

A Molecular Dynamics Model of Materials Flammability *

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Abstract

An expression for the global rate of mass-loss from polypropylene, as a function of temperature, was derived from a simple kinetic model using rate constants for the random scission initiation and β -scission propagation/termination reactions obtained from molecular dynamics (MD). The computed values for the activation energy and pre-exponential factor are compared with experimental values obtained from thermogravimetric analysis. The MD simulations were performed with a computer code (MD_REACT), which was developed in this laboratory to provide researchers with a computational tool for the development of new fire resistant materials.

Introduction

Recent work conducted in this laboratory has demonstrated the application of molecular modeling techniques to the design of flame retardants and fire resistant materials [Nyden et al.,1992-1997]This effort has culminated in the development of a novel computer program, hereafter called MD_REACT, that simulates the thermal degradation of polymers. The basis of this model is molecular dynamics (MD), which consists of solving Newton's equations of motion for each of the $3N$ degrees of freedom associated with the model polymer. The feature that distinguishes MD_REACT from other MD codes is that it allows for the formation of new bonds from free radical fragments that are generated when bonds in the polymer break and, thereby, accounts for the chemical reactions that play a major role in the thermal degradation process [Cullis and Hirschler,1981].

The motivation behind the development of MD_REACT was to create a versatile model that could be used to study thermal degradation at a molecular level in a wide range of polymers. The strategy employed to accomplish this objective was to interface our program for performing reactive dynamics on simple vinyl polymers [Nyden et al.,1992] with Discover 95 #, a commercially available molecular dynamics code offered by Molecular Simulations (MSI). The interface between the programs is established using an inter-process communication protocol (IPC) to pass coordinates, forces and connectivity information between MD_REACT, which computes the reactive forcefield, and Discover 95, which updates the molecular structure on the basis of the solution to the equations of motion.

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The purpose of this paper is to report the results of a validation study in which computer simulations, performed with MD_REACT, were used to derive an expression for the global rate of mass-loss from the thermal degradation of polypropylene as a function of temperature. The computed values for the activation energy and pre-exponential factor are compared to experimental values obtained from thermogravimetric analyses (TGA).

Theory

Molecular dynamics involves solving Hamilton's equations of motion, which are summarized in Eq.(1).

$$\begin{aligned}\frac{\partial H}{\partial p_i} &= \frac{dq_i}{dt} \\ \frac{\partial H}{\partial q_i} &= -\frac{dp_i}{dt}.\end{aligned}\tag{1}$$

The Hamiltonian,

$$H = \sum_i^{3N} \frac{p_i^2}{2m_i} + V(q_1, q_2, \dots, q_{3N}),\tag{2}$$

consists of the kinetic and potential energies associated with the thermal motion of the N atoms that make-up the model polymer. The central valence forcefield (CVFF) [Dauber-Osguthorpe, 1988], which is summarized in Eqs.(3) - (8), is used to represent the potential energy interactions between the atoms in MD_REACT.

$$\begin{aligned}V(q_1, q_2, \dots, q_{3N}) &= \sum_{ij}^{nbonds} V_b(r_{ij}) \\ &+ \sum_{ijk}^{nangles} V_a(q_{ijk}) \\ &+ \sum_{ijkl}^{ntorsions} V_t(\mathbf{f}_{ijkl}) + \sum_{ij}^{npairs} V_{nb}(r_{ij})\end{aligned}\tag{3}$$

What follows is a brief description of the components of the CVFF forcefield and how they have been modified to account for the chemical reactions represented in MD_REACT.

The energy required to stretch the covalent bonds is represented by the Morse potential

$$V_b = D[1 - \exp(-\alpha(r - r_e))]^2 - D, \quad (4)$$

where r is the distance between bonded atoms i and j , r_e is the equilibrium bond length,

$$k_b = \left(\frac{\partial^2 V_b}{\partial r^2} \right)_{r=r_e} \quad (5)$$

is the force constant, and $\alpha = [k_b/(2D)]^{1/2}$. The bond dissociation energies (D) have, in many cases, been altered from their original CVFF values in an attempt to provide a better description of the thermal decomposition reactions summarized in Figure 1. The new values were obtained from a variety of methods including experimental data and G2 calculations [Curtis et al., 1991] performed on monomers and other model compounds with representative bonds.

