New Reactive Molecular Dynamics Algorithm for Modeling the Thermal Decomposition of Polymers

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Introduction

High-accuracy quantum chemistry and molecular simulation methods, along with advances in computer technology, have introduced new capabilities for investigating thermal reactivity and its effect on materials flammability. One example is a molecular dynamics computer program called MD_REACT, which simulates the thermal degradation of polymers. MD_REACT has been applied in previous investigations into the effects of fire retardants and nano-additives on the thermal degradation of commodity polymers, including polyethylene, polystyrene, and polypropylene.[1-3]

Enhancements to the computer code and reactive force field were made as part of a recent collaboration between the Building and Fire Research Laboratory (BFRL) of the National Institute of Standards and Technology (NIST) and the Chemical Engineering Department of the University of Massachusetts Amherst. The purpose of this paper is to summarize the improvements we have made in the context of providing an overview of the theory and implementation of reactive molecular dynamics. The capabilities of MD_REACT and its potential as a tool for performing molecular level investigations of the mechanisms of thermal degradation are demonstrated by presenting results from comparative simulations performed on poly (methyl methacrylate) (PMMA) and poly (methacrylate) (PMA).

Despite their structural similarities, these polymers undergo dramatically different modes of thermal decomposition. Thus, while PMMA unzips almost exclusively to methyl methacrylate monomers[4], PMA decomposes to a distribution of products including CO, CO_2, CH_3OH and hydrocarbon chains of various lengths. In contrast to PMMA, only small amounts of the methacrylate monomer (less than 1% of the volatiles) are observed in the decomposition products of PMA[5]. These differences are commonly attributed to the presence of the methyl groups in PMMA.[5,6] In the thermal decomposition of most vinyl polymers, there is a strong competition between depolymerization reactions and hydrogen transfer reactions, which effectively shift the location of radical sites from chain ends to random positions on the polymer backbone (thereby producing a distribution of chain lengths via the ensuing β-scission reactions). In PMMA, however, it is thought that steric hindrance from the methyl groups inhibits the hydrogen transfer reactions, thereby making depolymerization the preferred decomposition pathway[6]. Results obtained in a previous study of the thermal degradation of PMMA[7], however, motivated us to examine this explanation in greater detail by performing comparative simulations on the two polymers.

Description of the Method

The basis of the MD_REACT method is molecular dynamics. In this method, atomic trajectories are computed by numerical integration of Hamilton's equations of motion:

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

where q_i and p_i are the coordinates and momenta of the atoms, and t is time. H is the Hamiltonian,

$$H = \sum_i^N \frac{\mathbf{p}_i^2}{2m_i} + V(q_1, q_2, \ldots, q_{3N}), \tag{2}$$

which is a mathematical expression for sum of the kinetic and potential (V) energies associated with atomic motion. In Eq. (2), N denotes the number of atoms in the system and $\mathbf{p}_i$ and m_i are the momentum vector and mass of the i^{th} atom, respectively. The potential energy, $V(q_1,q_2,\ldots,q_N)$, is represented by a modified form of the Consistent Valence Force Field[8] (CVFF), summarized in the equations 3 – 7.

$$V = \sum^{n_{bonds}} V_{bond} + \sum^{n_{angles}} V_{angle} + \sum^{n_{torsions}} V_{torsion} + \sum^{n_{pairs}} V_{nonbond} \qquad (3)$$

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 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 set of new potential bonds, consisting of all possible covalent interactions between the chemically active atoms, is generated. 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 of an atom is equal to its valence and the fractional bond order of each of its bonds is higher than *BDC*, the chemically active label is removed from the atom. Otherwise, if an atom retains its chemically active status, it is allowed to form one hypervalent bond. Thus, the maximum number of covalent bonds for a chemically active atom is equal to its valence + 1. This feature is introduced to describe chemical reactions that occur via hypervalent transition states (atom transfer reactions, for example). 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 equal to or higher than 0.3*D*.

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*). 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 (*D*) 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[7].

Simulation Procedures

Most of the simulations were performed on defect-free models of PMMA and PMA consisting of a single 15-unit polymer chain terminated with an H atom at one end and a CH_3 group at the other end (see Figure 1). Nonbond interactions were calculated using an atom-based summation method[9] with a cutoff 1distance 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 effects of reactions between chains, such as intermolecular atom transfer and

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* 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.

cross-linking, were assessed by performing additional simulations with model systems consisting of four polymer chains in the unit cell.

