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Molecular Modeling of the Thermal Decomposition of Polymers

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LIST OF ACRONYMS

BDC	Bond-dissociation criterion
BPC	Bisphenol C
EN	Enol
HA	Hydroxyamide
PHA	Poly(dihydroxybiphenylisophthalamide)
PIB	Polyisobutylene
RMD	Reactive molecular dynamics

EXECUTIVE SUMMARY

The applications presented here demonstrate the potential for using quantum chemical methods and molecular simulations to determine the mechanisms and rates of the thermal decomposition of polymers. The expectation is that these capabilities can be used to predict the flammability of materials and develop strategies to improve fire resistance. The thermal decompositions of poly(dihydroxybiphenylisophthalamide) and bisphenol C polycarbonate are investigated by performing density-functional calculations of potential energy surfaces of model compounds representing the polymers. Reactive molecular dynamics, a relatively new technique that extends conventional molecular dynamics to modeling chemical reactions, was used to simulate the thermal decomposition of polyisobutylene. The advantages and limitations of both computational approaches are discussed.

INTRODUCTION

Computational chemistry, which embraces the application of methods of quantum, classical, and statistical mechanics to molecules and molecular assemblies, offers new possibilities for the investigation of materials flammability. In principle, these methods can be used to determine the mechanisms and calculate the rates of thermal decomposition reactions, thereby providing guidance for the development of new and more fire-resistant materials. The ability of these methods to predict thermodynamics and kinetics of chemical reactions involving small gas-phase molecules is well established [1 and 2]. Unfortunately, the extension of the methods to large molecules, such as polymers, in the condensed phase introduces many conceptual and computational challenges. Nevertheless, the results from recent studies [3-6] demonstrate that it is possible to obtain valuable information about the mechanism and kinetics of polymer decomposition by means of computational chemistry.

Here, an overview of the studies of the thermal decompositions of poly(dihydroxybiphenylisophthalamide) (PHA) [3], bisphenol C (BPC) polycarbonate [4], and polyisobutylene (PIB) [6] are presented. PHA and BPC polycarbonate are among the most fire-resistant polymers ever tested. Their thermal degradation results in the formation of a large amount of char (about 50% by weight) and the release of nearly noncombustible gasses [7 and 8]. In an effort to determine the source of this exceptional fire performance, the decomposition chemistries of both PHA and BPC were investigated by performing quantum chemical calculations to determine the most probable reaction paths. Based on the results of these calculations, the chemical mechanisms responsible for the unusually high-temperature behavior of these materials were proposed. A relatively new method, called reactive molecular dynamics (RMD), was employed to study the thermal decomposition of PIB. The results of the RMD calculations provided a detailed, dynamic picture of the decomposition process and led to important observations about the kinetics of key elementary reactions.

QUANTUM CHEMICAL CALCULATIONS OF REACTION PATHS

The B3LYP density-functional method [9] was used in combination with the 6-31G(d) and 6-31G(d,p) basis sets [10] to calculate potential energies of model compounds representing the molecular structures of PHA and BPC. The model compounds contained up to 19 multielectron (nonhydrogen) atoms. This method was chosen to achieve the maximum accuracy within a reasonable computational time. A basis set with additional functions on the hydrogen atoms (the 6-31G(d,p) basis set) was used for the PHA calculations because of the expectation that these atoms play an important role in the decomposition process.

Potential energy surfaces of the model compounds (i.e., dependencies of potential energies of the compounds on internal atomic coordinates) were carefully examined to identify transition states leading to chemical transformations. Intrinsic reaction coordinate reaction-path-following calculations [11] were performed for the transition states to establish the connected reactants and products. The structures of the reactants, products, and transition states were optimized. The energies of the optimized structures were corrected for zero-point energy contributions. No corrections were made for the basis set superposition errors. These energies were subsequently used in the analyses of chemical mechanisms. During the analyses of competing reactions, it

was usually assumed that the most probable reaction channel was the one with the lowest energy barrier. However, only differences in energy larger than 40 kJ/mol, which is about twice the average error of the method [4], were considered as conclusive evidence of the domination of one reaction channel over the other. All quantum chemical calculations were carried out using the Gaussian 98 package of programs [12].

