Applications of Molecular Dynamics to the Study of Thermal Degradation in Aromatic Polymers. I: Polystyrene

MARC R. NYDEN*

Building and Fire Research Laboratory
National Institute of Standards and Technology
Gaithersburg, Maryland 20899

and

TERRY R. COLEY** *and* STEPHEN MUMBY

Molecular Simulations
San Diego, California 92122

This paper reports recent progress in the development of a generic molecular dynamics model that accounts for the major chemical reactions involved in the thermal degradation of polymers. The strategy employed in the design of the most recent version of this model was to interface our code for performing reactive dynamics on simple vinyl polymers with a commercial molecular dynamics package (Discover 95). The expanded range of applicability of the integrated model is illustrated by applying it to the study of thermal degradation in atactic polystyrene.

INTRODUCTION

The flammability of polymers is a major concern, affecting public safety and limiting their use in buildings, ships, aircraft, and clothing. Unfortunately, the traditional "trial and error" approach to the design of fire resistant materials is not cost effective. This realization has provided an impetus for the development of new methodologies. Research conducted in this laboratory has focused on using molecular dynamics modeling to identify factors that alter the condensed phase thermal degradation chemistries of polymers in ways that effect a reduction in their flammability.

The result of this ongoing research has been the development of a unique molecular dynamics model, hereafter referred to as MD_REACT, that accounts for the major reaction channels involved in the thermal degradation of polymers (1–3). The range of applicability of previous versions of this model was limited to the study of simple vinyl polymers such as polyethyl-

ene. Many commercially available molecular dynamics software packages have the capability to build a much wider range of molecular structures and have access to extensive compilations of the parameters needed to describe the atomic level forces that govern the thermal motion of polymers. Unfortunately, these commercial molecular dynamics codes do not allow for the formation of new bonds from the free radical fragments generated when bonds in the polymer break, and, therefore, cannot account for the subsequent chemical reactions that play a major role in the thermal degradation process.

The purpose of this paper is to provide an overview of the progress we have made in the development of an integrated model that possesses the capability to model thermal degradation in a wide range of polymers. The strategy employed to accomplish this objective was to make use of an inter-process communications protocol (IPC) to pass coordinates, forces, and connectivity information between MD_REACT, which computes the reactive force field, and Discover 95 (4), a commercially available molecular dynamics code offered by Molecular Simulations (5), which updates the molecular structure on the basis of the solution to the equations of motion. The capabilities of the present version of this model are illustrated by applying it to the study of thermal degradation in polystyrene.

* To whom correspondence should be addressed.
** Present address: Virtual Chemistry Inc., 7770 Regents Road Suite 251, San Diego, CA 92122.

THEORY

Molecular Dynamics

Molecular dynamics consists of solving Hamilton's equations of motion

$$\frac{\partial H}{\partial p_i} = \frac{dq_i}{dt}$$

$$\frac{\partial H}{\partial q_i} = -\frac{dp_i}{dt} \tag{1}$$

for each of the 3N molecular degrees of freedom. In this equation p_i and q_i denote the Cartesian components of momentum and position, respectively.

The Hamiltonian of the model polymers considered in this investigation, which is based on the CVFF forcefield (6) (one of several forcefields that are distributed with Discover 95), is summarized in *Eq 2*. The first term on the right-hand side of this equation represents the kinetic energy of the N atoms in the model polymers. The next terms are the potential energies for bond stretching (V_b) and bending (V_a) and a torsional potential (V_t), which restricts internal rotation around the covalent bonds. The last term represents the

$$H = \sum_i^{3N} \frac{p_i^2}{2m_i} + \sum_{ij}^{nbonds} V_b(r_{ij}) + \sum_{ijk}^{nangles} V_a(\theta_{ijk})$$
$$+ \sum_{ijkl}^{ntorsions} V_t(\phi_{ijkl}) + \sum_{ij}^{npairs} V_{nb}(r_{ij}) \tag{2}$$

nonbond potential energy (V_{nb}) resulting from the interactions between all pairs of atoms that are not part of the same covalent bond angle (i.e., between atoms separated by at least two atoms).

The potential energy for stretching the covalent bonds is described by a Morse function

$$V_b = D[1 - \exp(-\alpha(r - r_e))]^2 \tag{3}$$

where r_{ij} is the distance between covalently bonded atoms, r_e is the equilibrium bond length, D is the amount of energy required to dissociate the bond, and $\alpha = [k_b/(2D)]^{1/2}$, where k_b is the force constant.

The potential energy for bond bending is represented by the quadratic function

$$V_a = S(ij)S(jk)k_\theta(\theta - \theta_e)^2 \tag{4}$$

where θ denotes the angle defined by the dot product of the normalized bond vectors between three adjacent atoms (denoted $i, j,$ and k) and k_θ is the corresponding force constant.

