An Application of MALDI-MS and Reactive Molecular Dynamics in Determining the Mechanisms of Char-Formation During the Thermal and Oxidative Degradation of Polymers

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Introduction

The mechanisms by which polymers form carbonaceous chars as a result of thermal and oxidative degradation is an interesting scientific problem, which has important commercial (formation of carbon fibers and nanostructures) and public safety implications (materials flammability). In general, chars are thought to form from reactions involving polyene precursors, which in turn are produced by the abstraction and elimination of hydrogen atoms and functional groups from the polymer backbone. Many of these intermediates are amenable to standard metal cationization treatments and can, therefore, be monitored by MALDI mass spectrometry (MS).

In previous papers,[1,2] we have reported progress in using Reactive Molecular Dynamics (RMD) to model the thermal decomposition chemistries of polymers. In this technique, a reactive force field, which accounts for the dissociation and formation of covalent bonds, is employed in conjunction with standard methods for solving the classical equations of motion. It is computationally efficient compared to electronic structure calculations and, therefore, can be used to simulate chemical reactions in large molecular systems while still accounting for the effects of inter-molecular interactions in condensed phases. In this talk, we will report progress in using our RMD code (MD_REACT) in conjunction with MALDI-MS and FTIR analyses of pyrolysis residues to investigate mechanisms of char formation in vinyl and condensation polymers.

Theory of Reactive Molecular Dynamics

In its conventional formulation, molecular dynamics consists of solving the classical equations of motion for the time dependent positions (and velocities) of the atoms that comprise the system under investigation. The objective is usually to determine the time evolution of the molecular structure after it is subjected to a perturbation due to thermal motion and/or external forces. The perturbation is introduced in the form of a velocity distribution for the constituent atoms. The initial structures may be obtained from diffraction and spectroscopic data, from molecular calculations, or some combination of these sources of information. The classical equations of motion are given by

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

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

where q_i and p_i denote the coordinates and momenta of atoms and

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

is the Hamiltonian consisting of the sum of the kinetic and potential energies associated with the molecular motion. Typically, the potential energy, V, is represented by an analytical function of the form:

$$V = \sum^{nb_{onds}} V_{bond}(r_i) + \sum^{n_{angles}} V_{angle}(\theta_i) + \sum^{n_{torsions}} V_{torsion}(\varphi_i) + \sum^{n_{pairs}} V_{nonbond}(r_{ij}),$$

where the sums are over the covalent bonds, bond angles, torsion angles, and non-bonded pairs of atoms. The component terms correspond to the energies involved in distorting the structure from the equilibrium values of the internal coordinates by stretching, bending and twisting the bonds. These functions are collectively referred to as the "force field," even though the forces are actually obtained from the gradients of V. One of the most important attributes of a force field is that it provides a mechanism for describing the potential energy surface for a large molecular system from components that can be parameterized on the basis of experimental information and/or the results of quantum mechanical calculations on smaller, model compounds. This makes it possible, at least in principle, to obtain accurate representations of potential energy surfaces for nanoscale molecular structures, such as chars, which might otherwise be outside of the realm of computational chemistry.

During the past several years, we have made substantial progress in the development of force-field-based Reactive Molecular Dynamics as implemented in a computer program referred to as MD_REACT. The feature that distinguishes MD_REACT from other conventional implementations of molecular dynamics is that covalent bonds between atoms are allowed to break and form during the course of the simulation. 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 (S) is computed for every

$$S = \begin{cases} 1 & r \leq r_e \\ 1 - \dfrac{V_{bond}(r)}{D} & r > r_e \end{cases}$$

covalent bond in the system. Here r is the distance between bonded atoms and D is the bond dissociation energy. These bond orders are compared to a pre-defined criterion for bond-dissociation (*BDC*). If S 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 new set of potential bonds is generated, consisting of all possible covalent interactions between the chemically active atoms. 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 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. In other words, the 4 valence electrons are distributed over 5 bonds. This feature is introduced to describe chemical reactions that occur via so-called hypervalent transition states, such as atom transfer reactions. Once the bond analysis is complete and the structural information is updated, the next time step of molecular dynamics is executed.

Experimental

The MALDI-MS spectrum from a pyrolyzed sample of polyamide 6 (PA 6) is shown below. The MALDI was performed using the standard nitrogen laser with 2,5-dihydroxy benzoic acid (DHB) as a matrix and sodium trifluoroacetate to provide sodium cations. The decomposition products, which include cyclic and linear oligomers, have been identified on the basis of the observed mass to charge values and by FTIR spectroscopy[3]. Similar measurements will be made as a function of temperature for a series of polymers having a range of char yields in an effort to identify critical precursors and intermediates leading to the formation of carbonaceous chars. The experimental product distributions, obtained in this way, will be compared to the results of our RMD calculations.

REFERENCES

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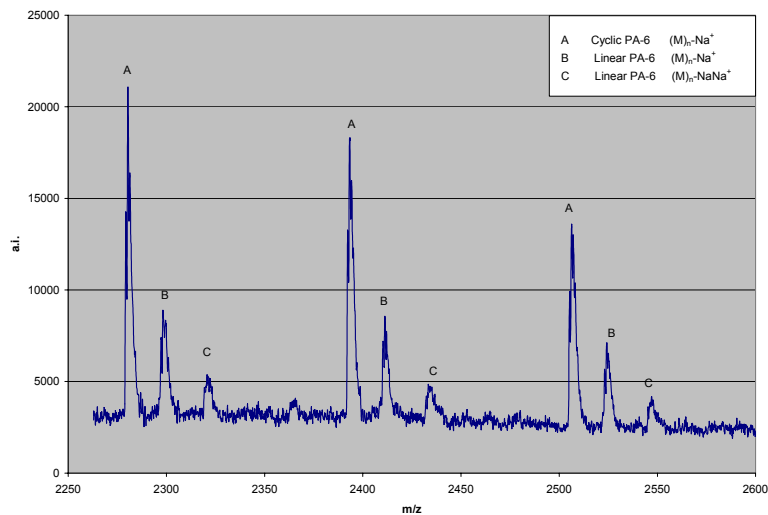
Figure 1. MALDI-MS spectrum of a pyrolized sample of PA 6.
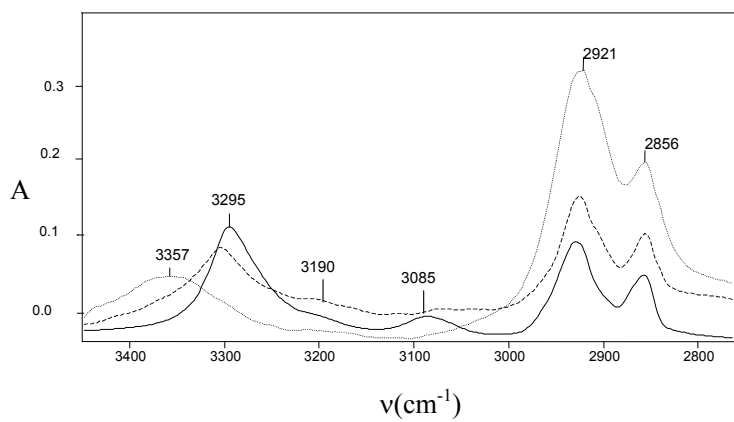
Figure 2. The spectra obtained from PA 6 just before ignition (dashed line) and after pyrolysis (dotted line) are compared to a spectrum measured at room temperature (solid line).