POLY(DIHYDROXYBIPHENYLISOPHTHALAMIDE).

It is well established [7] that, when heated, PHA converts to polybenzoxazole, which is an extremely thermally stable material. To a large degree, this explains the high fire resistance of PHA. However, the detailed mechanism of the decomposition reaction, which is shown in figure 1, is not known. To determine the mechanism, the potential energy surface of a model compound, hydroxyamide (HA), was analyzed as shown in figure 2. This compound represents a PHA fragment that undergoes the cyclodehydration reaction. The analysis led to the conclusion that this reaction is not a single-step process. Before HA cyclizes, it has to undergo a keto-enol rearrangement. Two possible mechanisms for this rearrangement are shown in figure 2. The direct transfer of a hydrogen atom (top diagram) has a substantial energy barrier. However, this barrier is reduced by almost a factor of 3 when an external hydroxyl group participates in the rearrangement (bottom diagram). Presumably, the hydroxyl group comes from an adjacent PHA chain (which was represented by vinyl alcohol in the calculations) or a water molecule, which is an expected contaminant.

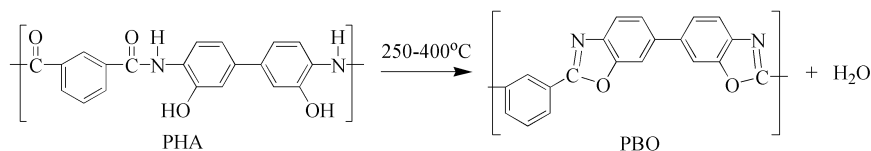


FIGURE 1. THERMAL DECOMPOSITION OF PHA

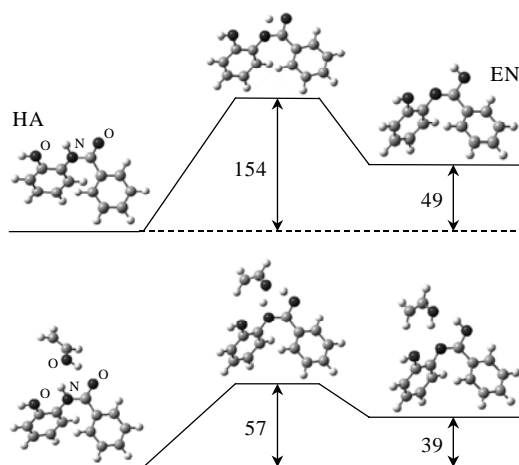


FIGURE 2. KETO-ENOL REARRANGEMENTS
(Energy values are in kJ/mol)

Two conformations of the enol (EN) compound, which is formed as a result of the keto-enol rearrangement, were found to be capable of cyclization. These conformations are depicted in figure 3. Transformations between EN conformers require between 30 and 70 kJ/mol and are omitted here. A detailed description of these transformations can be found in reference 3. According to the mechanisms presented in figure 3, the cyclization of EN may proceed through a single transition state (top diagram) or through a sequence of two transition states separated by an intermediate state (bottom diagram). The latter reaction path is much more energetically accessible and, thus, more probable. Regardless of whether or not an external hydroxyl group is involved in the keto-enol rearrangement, the total energy required for the cyclodehydration of HA is about 170 kJ/mol. This is significantly less than 320 kJ/mol that is required to break the backbone of PHA [3]. On this basis, it was concluded that the polymer should convert to polybenzobisoxazole before any fragmentation of the chains takes place, which is consistent with experimental observations.

