies are almost exclusively based on indirect experimental observations (such as analysis of gaseous products) and/or analogies with the behavior of smaller, gas-phase molecules.

Recent advances in computer hardware and the development of high accuracy quantum chemistry, molecular mechanics, molecular dynamics, and Monte-Carlo-based methods have opened up a new dimension for investigating the condensed-phase processes. The present work presents and employs an extension of classical force-field-based molecular dynamics to modeling chemical reactions. The method, which may be called Reactive Molecular Dynamics (RMD), is being developed as a tool for analysis of the thermal decomposition of polymeric materials. Earlier implementations of this method have been successfully applied in studies of the mechanisms of thermal degradation in a number of polymers and polymer composites (4-7).

In what follows, we provide a description of the RMD, including recent enhancements, and report preliminary results of simulations on the homologous series of polyolefins: polyethylene (PE), polypropylene (PP), and polyisobutylene (PIB). Despite similarities in their structures, there are substantial differences in the experimental product distributions, which result from the thermal decomposition of these polymers (2-3). The purpose of this on-going investigation is, therefore, to gain insights into the factors, which determine the predominant decomposition pathways.

## 2. METHOD

The basis of Reactive Molecular Dynamics is solving the classical equations of motion for the atoms of the molecular system under study. The feature that distinguishes RMD from other force-field-based implementations of molecular dynamics is that covalent bonds between atoms are allowed to break and form during the course of the simulations.

In this method, atomic trajectories are computed by numerical integration of Hamilton's equations of motion:

$$\begin{aligned}\frac{\partial H}{\partial p_i} &= \frac{\partial q_i}{\partial t} \\ \frac{\partial H}{\partial q_i} &= -\frac{\partial p_i}{\partial t},\end{aligned}\quad [1]$$

where  $q_i$  and  $p_i$  are the coordinates and components of momenta of the atoms, and  $t$  is time. The classical Hamiltonian,

$$H = \sum_j^N \frac{p_j^2}{2m_j} + V(q_1, q_2, \dots, q_{3N}), \quad [2]$$

is a mathematical expression for the sum of the kinetic and potential ( $V$ ) energies associated with atomic motion. In Eq. 2,  $N$  is the number of atoms in the system;  $p_j$  and  $m_j$  are the momentum vectors and masses of the atoms. In our present implementation, the potential energy is a modified form of the Consistent Valence Force Field (CVFF) (8). It is summarized by Eq. 3:

$$V = \sum^{N_{\text{bonds}}} V_{\text{bond}} + \sum^{N_{\text{angles}}} V_{\text{angle}} + \sum^{N_{\text{torsions}}} V_{\text{torsion}} + \sum^{N_{\text{pairs}}} V_{\text{nonbond}} \quad [3]$$

What follows is a description of the basic components of the CVFF, including how the force field has been altered to account for chemical reactivity.

The potential energy for stretching a covalent bond is represented by a Morse function,

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

$$\alpha = \sqrt{k_b / (2D)},$$

where  $D$  is the bond dissociation energy,  $r$  is the distance between the bonded atoms,  $r_e$  is the equilibrium bond length, and  $k_b$  is the force constant. The potential energy term associated with changing the bond angle,  $\theta$ , between adjacent atoms  $a, b, c$  is

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

where  $\theta_e$  is the equilibrium angle,  $k_\theta$  is the angular force constant, and  $S(ab)$  and  $S(cd)$  are 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,  $\phi$ , is defined by the three bonds between four adjacent atoms:  $a, b, c$ , and  $d$  (planes  $abc$  and  $bcd$ ). Parameters  $k_\phi$ ,  $n$ , and  $\phi_e$  determine the height, multiplicity, and position of the barrier to internal rotation. The switching functions,  $S$ , are fractional bond orders defined as:

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

where  $V_{\text{bond}}$  is the bond energy defined by the Morse potential, which is a function of the interatomic distance,  $r$ ;  $D$  is the bond dissociation energy and  $r_e$  is the equilibrium bond length.

The purpose of the switching functions is to simulate the decay of the bending and twisting forces as the covalent bonds are stretched.

In case of a stretched double bond, only potentials representing torsional angles with the double bond in the middle are scaled by a switching function. This switching function is equal to the fractional bond order of the  $\pi$  bond corresponding to the double bond. The energies of  $\pi$  bonds ( $V_{bond}^{\pi}$ ) are calculated using the double bond Morse potentials ( $V_{bond}^{double}$ ):

$$V_{bond}^{\pi} = \begin{cases} V_{bond}^{double} & V_{bond}^{double} \leq D^{\pi} \\ D^{\pi} & V_{bond}^{double} > D^{\pi} \end{cases}, \quad [8]$$

where  $D^{\pi}$  is the  $\pi$  bond dissociation energy (which is equal to the difference between the double bond and corresponding  $\sigma$  bond dissociation energies). The nonbond term ( $V_{nonbond}$ ) in the CVFF expression (Eq. 3) is equal to the sum of the Lennard-Jones 6-12 and Coulomb potentials as defined in the reference (9).