Rotations about covalent bonds are restricted by the torsional potential

$$V_t = S(ij)S(jk)S(kl)K_\phi[1 + \cos(n\phi - \phi_e)], \tag{5}$$

where the dihedral angle, ϕ, is defined by the three bond vectors between four adjacent atoms $(i, j, k,$ and $l)$. The parameters, K_ϕ, n, and ϕ_0 determine the height,

multiplicity, and position of the barrier to internal rotation.

The switching functions, which are used to turn off the forces due to bending and twisting as the relevant bonds approach dissociation, are determined from *Eq 6*

$$S(ij) = \frac{1}{2}(1 - \tanh(a(r_{ij} - r_d))) \tag{6}$$

with $a = 40$ nm^{-1}. The dissociation distances, r_d, depend on the nature of the bond and are determined from an energy-based criterion, which is discussed in the following subsection. It is the presence of the switching functions in *Eqs 4* and *5* that distinguishes the reactive forcefield used in our model from the CVFF forcefield, which is included with Discover 95.

The nonbond potential energy is represented by the Lennard-Jones function

$$V_{nb} = \epsilon\left[\left(\frac{r^*}{r}\right)^{12} - 2\left(\frac{r^*}{r}\right)^6\right] \tag{7}$$

where r is the distance between nonbonded atoms. No explicit accounting is made for electrostatic interactions or hydrogen bonds in the present version of the model.

Reactions

Bond dissociation and formation are simulated in MD_REACT by the following algorithm. A list of the free radical sites, which are generated when bonds in the polymer break, is updated at every time step. These free radicals are eligible to react with each other to form new bonds. The specific criterion used in MD_REACT is that two free radical sites are formed whenever the energy stored in a bond approaches the average thermal energy, kT. The program generates a new set of bonds consisting of all possible covalent interactions between the available free radicals and retains those corresponding to the lowest energy subject to the constraints implicit in the valency of the atoms. That is, a section of code is implemented that ensures that there are never more than 4 bonds to any carbon atom, more than 1 bond to any hydrogen atom, and so on. Of course, the number of bonds to an atom can, and frequently does, decrease from its maximum value as a result of bond scission reactions. The bond table in Discover 95 is modified and the trajectory of the polymer is updated accordingly.

In this way, the model accounts for many of the reaction pathways that are involved in the thermal degradation of polymers (7). Some of these reactions are illustrated, using atactic polystyrene as the prototype, in *Fig. 1*. Listed from top to bottom, these include: bond scission, depolymerization, intramolecular hydrogen transfer, chain stripping, intramolecular cyclization, intermolecular crosslinking, and radical recombination reactions.
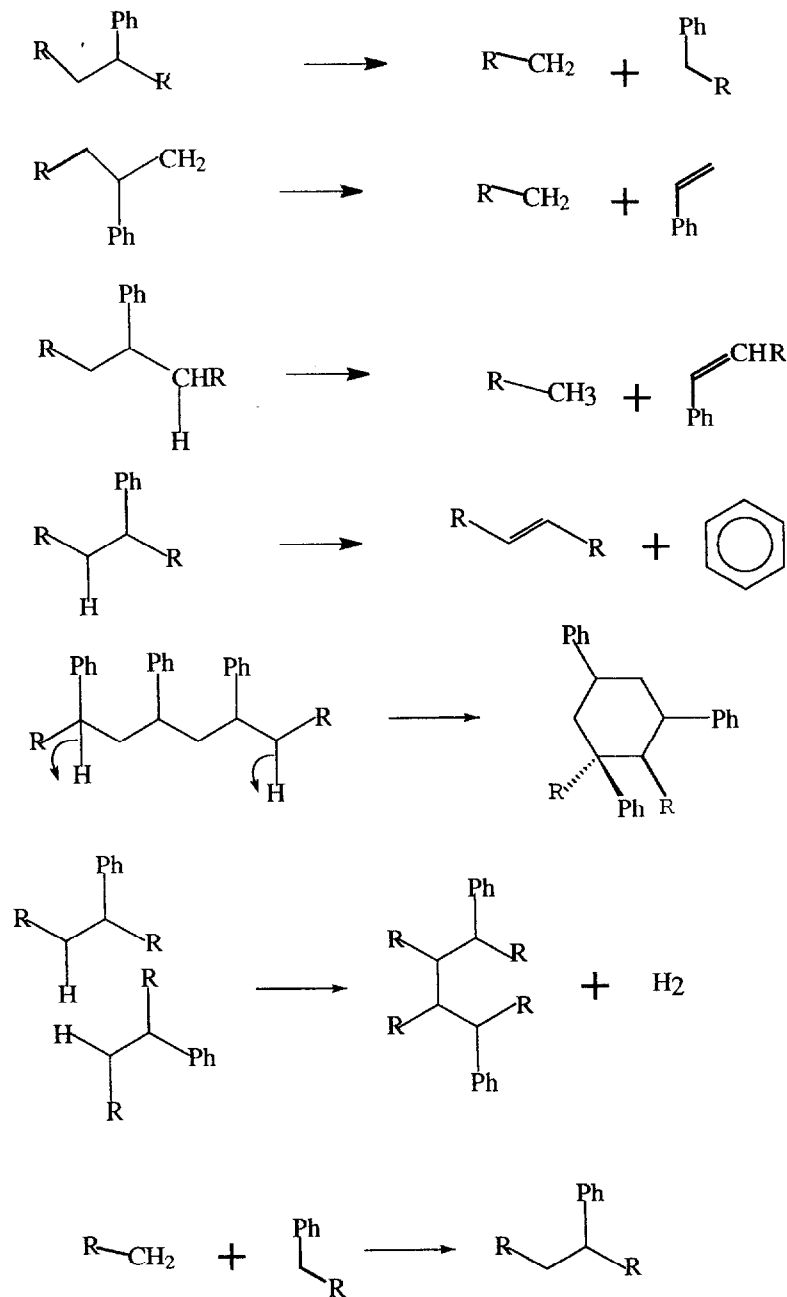
Fig. 1. Reaction channels used in simulations of the thermal degradation polystyrene.