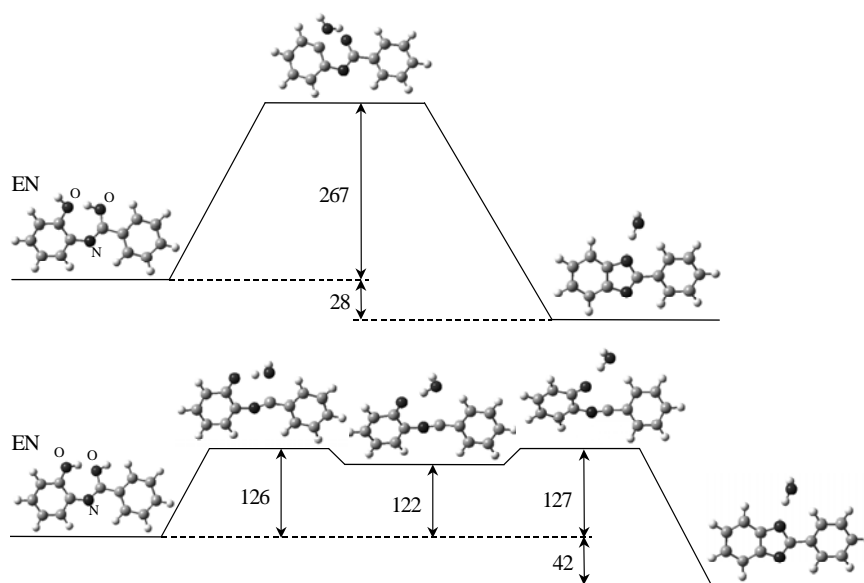


FIGURE 3. CYCLIZATIONS
(Energy values are in kJ/mol)

BISPHENOL C.

As shown in figure 4, hydrogen chloride, carbon dioxide, and char are among the major products of the thermal decomposition of BPC [8]. The unusually high char yield suggests that cyclization and cross-linking dominate the decomposition process. To determine the mechanism of the process, a number of reactions that could potentially lead to cyclization or cross-linking of the polymer was examined. The reaction paths for Cl_2 elimination, one-step HCl elimination, C-Cl bond dissociation, and Cl-atom shift were calculated. According to the calculations, the energy barriers of these reactions were 400, 380, 330, and 300 kJ/mol, respectively. The first two reactions were ruled out based on energetics. A detailed description of these reactions is given in reference 4. The last two reactions were found to be both energetically and mechanistically similar. The Cl-atom shift was identified as the key reaction that takes place at

the initial stages of the thermal decomposition. However, the possibility that the C-Cl bond dissociation also plays a major role in the decomposition process could not be ruled out.

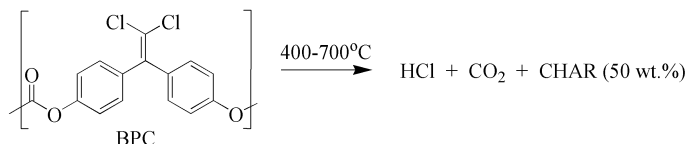


FIGURE 4. THERMAL DECOMPOSITION OF BPC

The Cl-atom shift is a reaction where a chlorine atom moves from its original position in BPC onto the adjacent phenyl ring. The reaction path, which was calculated using the β,β -dichlorostyrene model compound, is shown in figure 5. Once the shift occurs, the Cl atom can move freely around the ring structure. The fact that a Cl atom can bond with one as well as two phenyl rings [4] indicates that, in an environment with a high density of the rings, migration of the atom from one ring to another will also require little or no energy. Thus, the Cl-atom shift in BPC should be similar to the C-Cl bond dissociation, with the exception that the energy required for the former reaction is lower due to the stabilization provided by Cl-phenyl interactions.