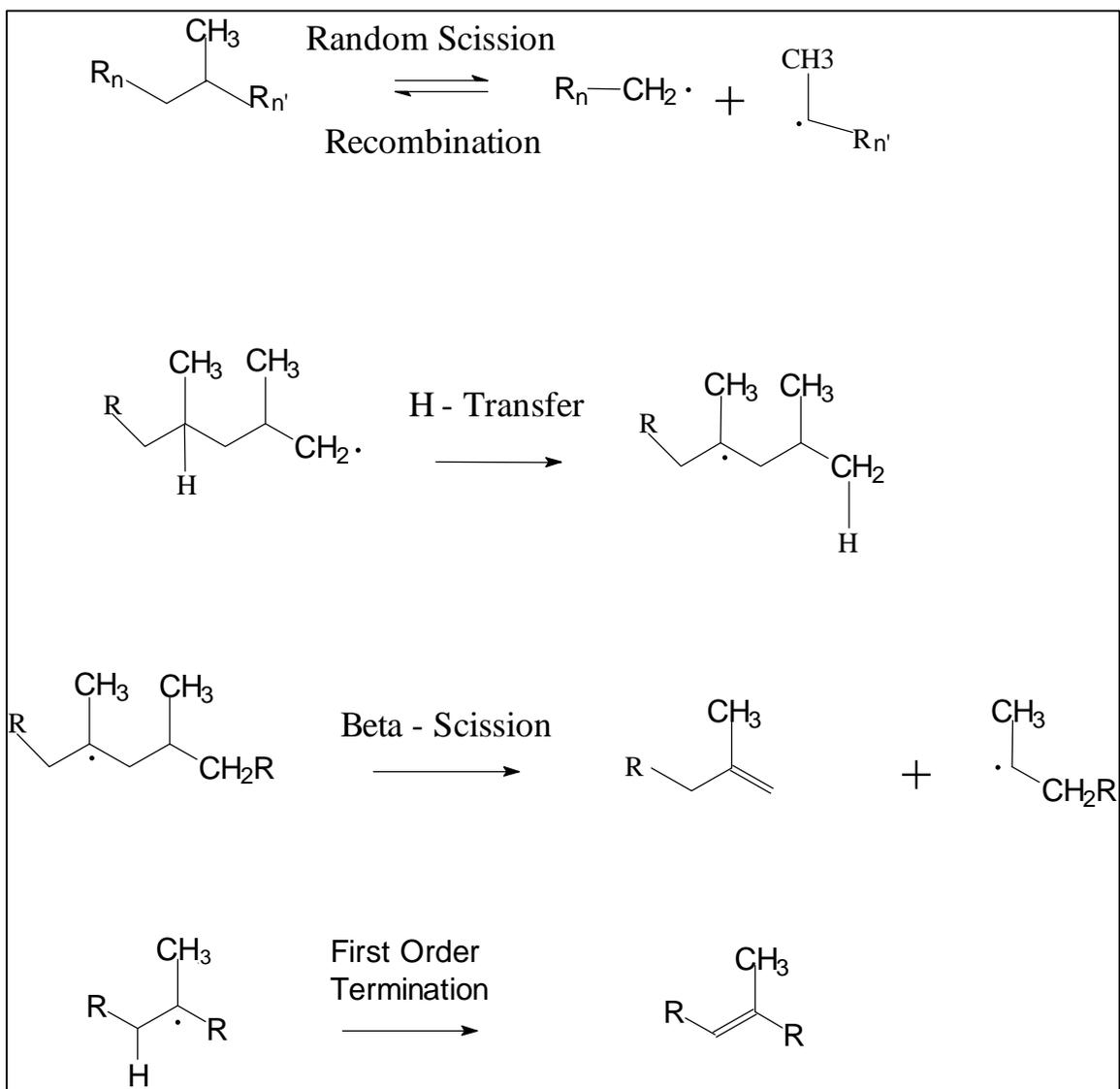


Figure 1. Major Reaction Channels in the Thermal Degradation of Polypropylene.

The potential energy for bond bending is represented by

$$V_a = S(ij)S(jk)k_\theta(\theta - \theta_e)^2, \quad (6)$$

where θ denotes the angle determined from the dot product of the normalized bond vectors between three adjacent atoms (i, j and k) and the $S(ij)$ and $S(jk)$ are switching functions, which are defined below. The force constant, k_θ , is defined, in analogous fashion to k_b , as the second derivative of the potential energy evaluated at the equilibrium bond angle (θ_e).

