



# Modeling differential scanning calorimetry of thermally degrading thermoplastics



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## ABSTRACT

Differential scanning calorimetry (DSC) of thermally degrading thermoplastics is modeled using a discrete population balance equation (PBE). The PBE allows for species mole change due to pyrolysis and bubbling mass loss. Efficient solution is achieved by lumping non-volatile species into a single, notional “polymer” species. Thermodynamic properties are calculated by group additivity techniques, and empirical corrections are made to account for the changes in specific heat capacity and enthalpy upon mixing. Simulation results for high-density polyethylene (HDPE) are compared to literature data for DSC at heating rates of 5, 10, and 20 K/min. The model predicts peak energy absorption rates to within 4% at the lowest heating rate. The heat of decomposition was found to be within 17% of literature values at all three heating rates. The predicted pyrolysis gas species distribution agrees well with literature gas chromatography–mass spectrometry (GC–MS) data.

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## 1. Introduction

Mechanistic models of pyrolysis have the potential to improve the way polymers are formulated and processed. Specific applications include engineering less flammable materials, improving gasification reactors, and development of recycling systems. Unfortunately, the use of detailed models for engineering problems has been limited by computational cost and a lack of relevant validation data. In this article, both of these limitations are addressed by introducing an efficient model for predicting the outcome of differential scanning calorimetry (DSC) experiments based on molecular scale information.

Differential scanning calorimetry is a common tool for the thermal analysis of materials. A DSC apparatus heats a small sample (~10 mg) at a constant temperature ramp rate,  $\beta \equiv dT/dt$ . Thermal events (e.g., chemical reactions, phase changes, etc.) are quantified by the power needed to heat the sample at the prescribed  $\beta$  relative to the power needed to heat a reference cell being heated at the same rate. The resultant data is the heat input difference as a function of temperature,  $\Delta\dot{Q}(T)$ . Typical DSC applications include measuring glass transition temperatures, enthalpies of crystallization, and enthalpies of melting. DSC has also been used to quantify the enthalpy change associated with the thermal degradation of

polymers [1,2]. Thermally degrading polymers undergo endothermic chemical reactions and devolatilization. Since these processes are complex, detailed models could be particularly helpful for analyzing thermal degradation DSC.

Detailed models of DSC can be useful for calibration and validation of microscale models as well as prediction of material behavior at high temperatures. Because mechanistic models depend on well-defined physical properties, calibration with detailed models provides fundamental information that can be used in scenarios much different than the calibration experiment. It is often difficult to validate molecular scale and condensed phase material models due to experimental limitations. However, an accurate, mechanistic DSC model is a means for testing microscale theory against easily obtainable data. Finally, a material's performance in thermal degradation DSC can be a partial indicator of its engineering performance (e.g., flammability), and so a well-validated model can be used to inexpensively evaluate novel polymers.

In the next section, submodels for pyrolysis and devolatilization are presented for the case of linear thermoplastics. It is then shown how to formally reduce the dimensionality in order to increase simulation efficiency. Conservation of mass and energy equations are derived for DSC systems, and the thermal degradation submodels are incorporated into these conservation equations. In order to produce simulation results, material properties for polyethylene were modeled or collected from the literature. Finally, simulated DSC results are presented and compared to literature data.

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## 2. Thermal degradation model

In a macroscopic, non-porous polymeric system, thermal degradation is primarily non-oxidative. The presence of flaming combustion further reduces the degree of oxidative degradation by depriving the polymer surface of oxygen. Therefore, DSC experiments are typically performed in an inert atmosphere. Non-oxidative thermal degradation physics are dominated by pyrolysis and devolatilization. Pyrolysis is the chemical conversion of polymer chains to successively smaller molecules due to heating. Devolatilization is the mass transport of small molecules across the interface of the condensed phase to the gas phase. The effects of these two processes on the chemical composition of a sample can be described by a population balance equation (PBE) that includes appropriate submodels. A PBE is a transport equation for a population of particles distributed over some state space [3]. Particle state spaces are typically divided into external and internal coordinates. External coordinates refer to locations in physical space, and internal coordinates refer to properties of individual particles. Since the samples in DSC experiments are small, it is assumed that there are no significant temperature or concentration gradients so that the state space contains only internal coordinates.