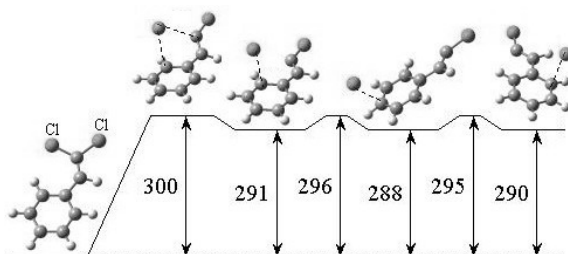


FIGURE 5. Cl-ATOM SHIFT
(Energy values are in kJ/mol)

Cl atoms migrating around and between the phenyl rings are likely to abstract hydrogens attached to the rings. According to the mechanisms shown in figure 6, these abstraction reactions have relatively low energy barriers. The reactions lead to cyclization and to the formation of phenyl radical sites. In the context of decomposing BPC structure, this results in internal cyclization of the polymer and the formation of highly reactive centers capable of establishing strong covalent cross-links between the chains. Chlorovinyl radical sites, which are formed as a result of the Cl-atom shifts, may also be involved in cross-linking. In addition, these radical sites may participate in phenyl-ring shifts followed by eliminations of the Cl atoms [4], which, in turn, lead to the formation of diphenylacetylene structural elements in the decomposing polymer. The cyclization and cross-linking reactions, which result in the formation of char, are expected to compete with the scissions of the O-C(O) backbone bonds (the weakest covalent bonds in BPC [4]), which result in fragmentation of the polymer chains and the subsequent elimination of CO₂.

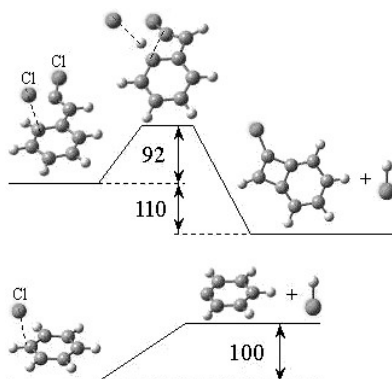


FIGURE 6. ABSTRACTIONS OF HYDROGEN ATOMS BY Cl ATOMS
(Energy values are in kJ/mol)

REACTIVE MOLECULAR DYNAMICS

The RMD method is based on conventional molecular dynamics, which makes use of analytical expressions (force field) that define the interactions between atoms. The atomic trajectories, obtained by numerical integration of the classical equations of motion, provide a time-resolved description of the system under study. The feature that distinguishes RMD from other force field-based implementations of molecular dynamics is that it is capable of modeling chemical reactions.

The current implementation of RMD, a detailed description of which is given in reference 6, uses a version of the consistent valence force field [13], which was modified and calibrated to accommodate some general features of reactive potential energy surfaces. In this force field, the energy of a molecular system is represented as a sum of contributions from covalent bonds (defined by Morse potentials), bond angles (including torsions), and nonbonded interactions. To model chemical transformations, the RMD employs the following algorithm: after every time step of molecular dynamics, fractional bond orders, which are defined as $1 - V/D$, where V/D is the ratio of the bond energy to the bond dissociation energy, are computed for every covalent bond. The bond orders are then compared to a predefined bond-dissociation criterion (BDC). If a fractional bond order is less than or equal to BDC, the bond is eliminated and the atoms that had been connected are labeled as chemically active (if the bond order is higher than BDC, no action is taken with respect to that bond). Next, a set of new bonds is generated, consisting of all possible covalent interactions between the chemically active atoms. The most energetically favorable subset of the new bonds that complies with the rules of atomic valence is selected. 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. This feature is used to describe chemical reactions that occur via so-called hypervalent transition states, such as abstraction or radical disproportionation 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 procedure described above, 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 $0.25RT$ (R is the ideal gas constant and T is the simulation temperature) of the dissociation energy. The BDC determines whether covalently bonded atoms are eligible to participate in chemical reactions. In the simulations described below, BDC was set to 0.8, which means that an atom was labeled as chemically active when at least one of its stretched covalent bonds reached the energy that was equal to or higher than 20% of the bond dissociation energy. The RMD 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 is to compute the reactive force field, while Discover 95 updates the molecular geometry based on the solution of the equations of motion.

The thermal decomposition of PIB has been studied experimentally by a number of investigators [14-16]. According to these studies, the mechanism of the decomposition can be summarized by the set of reactions shown in figure 7.