Rotations about covalent bonds are restricted by the torsional potential

$$V_t = S(ij)S(jk)S(kl)k_\tau[1 + \cos(n\phi - \phi_e)]. \quad (7)$$

The dihedral angle, ϕ , is defined by the three bond vectors between four adjacent atoms (i,j,k and l). The parameters, k_τ , n , and ϕ_e determine the height, multiplicity, and position of the barrier to internal rotation.

The nonbond potential energy consists of two terms corresponding to the Van der Waals and electrostatic interactions. These are represented by

$$V_{nb} = \mathbf{e} \left[\left(\frac{r^*}{r} \right)^{12} - 2 \left(\frac{r^*}{r} \right)^6 \right] + \frac{q_i q_j}{r}, \quad (8)$$

where q_i and q_j are the partial charges on nonbonded atoms separated by a distance, r . The parameters r^* and ϵ in the Van der Waals term determine the position of the minimum and the depth of the potential well, respectively.

The switching functions, that are defined in Eq.(9), are used to turn the bending and twisting forces on and off as the corresponding bonds are formed and broken.

$$S(ij) = \begin{cases} 1 & r \leq r_e \\ \frac{-V_b(ij)}{D(ij)} & r > r_e \end{cases} \quad (9)$$

It is the presence of these terms that distinguishes the reactive forcefield used in MD_REACT from the CVFF and other forcefields used in more conventional MD codes. The ratio of the bond energy to its dissociation energy, which appears on the right hand side of Eq.(9), corresponds to a fractional bond order. The use of switching functions based on fractional bond orders was implemented to facilitate the description of hypervalent transition states for hydrogen transfer and similar reactions that play a major role in the thermal degradation process (*vide infra*). The energy and forces calculated in Discover 95 do not include the contributions due to the presence of these switching functions. These corrections are computed in MD_REACT and passed to Discover 95 in the form of restraints on the energy and forces.

Bond dissociation and formation are simulated in MD_REACT by the following algorithm. A list of the free radical sites, that 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 covalently bonded atoms become free radicals when their potential energy comes within RT (or a small multiple of RT which can be specified in the input file) of the bond dissociation energy, where R is the gas constant. 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 imposed by the rules of atomic valence. That is, new bonds are disallowed when the sum of the bond orders exceed the maximum valence of the participating atoms.

In order to make meaningful comparisons, the disparity between the time scales associated with laboratory measurements, such as the cone calorimeter (seconds) and those accessible to atomistic simulations (picoseconds) must be overcome. Our approach to this problem is to substitute the rate constants obtained from the MD simulations into a simple kinetic model for the rate of mass-loss from the degrading polymer. We adapted a global rate expression derived by Boyd [Boyd, 1970] for this purpose, which is summarized in Eq.(10).

$$\frac{1}{m(t)} \frac{dm(t)}{dt} = -(2k_i(T) + [R]k_t(T))Z(T) \quad (10)$$

In this equation, $m(t)$ denotes the mass of the residual polymer at time, t , $k_i(T)$ is the rate constant for the random scission initiation reaction, and $k_t(T)$ is the rate constant for chain transfer scission. In the latter case, a \dagger -scission occurs on a polymer after it transfers a hydrogen atom to a free radical polymer fragment (frpf). The steady-state concentration of frpfs, $[R]$, which is assumed to be constant throughout the data collection process, is given by Eq.(11)

$$[R] = \frac{2k_i(T)d_0}{k_t(T)m_0}, \quad (11)$$

where $k_t(T)$ is the rate constant for termination, d_0 is the density of the polymer sample and m_0 is the molecular weight of the repeat unit. The zip-length,

$$Z(T) = \frac{k_p(T)}{(k_t(T) + k_l(T) \frac{d_0}{m_0})}, \quad (12)$$

is the number of volatile fragments (including, but not restricted to, monomers) produced before the frpf is terminated (*i.e.* converted back to a stable, nonvolatile molecule) either by the transfer of a hydrogen from a neighboring polymer chain or by the dissociation of a hydrogen or methyl group from the β -bond. In principle, the value of $Z(T)$ cannot exceed the average degree of polymerization, n . Although this limit is approached in some polymers, such as poly(methyl methacrylate), in the case of polypropylene, $Z(T)$ would be expected to be much less than n over the full temperature range that prevails in fire environments. Indeed, the thermal degradation of polypropylene appears to be dominated by chain transfer scission reactions (*vide infra*), which transfer the site of the radical and, thereby, the site of β -scission propagation, from one chain to

the next. The effect of this process on the rate of mass-loss is accounted for by the presence of the term, $[R]k_t(T)Z(T)$ in Eq.(10).