Interface

The interface to Discover 95 is established using the IPC protocol developed by MSI. The input file for the Discover 95 run contains a BTCL (8) command string, which initializes an IPC connection in server mode and launches MD_REACT as an external process. A series of database operations that identify and replace the high energy bonds are executed at every time step. The energy and forces calculated in Discover 95 do not include the contributions due to the presence of the switching functions in *Eqs 4* and *5*. These corrections are computed in MD_REACT and passed to Discover 95 in the form of a BTCL restraint.

Procedure

Simulations of thermal degradation were performed on two models of isotactic polystyrene. The models consisted of 3 chains with 20 styrene monomers in each chain, which were predominately bonded in a head-to-tail fashion (i.e., the phenyl rings were bonded to alternating backbone carbons). The effect of head-to-head bond defects (i.e., phenyl rings bonded to adjacent carbons) was investigated by introducing a total of 9 head-to-head bonds (3 per chain) in one of the model polymers. The initial geometries were ob-
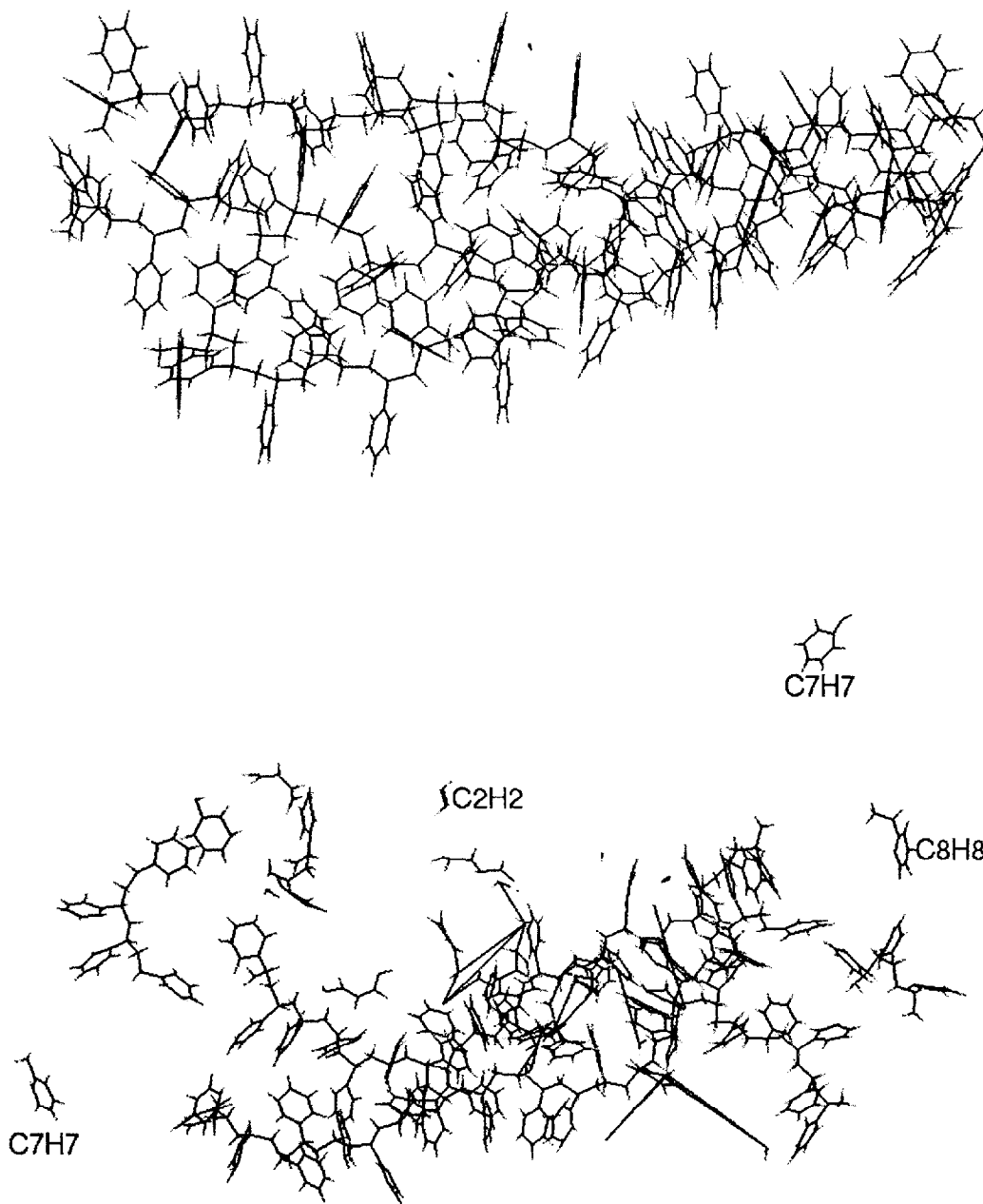
Fig. 2. Still frames from a computer animation of a representative trajectory depicting the structures of polystyrene at the onset of the simulation (top) and after 1200 time steps of reactive dynamics at 2000 K (bottom).