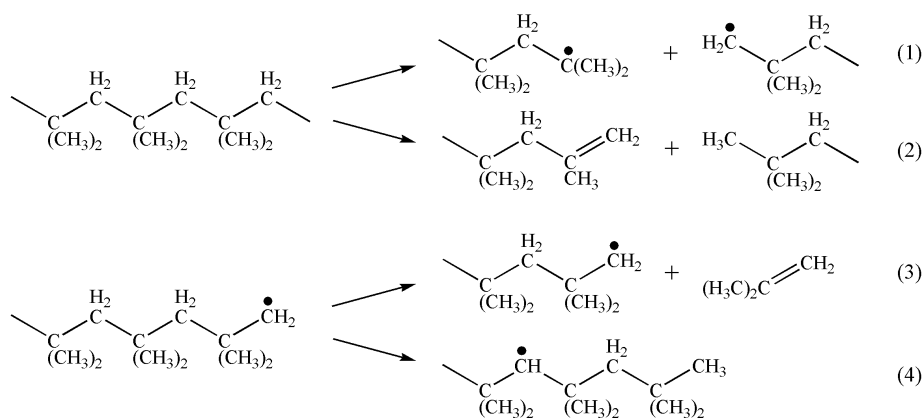


FIGURE 7. MECHANISM OF THE THERMAL DECOMPOSITION OF PIB

In all studies, homolytic scissions of the backbone and depolymerization reactions (reactions 1 and 3 in figure 7) are considered to be important. There are, however, notable disagreements between investigators regarding the roles and mechanisms of reactions involving transfer of a hydrogen atom (reactions 2 and 4 in figure 7).

Four single-chain models of PIB consisting of 4, 14, 50, and 150 isobutylene units were used in the RMD simulations of the decomposition process. Periodic boundary conditions were employed in the simulations involving the 14-, 50-, and 150-unit models to account for the condensed-phase environment. The 4-unit model, however, was treated as a single gas-phase molecule. Simulations were performed at a series of temperatures between 1300 and 1750 K.

^{*}Certain commercial equipment, instruments, materials, or companies are identified in this paper to adequately specify the procedure. This in no way implies endorsement or recommendation by the National Institute of Standards and Technology.

The lowest temperature was dictated by the necessity to observe reactive events within computationally feasible simulation times. The thermal motion was initiated by assigning each atom a velocity with Cartesian components chosen at random from a Maxwell-Boltzmann velocity distribution. The reactive dynamics were run for 5-100 ps (longer times were used at lower temperatures and with smaller models). To accumulate statistics on chemical reactions, between 11 and 70 RMD simulations were done for each model at every temperature.

A still frame from an RMD trajectory of the 150-unit model of PIB is shown in figure 8. According to the results of the simulations, homolytic backbone scission and subsequent depolymerization of the resulting radicals (reactions 1 and 3 in figure 7) are the dominant decomposition reactions for all models within the examined range of temperatures. The only hydrogen transfer reactions observed in the simulations were hydrogen abstractions involving small molecules (smaller than the dimer). Aside from occasional terminations of the depolymerization process, these reactions had little effect on the decomposition of the polymer chains.