Due to the assumptions made in the derivation of this model, the range of applicability is limited to cases where end group initiation and second-order (inter-molecular) termination reactions are unimportant. The first condition is satisfied by virtue of the symmetric nature of the molecular models used in the simulations. Of course, some care must be exercised in comparing these results to experimental values, which may very well be influenced by the presence of end groups in the actual polymer. The extent to which the restriction to first order (intra-molecular) termination is satisfied in the thermal degradation of polypropylene is discussed below and will be examined further in subsequent investigations.

The computer simulations, which indicate that the degradation process is initiated by random scission of the C-C bonds and propagated by β -scission of the resulting free radical fragments, are consistent with the model summarized in Eq.(10). However, the simulations indicate that a distribution of small volatile molecules, as opposed to just monomers, is formed as the result of hydrogen transfer reactions, which occur in the interval between the β -scissions. The effect of these reactions is to move the free radical sites from the chain ends, where they were created by β -scissions of the backbone C-C bonds, to interior carbon atoms. This does not alter the form of the rate expression as long as the rate of hydrogen transfer is fast compared to propagation and the rate constant for random scission is normalized appropriately by dividing it by the number of repeat units, as determined from the average size of the volatile fragments (*vide infra*). The chain reaction is terminated by β -scissions of C-CH₃ and C-H bonds (intra-molecular) leading to the formation of a double bond in the polymer chain or by recombination with another free radical fragment (inter-molecular). These reactions are depicted in Figure 1.

The disparity in the time scales corresponding to the initiation reactions, which have activation barriers on the order of 320 kJ/mol or more, and the propagation and termination reactions, which have activation barriers of 160 kJ/mol or less, is resolved by performing independent simulations at temperatures appropriate for each of these processes. Thus, a typical computer experiment involves at least two sets of simulations. An artificially high temperature (typically, > 2000 K) is used in the first series of simulations for the purpose of generating a sufficient population of frpfs to initiate the propagation/termination reactions, which constitute the second stage of the computer experiment. These simulations can be performed at lower temperatures because of the relatively small activation energies associated with β -scission, which is the dominant mechanism in the propagation and first order termination reactions. The global rate of mass-loss at thermal degradation temperatures, T_d , may then be obtained from Eq.(10) by extrapolation of the temperature dependent rate constants computed using data collected in this sequence of MD simulations.

The reactions, which are the focus investigation, also occur in small gas phase molecules that can be studied in detail. On the basis of these investigations, it is known that they proceed via the unimolecular mechanism summarized in Eq.(13).



The asterisk is used to indicate that the molecule of interest is thermally excited by collisions with other molecules (M). Once excited, the molecule can either be deactivated by another collision, or undergo unimolecular decomposition to products (P). When the frequency of collision is high, the rate of deactivation would be expected to be much greater than the rate of unimolecular decomposition. In mathematical terms, we have $k_{de}[M][B^*] \gg k_{uni}[B^*]$, which defines the high pressure limit. The corresponding rate constant is given by

$$k_{\infty}(T) = \int_{E_0}^{\infty} P(E, T) k_{uni}(E) dE. \quad (14)$$

The function, $P(E, T)$, gives the probability that a molecule, which is in equilibrium with its surroundings at temperature T , will have an energy, E . Thus, the experimental high pressure rate constant corresponds to the microcanonical ensemble average of the energy dependent rate constant, $k_{uni}(E)$. According to the theory of unimolecular reactions [Benson, 1960], the result of the integration indicated in Eq.(14) is

$$k_{\infty}(T) = \nu^* \exp\left(\frac{S^{\#}}{R}\right) \exp\left(-\frac{E_0}{RT}\right), \quad (15)$$

where, ν^* represents an average of the vibrational frequencies of the transition state, $S^{\#}$ is the activation entropy corresponding to the difference in the entropy of the reactant and transition state, and E_0 is the minimum or critical energy required for the unimolecular reaction. A comparison of Eq.(15) with the Arrhenius equation leads to the identification of $\nu^* \exp(S^{\#}/R)$ and E_0 with the experimentally determined pre-exponential factor (A) and activation energy (E_a), respectively.

