

APPLICATIONS OF MOLECULAR DYNAMICS TO THE STUDY OF THERMAL DEGRADATION IN POLYMERS

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The flammability of polymeric materials is a major concern which impacts public safety and limits 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 research conducted in this laboratory which has focused on using molecular dynamics modeling to identify factors which alter the condensed phase thermal degradation chemistries of polymers in ways which effect a reduction in their flammability.

The result of this ongoing research effort has been the development of a unique molecular dynamics model, hereafter referred to as MD_REACT, which 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, however, were limited to the study of simple vinyl polymers such as polyethylene. 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 which are needed to describe the atomic level forces which 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 chemical reactions which 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 which 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 of polypropylene in the presence of a silica gel additive.

Molecular dynamics consists of solving Hamilton's equations of motion for each of the $3N$ molecular degrees of freedom. The Hamiltonian of the model polymers considered in the present investigation is based on the CVFF forcefield [6] (one of several forcefields which are distributed with Discover 95) except that switching functions are used to turn off the forces due to bending and twisting as the relevant bonds approach dissociation.

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 after a specified number of timesteps. 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 which 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 computer model accounts for many of the reaction pathways which are involved in the thermal degradation of polymers. Some of these reactions are: bond scission, depolymerization, intramolecular hydrogen transfer, chain stripping, intramolecular cyclization, intermolecular crosslinking and radical recombination reactions. The depolymerization and intramolecular hydrogen transfer reactions, in particular, are modeled by introducing two new atom types (cf and ccf) into the CVFF forcefield to account for beta scission. The ccf atom type corresponds to an aliphatic carbon (c) bonded to a free radical carbon (cf). Once a free radical is formed, the dissociation energies of the c-ccf and h-ccf bonds (beta to cf) are reduced by the energy of the pi bond (corresponding to ccf=cf) which is presumed to form at the same time that the c-ccf (or h-ccf) bond breaks. Thus, the activation energies for the formation of the alkene, via intramolecular hydrogen transfer, or the monomer, are about 40 and 20 kcal/mol, respectively.

MD_REACT was recently upgraded to provide the capability to use periodic boundary conditions. This was implemented by replicating the degrading polymer chains in space (Figure 1), thereby creating ghost atoms, and keeping track of all of the new bonds which form from reactions involving actual free radical fragments and their ghosts. The use of periodic boundary conditions increases the utility of the model by making it possible to maintain realistic densities in simulations of the thermal degradation of isolated chains within the bulk polymer.

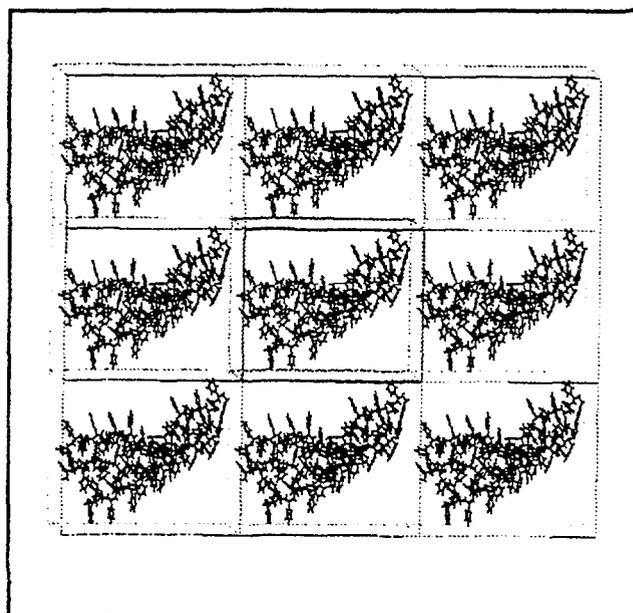


Figure 1. Periodic display of polystyrene.