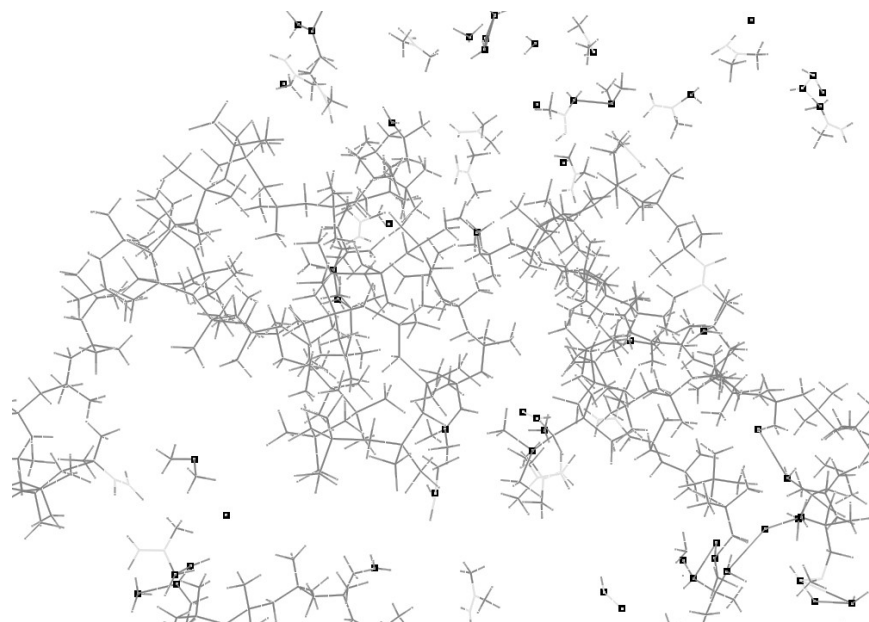


FIGURE 8. THE 150-UNIT MODEL OF PIB AFTER 10 ps OF REACTIVE DYNAMICS AT 1525 K
(The black dots are chemically active atoms.)

The times to the first backbone scission determined from the simulations were used to calculate the rate constants of the initiation reaction. The rate constants were normalized by the initial number of backbone bonds in the PIB models to provide a common basis for comparing the results from models having different chain lengths. Arrhenius fits of the temperature dependence of the rate constants revealed that the pre-exponential factors and activation energies decrease systematically with increasing size of the model. The Arrhenius parameters change from a pre-exponential factor of $2 \times 10^{17} \text{ s}^{-1}$ and an activation energy of 240 kJ/mol, obtained for the 4-unit model (gas-phase tetramer), to a pre-exponential factor of $1 \times 10^{15} \text{ s}^{-1}$ and an activation

energy of 170 kJ/mol, obtained for the 150-unit model. Based on the observation of these trends, it was concluded that the kinetics of the backbone scission reaction is affected by the density and by the degree of polymerization of the decomposing polymer. This means that the conventional approach to the kinetic modeling of polymer decomposition, in which the chain scission rate constants are assigned values obtained from the measurements performed on small gas-phase molecules, is not generally valid. This approach should be modified to account for the potential effects of the macromolecular environment on the rate of the scission reactions. For a complete description of the RMD simulations and comparison of the simulation results with experimental observations, see reference 6.

Each of the computational approaches discussed in this report has its own advantages and limitations. The quantum chemical approach is an effective tool for mapping complex chemical transformations that are localized on a small segment of a polymer structure. The information obtained from the quantum chemical calculations can be used in combination with statistical reaction rate theories [17] to determine rate constants of the model reactions. However, it is not clear whether the calculated rate constants would represent the kinetics of the corresponding reactions in the polymer melt because the presence of the surrounding molecular structure (the condensed-phase) is ignored in the calculations.

CONCLUDING REMARKS

The application of reactive molecular dynamics (RMD) makes it possible to capture the effects of the condensed-phase environment. Unlike the case of the quantum chemical approach, RMD simulations do not require a priori assumptions about reaction mechanisms. However, despite these advantages, RMD does have several drawbacks. Currently, the computationally accessible time scales of these calculations are several orders of magnitude shorter than what is needed to make direct comparisons with experimental measurements on burning polymers. Even more important is the issue of force field accuracy. For RMD to produce reliable quantitative results, the force field should be able to reproduce reactive potential energy surfaces with chemical accuracy (be accurate within about 5 kJ/mol). The development and validation of a force field that is capable of this level of accuracy, even for a small number of chemical elements, is a grand challenge. Further complications arise from the fact that RMD uses classical mechanics to simulate quantum mechanical systems. That is, there is no accounting for the discrete nature of molecular vibrations or tunneling. It is apparent that, to a large degree, RMD and the quantum chemical approach (combined with statistical reaction rate theories) are complementary. The development of methodologies that combine best features of both approaches are actively being pursued.

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