The energy dependent rate constant for a unimolecular reaction can be computed on the basis of MD simulations from Eq.(16)

$$k_{uni}(E) = \frac{N_{rxn}}{\Delta t}, \quad (16)$$

where N_{rxn} is the number of reactions observed in a MD simulation performed at a constant energy, E , during the time interval, Δt . In the case of polymers, the number of degrees of freedom is large so that the average thermal energy, $+E$, is much greater than E_0 and all of the polymers have sufficient energy to react. Furthermore, the fluctuations from $+E$, are negligible

(again because each polymer chain has so many degrees of freedom) which implies that $P(E,T)$ behaves like a delta function at $E = +E_0$. Thus, from Eqs. (14) and (15) we obtain

$$\lim_{N \rightarrow \infty} k_{\infty}(T) = k_{uni}(\langle E \rangle) = \mathbf{n}^* \exp\left(\frac{S^{\#}}{R}\right) \exp\left(-\frac{E_0}{RT}\right), \quad (17)$$

so that the temperature dependent rate constants for the unimolecular reactions involved in the thermal degradation of polymers can be obtained directly from Eq.(16) without performing the integration indicated in Eq.(14), which is necessary in smaller molecules.

The result given in Eq.(17) is not unexpected. It is a simple consequence of the fact that a polymer has a well-defined temperature because it is made up of a large number of fragments with individual energies that constitute a representative sampling from the Boltzmann distribution. That is, each polymer may be viewed as an ensemble. Since the collisions that transfer energy between modes are largely intra-molecular events, it may be argued that the mechanism for these reactions more closely approaches unimolecularity in polymers than it does in small gas phase molecules, where the activation reactions are actually bimolecular. In principle, this analysis implies that only a single MD simulation is needed to evaluate the unimolecular rate constants for a polymer reaction at the specified temperature. In practice, however, many simulations are needed to obtain reliable averages due to the statistical nature of

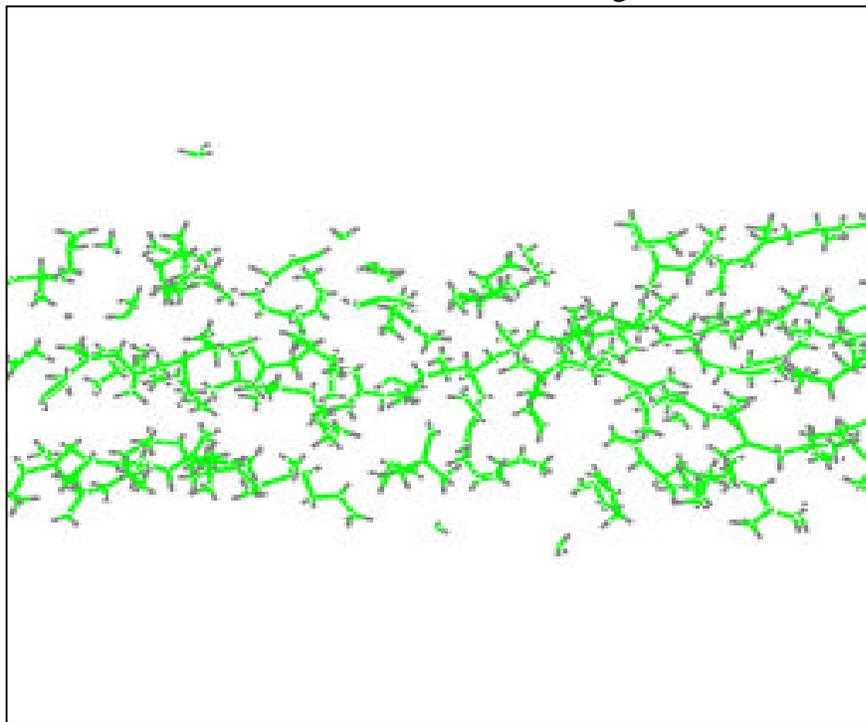


Figure 2. Still frame from an MD simulation of the thermal degradation of a model polypropylene consisting of 6 polymer chains, each with 21 monomers.

the interaction between vibrational modes. The rate constants corresponding to the temperature range that is appropriate for polymer degradation ($T_d = 600 - 1000$ K) may be estimated by extrapolation of Eq.(15) using kinetic parameters determined from a small number of MD simulations performed at high temperatures, where the rate constants are large and the simulation times are correspondingly short.