tained for both models by minimizing the CVFF energies until the maximum derivative was <0.001 using the conjugate gradient algorithm in Discover 95.

The CVFF forcefield was augmented with new atom types, denoted as ccf for a carbon atom bonded to a free radical site (cf) and ccp corresponding to an aliphatic carbon bonded to an aromatic carbon (cp), to account for the formation of monomers via β-scission and the special stability of benzyl radicals. These atom types were equivalenced to the generic aliphatic carbon atom type (c) for all potential energy terms except

bond stretching. The dissociation energies (D) of bonds to ccp atoms were lowered by the resonance stabilization energy of 50 kJ/mol (12 kcal/mol) for each benzyl radical formed (9). On this basis, the parameters used to represent the dissociation energies of the ccp-ccp and ccp-c bonds was reduced from the CVFF value of 368 kJ/mol for c-c bonds to 268 and 318 kJ/mol, respectively, and the value for ccp-h bonds was reduced from 454 to 404 kJ/mol. The formation of pi bonds during β-scission was modeled by reducing the dissociation energies of c-ccf and h-ccf

bonds by 317 kJ/mol (to 51 and 137 kJ/mol, respectively), which corresponds to the difference between a carbon-carbon single and double bond.

The simulations of thermal degradation were performed in two steps. First, the model polymers were equilibrated by integrating the equations of motion over a constant temperature path at 1500 K for 0.1 picosecond (100 time steps) using the full CVFF forcefield with cross terms. The purpose of including cross terms in the equilibration was to facilitate an efficient transfer of thermal energy into the stretching modes responsible for bond dissociation. The reactive dynamics were then carried out at constant temperatures of 2000 K, 1000 K and 500 K for 5.0 picoseconds (5000 time steps) using the reactive forcefield summarized in *Eqs 2–7*.

Results

Displayed in *Fig. 2* is a still frame from the computer animation of a representative trajectory, which indicates the formation of styrene monomers via β-scission and benzyl radicals by dissociation of c-ccp bonds. These, and other reactions producing styrene oligomers, toluene, benzene, ethene and acetylene, were observed to occur with regularity in all the simulations performed in this study. Although these results are in reasonable accord with experimentally determined product distributions (10), the preponderance of free radical over molecular products suggests that the densities of the model polymer systems used in these simulations were unrealistically low. We are attempting to overcome this deficiency by introducing the capability to use periodic boundary conditions in future versions of MD_REACT.

The presence of the head-to-head bond defects in one of the models was apparent only in the simulations where the reactive dynamics was carried out at 500 K. In this case, the predominant reaction paths involved dissociation of the head-to-head bonds, which are by far the weakest bonds in these polymers. This behavior, however, was not observed in the higher temperature simulations.

SUMMARY AND CONCLUSIONS

A series of computer simulations of the thermal degradation of polystyrene were performed. The major

reaction paths observed in these simulations were β-scission, producing styrene monomer, random scission, resulting in the formation of styrene oligomers, and dissociation of c-ccp bonds, yielding benzyl radicals and toluene. The formation of benzene, ethene, and acetylene was also frequently observed. The effect of head-to-head bond defects on the thermal degradation of the model polymers was apparent only in the low temperature simulations.

ACKNOWLEDGMENTS

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