Fully specifying the chemical composition of a thermoplastic requires quantifying the amounts of a very large ( $\sim 10^5$ ) number of species. For a linear homogeneous thermoplastic, the various species differ only in terms of their chain length. Once degradation begins, various families of polymer species evolve. However, for many materials such as polyethylene, it appears that the dominant pyrolysis mechanism preserves the linear chain nature of the species population [4]. It is therefore possible to describe the composition of such systems as a size-distributed population. In the following discussion, it is convenient to quantify the composition of the polymer system with a molar distribution function,  $n_i$  for  $1 \leq i \leq N$ , defined as the total number of moles of chains with carbon number  $i$ . The dynamics of this population are described by a discrete PBE of the form

$$\frac{dn_i}{dt} = K_i(\mathbf{n}, T) - L_i(\mathbf{n}, T), \quad i = 1, \dots, N \quad (1)$$

where  $\mathbf{n}$  is the  $N$ -dimensional vector formed by the species mole numbers  $n_i$  and the functions  $K_i$  and  $L_i$  account for changes due to pyrolysis (kinetics) and devolatilization (loss), respectively. The kinetic term must be mass conserving. That is, if  $L_i = 0$  for all  $i$ , then the total mass in the system cannot change. For linear homogeneous molecules, molecular weight is proportional to the carbon number and so conservation of mass requires that  $\sum_i iK_i = 0$ . Consequently, the time rate of change of mass in the system is

$$\frac{dm}{dt} = -M_0 \sum_i iL_i \quad (2)$$

where  $M_0$  is the molecular weight of a single chain unit. The mathematical forms of  $K_i$  and  $L_i$  depend upon the mechanisms of pyrolysis and loss. In the remainder of this section, models for these processes are presented, and a simplified solution procedure is proposed.

### 2.1. Pyrolysis model

A chemically consistent random scission pyrolysis mechanism will be assumed for the development of the kinetic term,  $K_i$ , in Eq. (1). Random scission mechanisms have been used in much of the literature of detailed pyrolysis modeling [5–7]. Furthermore, evolved gas analysis indicates that the pyrolysis products of polyethylene are similar to what would be produced by pure random scission [4]. Previous random scission models have been chemically inconsistent in assuming that chain scission only changes the size of molecules in the distribution. This is not strictly

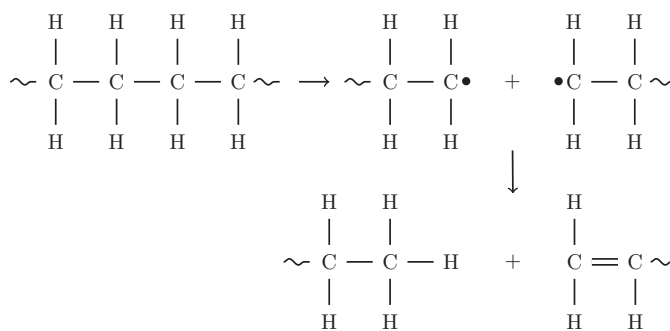


Fig. 1. Chemically consistent random scission pyrolysis mechanism consisting of random initiation and disproportionation.

correct since the breaking of a backbone bond results in two radical molecules with significantly different reactivities. To avoid introducing another population of radical chains, many authors have neglected the chemical composition of the chains [5,6,8]. This approach is inadequate for detailed DSC modeling since the thermodynamic properties of the system depend upon its precise chemical composition.

A chemically consistent version of random scission is possible for a population of linear  $\alpha$ -olefins. It is assumed that the pyrolysis mechanism is random backbone bond scission immediately followed by disproportionation to convert the radicals back to olefins. The two reaction steps are shown in Fig. 1. These reactions may be lumped together such that

$$P_i \xrightarrow{k} P_j + P_{i-j}, \quad i = 4, \dots, N, \quad j = 2, \dots, i-2 \quad (3)$$

where  $P_i$  is a label for the olefin with  $i$  carbon atoms and  $k$  is the rate constant. The scission is random in the sense that  $k$  is independent of both  $i$  and  $j$ . This mechanism does not fully capture the chemistry of polyethylene pyrolysis, but it will be used in the following model since the focus of this paper is on the development of a mechanistic DSC model rather than a polyethylene pyrolysis mechanism. The modeling framework is amenable to more sophisticated pyrolysis mechanisms. In fact, as was discussed in the introduction, the mechanistic DSC model can be used for validating different proposed mechanisms against easily obtainable DSC data.

The pyrolysis mechanism of Eq. (3) implies a species  $i$  generation rate of

$$K_i = \begin{cases} k[-(i-3)n_i + 2 \sum_{j=i+2}^N n_j], & i \geq 3 \\ 2k \sum_{j=4}^N n_j, & i = 2 \end{cases} \quad (4)$$

The two cases are necessary since ethene,  $i=2$ , is assumed to be stable. For larger molecules, species are lost due to scission at a rate proportional to the number of bonds available for breakage,  $i-3$ . It can be shown that Eq. (4) is mass conserving.

### 2.2. Multicomponent bubbling mass loss

It is observed that thermally degrading polyethylene boils vigorously at temperatures greater than around  $400^\circ\text{C}$  [9,10]. As the sample is heated, volatiles are formed by pyrolysis. When the concentration of these volatiles is sufficiently large, the melt becomes supersaturated and bubbles nucleate. Volatiles diffuse to the bubble surfaces resulting in bubble growth. Eventually, buoyancy forces drive the bubbles out of the sample. This loss process favors smaller molecules that diffuse and exit the melt phase (devolatilize) at faster rates than large molecules.

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