Computer Experiments

A series of computer experiments were performed to determine the temperature dependent rate constants in Eq.(10) for polypropylene. Constant temperature simulations were carried out at $T = 2250$ K, 2500 K, 2750 K and 3000 K, to evaluate the rates of random scission initiation, and at $T = 1500$ K, 1750 K and 2000 K, for the rates of β -scission propagation and termination. The model polymer used in these simulations consisted of 6 chains of isotactic polypropylene each containing 21 monomers. A still frame taken from a computer animation of a representative simulation is reproduced in Figure 2. The propagation/termination reactions were initiated from a single chain (also consisting of 21 propylene monomers) with a free radical site on one of the ends. In fact, two types of free radical polymer fragments (frpfs), a primary radical ending with a $-\text{CH}_2\bullet$ group and a secondary radical with a $-(\text{CH}_3)\text{CH}\bullet$ end group, are produced in a random scission reaction. Independent simulations of the propagation/termination reactions were initiated from each type of frpf in an effort to determine whether there is a difference in their relative reactivities. A fragment with a $-\text{CH}_2\bullet$ end group is

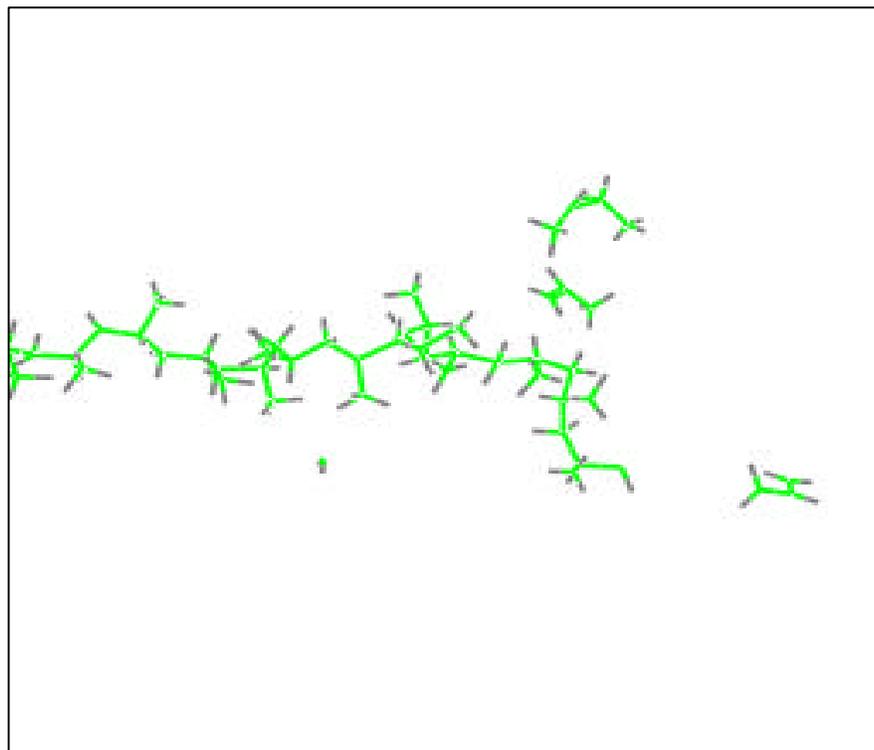


Figure 3. Single chain model of polypropylene undergoing successive β -scission reactions.

shown undergoing successive \dagger -scission reactions in Figure 3.

The temperature dependent rate constants for the random scission, propagation and termination reactions were determined from Eqs.(16) and (17), with $E = +E_a = (3N-6)/RT$. The corresponding uncertainties were estimated by propagation of the standard errors in the reaction times. The kinetic constants (E_a and A) for each of these reactions were determined from Arrhenius plots. The uncertainties in these values were estimated from the standard deviations in the slope and intercept of the linear regression lines. The zip-lengths were obtained from single molecule simulations, thereby ignoring the contribution from second order termination reactions; which was done to make the calculations more computationally tractable.