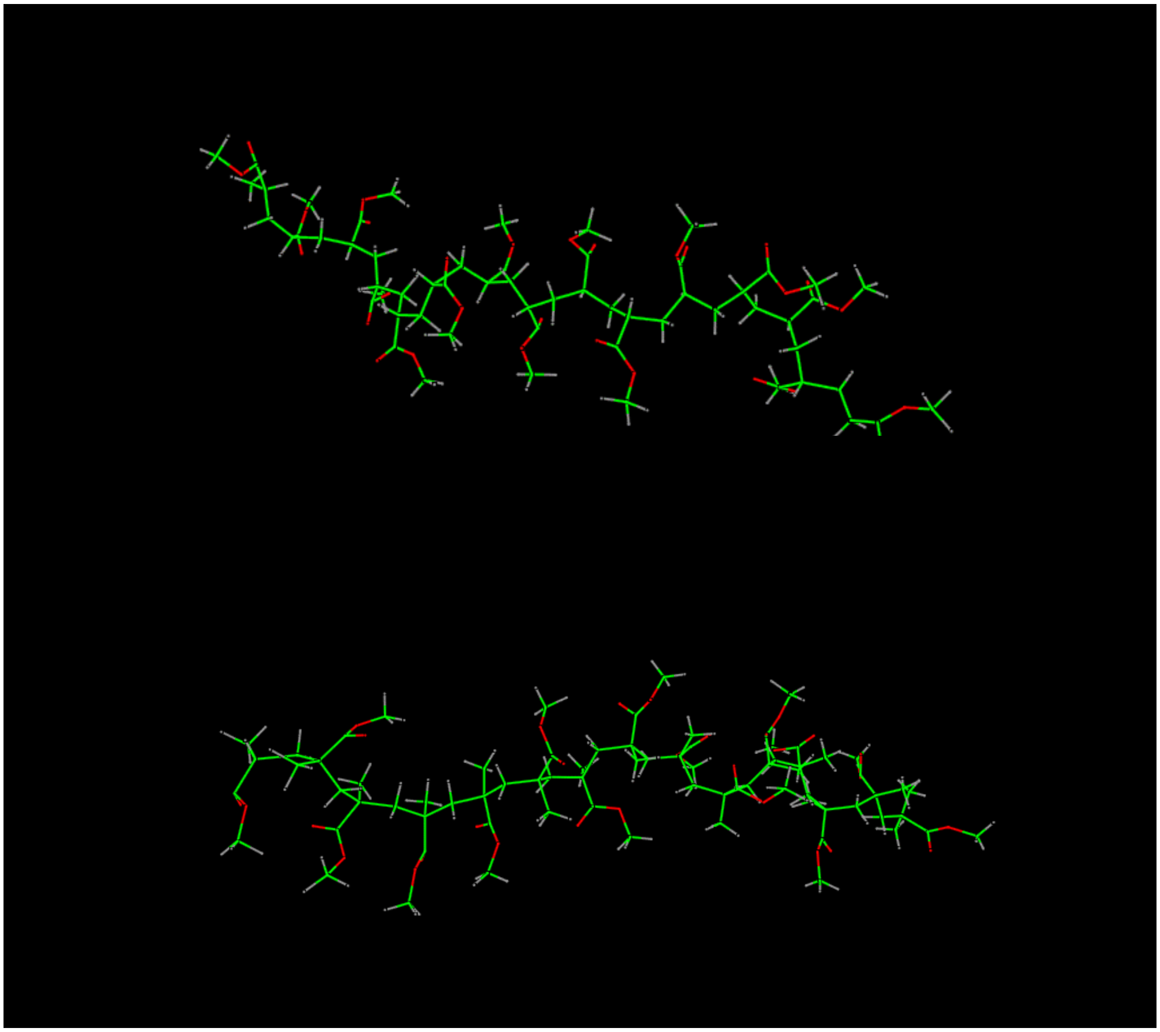

Figure 1. Initial single chain structures for simulations of the thermal degradation of PMA and PMMA.

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 after decrementing the temperature by 10 degrees until the specified temperature for the dynamics was reduced to 0 K. The densities of the single chain PMMA and PMA models at typical simulation temperatures were approximately 1.0 g/cm^3 and 0.7 g/cm^3, respectively.

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 (Eq. (4)) in the CVFF was substituted for by a harmonic potential with $r_e^{harmonic}=r_e^{Morse}$ and $k_b^{harmonic}=k_b^{Morse}$. The durations of the equilibration dynamics varied between 0.5 and 12 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 varied between 2 and 40 ps.

Simulations were performed at a series of temperatures between 900 K and 1600K in 100K increments. The temperature was controlled by velocity scaling with a variance of ? 10 K. Our observations about the differences in product distributions and the relative thermal stabilities of the polymers were made on the basis of results obtained from at least three independent simulations at each temperature.

Results and Discussion

The final frames from representative simulations for each polymer are compared in Figure 2. The mechanism derived from analysis of the results obtained for PMMA[7] is consistent with the experimental observation that PMMA decomposes at low temperatures almost exclusively into monomers and is in agreement with the mechanism advanced by Inaba, Kashiwagi, and Hamins based on their analysis of kinetic measurements of molecular weight distributions[10]. In contrast, the PMA simulations required much higher temperatures to initiate thermal decomposition and yielded fewer monomers and a greater variety of low molecular weight hydrocarbons and esters.