Chemical reactions are modeled in the RMD by the following algorithm. After every time step of molecular dynamics, fractional bond orders are computed for every covalent bond in the system (in case of double bonds, the bond orders of  $\pi$  bonds are computed). The bond orders are compared with a pre-defined bond-dissociation criterion ( $BDC$ ). If a fractional bond order,  $S$ , is less than or equal to  $BDC$ , the bond is eliminated (i.e., the information about the covalent connection is erased from the database) and the atoms that had been connected by the eliminated bond are labeled as chemically active.

At the next stage, a set of bonds is generated, consisting of all possible covalent interactions between the chemically active atoms. Bonds with the largest value of  $[D - V_{bond}]$  (the most energetically favorable bonds) 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 5 bonds as long as the sum of the bond orders associated with these bonds does not exceed 4. This feature is introduced to describe chemical reactions that occur via so-called hypervalent transition states, such as disproportionation or 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/bond-making routine, the bonds between atoms are not formally removed unless they are replaced by new more energetically favorable bonds. For the purpose of quantifying chemical events, a covalent bond between atoms is considered to be broken when its energy is within  $[0.5kT]$  of the dissociation energy, where  $k$  is the Boltzmann constant and  $T$  is the simulation temperature. The only role of the bond-dissociation criterion is that it 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 labeled as chemically active when the energy of at least one of its covalent bonds is equal to or higher than [0.3*D*].

The atom types of chemically active atoms are updated during every bond-breaking/bond-making procedure to reflect the new arrangement of covalent bonds (see reference (7) for information on the atom types used in the force field). When the "chemically active" label is removed from an atom, the types of the atoms adjacent to the former chemically active atom are also updated. The "chemically active" label does not itself alter properties of the atoms.

The set of the force-field parameters describing interactions between different atom types is based on the version 2.3 of the CVFF provided by Accelrys Inc. (formerly, Molecular Simulations Inc.). As an attempt to improve the parametric description of reactive potential energy surfaces, the dissociation energies and the equilibrium bond lengths used in the force field have been calibrated against the results of high-level quantum chemical calculations performed on small (up to 20 atoms) model compounds. Details of the methods, procedures, and results of these calculations are reported in the reference (7).

In the present version of RMD, only homogeneous bond dissociation is permitted (i.e., no ions are formed). Partial charges on the atoms participating in breaking and making of covalent bonds are adjusted accordingly. The method is designed to model any chemical reaction involving  $\sigma$  and/or  $\pi$  bonds in a carbon-hydrogen-oxygen molecular system, with the exception of triple bonds and  $\pi$ -conjugated and aromatic systems (which we intend to include in the future).

The reactive molecular dynamics algorithm is implemented as a Fortran/C computer code (MD\_REACT program) interfaced with Discover 95, which is commercially available molecular dynamics software offered by Accelrys Inc. 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.

### 3. RESULTS AND DISCUSSION

The RMD simulations were performed on single-chain 20-monomer models of PE, PP, and PIB. Interactions between atoms in the chain(s) and those in the bulk polymer were accounted for by imposing periodic boundary conditions (PBC) (9). The initial structures of the models were obtained via a simulated annealing procedure described elsewhere (7). The simulations were performed at a series of temperatures between 1200 K and 2300 K. The temperature was controlled by a direct velocity scaling (9). The value of 1200 K as the lowest temperature was dictated by the necessity to observe reactive events within computationally feasible simulation times (< 100 ps). Each RMD run was preceded by a shorter (1-5 ps) equilibration molecular dynamics (EMD) performed using a non-reactive variant of the CVFF with the Morse terms substituted for by harmonic potentials ( $r_e^{\text{harmonic}} = r_e^{\text{Morse}}$  and  $k_b^{\text{harmonic}} = k_b^{\text{Morse}}$ ). The EMD was initiated by giving each atom a three-dimensional velocity chosen at random from the Maxwell-Boltzmann distribution and performed at a constant temperature and constant pressure of 101 kPa. The last point on the EMD trajectory was used as a starting point for the RMD, which was performed at a constant volume.

The preliminary results indicate that the decomposition processes are initiated by chain scission reactions. Fragmentation of PIB could be observed at temperatures as low as 1300 K. The main low-molecular-weight product of decomposition of PIB is the monomer (isobutylene). In contrast to PIB, the simulations on both PP and PE required much higher temperatures (>1700 K for PP and close to 2000 K for PE) to initiate the chain scission within the computationally feasible simulation times. The PP and PE yielded a smaller percentage of monomers and a greater variety of low molecular weight hydrocarbons.

Preliminary estimates of the rate constants for the chain scission reactions (computed as  $t_s^{-1}$ , where  $t_s$  is the time of the first scission event) indicate that the activation energy for these reactions depends on the structure of the polymer chains. For PE, we found that the activation energy for chain scission is comparable to the bond dissociation energy of the Morse potential used for the C-C bonds that comprise the polymer backbone. In the cases of PP and PIB, however, we found that the activation energies were much lower (on the order of 60 % and 30 % of the corresponding bond dissociation energies, respectively) even though the bond dissociation energies used for the backbone bonds of all three polymers were very comparable (7). In fact, there is a clear trend of decreasing activation energy with successive substitutions of hydrogen atoms by the bulky methyl groups. This effect, so dramatic in our simulations of the thermal decomposition of the 20-monomer polymers, was no longer apparent when we performed RMD simulations on an isobutylene dimer, for which we found that the activation energy for the backbone scission was close to the bond dissociation energy.

The unusually low values of the activation energy obtained for the backbone scission reaction in PIB may actually be due to approximations used in the description of the reactive potential energy surfaces. Substantial additional work needs to be done before we can completely rule out this possibility. However, we believe that there are more fundamental reasons for the observed trends. The results of the simulations can be explained within the framework of the Canonical Variational Transition State Theory (see, for example, reference 10). According to this theory, an increase in the entropy contribution to the free energy along the reaction coordinate results in a reduction of the activation energy with increasing temperature. This happens because the position of the transition state, defined by the maximum value of the free energy, shifts towards the reactant (lower entropy) as the temperature increases. The magnitude of this effect depends on the structures of the reacting molecules. For most small gas-phase molecules, the difference between the activation energies (typically measured within 500 – 1500 K temperature interval) and bond energies is minor and is frequently ignored. However, according to the RMD simulations, this disparity becomes greater with increasing size of the decomposing molecules. Our results also indicate that this effect is much more dramatic in branched polymers with large pendant groups. On the basis of these trends, it seems reasonable to suggest that the source of the reduction in the activation energies for backbone scission reactions is the increase in conformational entropy, which occurs as atoms, whose motion was constrained by the presence of the dissociating bond, become free to move. This effect is more dramatic for branched polymers because the steric forces, which restrict the orientations of the pendant groups in the fully associated polymer, fall rapidly to zero when bonds along the backbone of the polymer break, thereby resulting in a large increase in entropy.

Recently, we have undertaken a detailed study of the effects of polymer chain structure and length on the kinetics and mechanism of the thermal decomposition process. Three single-chain models containing 14, 50, and 150 monomer units with PBC imposed were made for each of the polymers, PE, PP, and PIB. Additional two single-chain models without PBC containing 4 and 50 monomer units were made for PE and PIB (two models for each of the polymers). The initial structures of the models were prepared using the Materials Studio software package (11) and annealed as follows. A 100 ps molecular dynamics calculation was performed on each model using the non-reactive variant of the CVFF. From each trajectory, we sampled 100 structures and proceeded to minimize their energies with respect to both the molecular geometries and cell parameters (in the case of the PBC models). This procedure was repeated until no reduction in energy could be achieved from five consecutive 100 ps runs of molecular dynamics. All of the molecular dynamics calculations were performed at a constant temperature of 1000 K and constant pressure of 101 kPa (for the PBC models). Some of the PBC models required excessive pressures (up to 100 MPa) in order to accelerate convergence to the correct density ( $\approx 0.85 \text{ g cm}^{-3}$  at  $T=300 \text{ K}$  for all the polymers (12)). The results of the RMD simulations performed on these models will be reported at the conference. A related manuscript, which focuses exclusively on the thermal decomposition of PIB, was also submitted to the conference proceedings (13).

#### 4. REFERENCES

1. T. Kashiwagi, Symp. (Int.) Combust., Proc., **25**, 1423 (1994).
2. S.L. Madorsky, Thermal Degradation of Organic Polymers, Interscience Publishers, New York, 1964.
3. C.F. Cullis and M.M. Hirschler, The Combustion of Organic Polymers, Clarendon Press, Oxford, 1981.
4. M.R. Nyden, G.P. Forney, J.E. Brown, Macromolecules, **25**, 1658 (1992).
5. M.R. Nyden, T.R. Coley, S. Mumby, Polym. Eng. Sci., **37**, 1496, (1997).
6. M.R. Nyden, International Aircraft Fire and Cabin Safety Research Conference, Atlantic City, 1998.
7. S.I. Stoliarov, et al. Polymer, **44**, 883 (2003).
8. P. Dauber-Osguthorpe, et al. Structure, Function and Genetics, **4**, 31 (1988).
9. Discover 95. User Guide., Biosym/MSI, San Diego, 1995.
10. R.G. Gilbert, S.C. Smith, Theory of Unimolecular and Recombination Reactions, Blackwell, Oxford, 1990.
11. Materials Studio Version 2.1, Accelrys Inc., 2001.
12. D.W. Van Krevelen, Properties of Polymers, Elsevier, Amsterdam, 1990.
13. C.S.Y. Jee, et al. "Study of The Thermal Degradation of Polyisobutylene Binder for The Production of Titanium Matrix Composites via Experiment and Reactive Molecular Dynamics Simulations", SAMPE Conference, Long Beach, CA, 2003.