The difference in the product distributions can be accounted for by the fact that more decomposition pathways are available at the higher temperatures required to initiate thermal degradation in PMA. The source of this disparity in the thermal stabilities of these polymers,

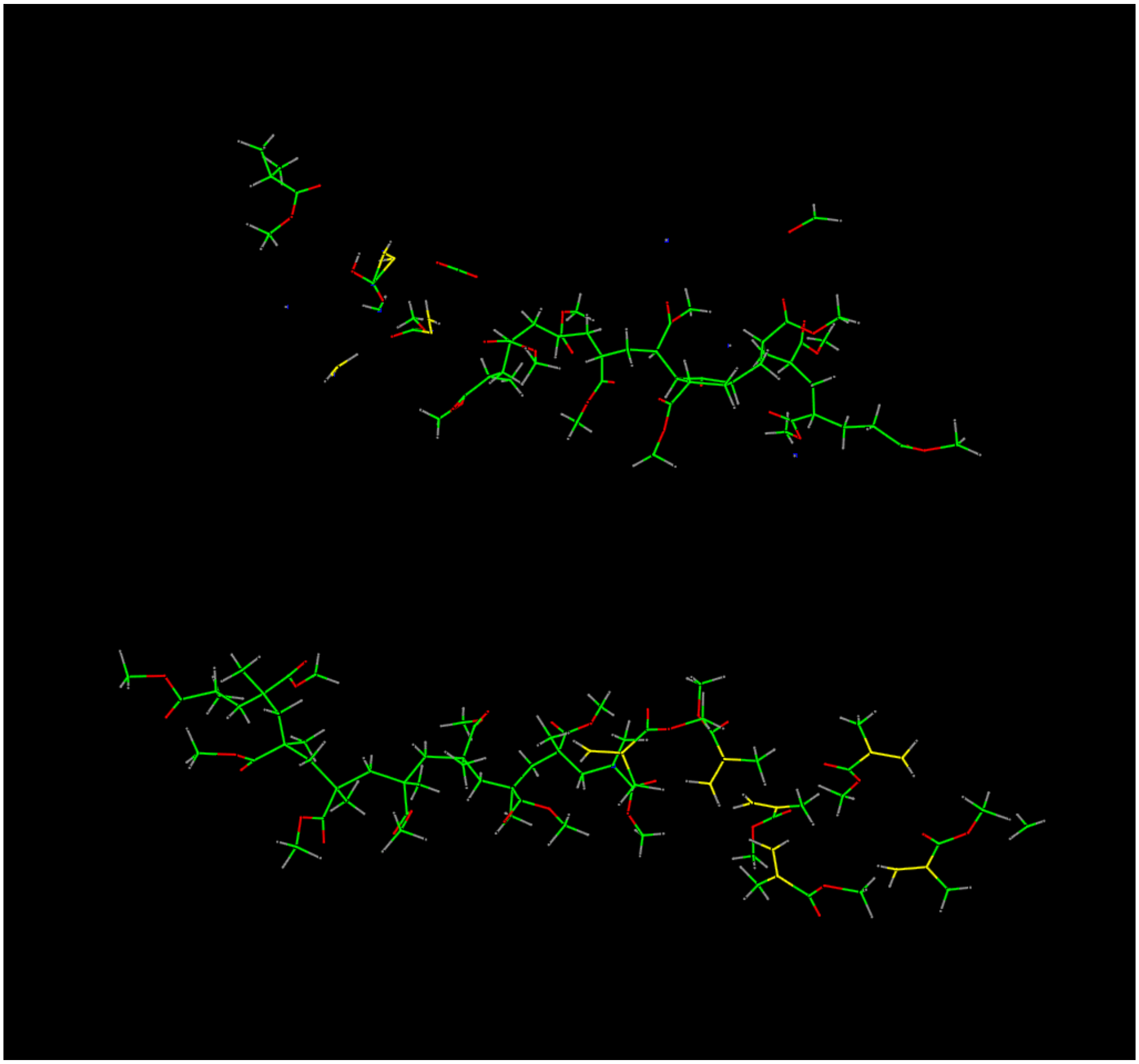

Figure 2. Final frames from simulations of the thermal degradation of PMA and PMA.

however, is open to discussion. We think that there are at least two contributing factors. First, the simulated annealing calculations, used to generate the initial structures for our reactive simulations, gave a higher density for PMMA than for PMA. Consequently, the excitation energies per unit volume were proportionately greater in the PMMA simulations, even though the average energies per degree of freedom were the same. This implies that the energy exchange between vibrational modes is more efficient in PMMA than it is PMA. Another consideration is that the dissociation energies of the C-C bonds that comprise the polymer backbones are somewhat smaller in PMMA due to both steric and electronic effects associated with the pendant methyl groups.

Summary and Conclusions

The theory and implementation of MD_REACT, a molecular dynamics model for simulating the thermal degradation of polymers, were reviewed in the context of presenting an overview of recent enhancements that we made to the computer code and reactive force field. The improved model was used in performing comparative simulations on poly(methylacrylate) and poly(methylmethacrylate), which, despite their structural similarities, are known to undergo dramatically different modes of thermal degradation. The results, which are consistent with experimentally determined product distributions, indicate that these differences derive from the higher temperatures needed to initiate thermal decomposition in PMA. Some of the factors responsible for increasing the thermal stability of PMA with respect to PMMA were identified and discussed.

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