Results and Discussion

The temperature dependent rate constants for the random scission reactions, that are reported in Table 1, were computed from the mean reaction times obtained from a series of 9 independent simulations performed at each temperature. The values were normalized by

Table 1. Rate Constants for the Random Scission Reactions

$T (K)$	$k(T) \times 10^{-9} s^{-1}$
3000	3.0 0.5
2750	1.2 0.4
2500	0.3 0.1
2250	0.04 ± 0.01

dividing by the number of monomers in the chain in accordance with the convention used by Boyd. A small error was introduced as a consequence of this procedure because the average size of the volatile fragments that were produced in the simulations was slightly larger than a monomer (*vide supra*).

The kinetic constants, derived from the Arrhenius plot of this data, are $E_a = 323 \pm 25$ kJ/mol and $A = 2.6 \times 10^{15} s^{-1}$. These values are in line with experimental values for bond scission reactions in small gas phase molecules [Tsang and Kiefer, 1995]. The activation energy is comparable to the bond dissociation energy. Indeed, the value used in the forcefield was 322 kJ/mol. The large pre-exponential factor may be attributed to the increase in entropy associated with the free rotation around the dissociating bond [Benson,1960].

The simulations of the propagation/termination reactions were initiated from single chain frpfs and stopped shortly after a termination reaction occurred. Three modes of termination were observed: intramolecular cyclization, and \dagger -scission of either a C-H, or C-CH₃ bond. The occurrence of the latter two reactions was indicated by the appearance of a double bond (usually, but not always, at the end of the chain), whereas the former reactions were indicated by the presence of a cyclic moiety in the polymer chain. The zip-lengths, $Z(T)$, were determined as the average number of propagation reactions, $N_{rxn}(T)$, observed in the time required for a termination reaction, $\ast t_{avg}$. The values of $Z(T)$, $N_{rxn}(T)$ and $\ast t_{avg}$ obtained from simulations initiated from both primary and secondary frpfs, are listed in Table 2. No distinction was made

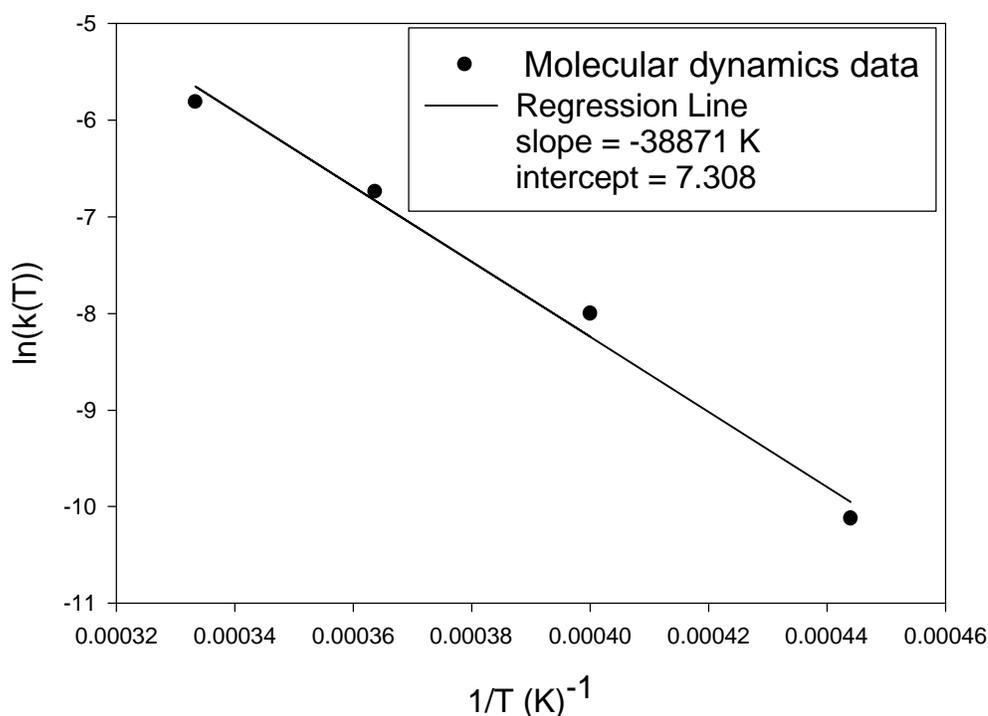


Figure 4. Arrhenius plot of the rate constants for the random scission reactions.

between the three modes of termination, alluded to above, in calculating these quantities. The uncertainties reported in this table are the standard errors of the data obtained in the 7 simulations performed at each of the specified temperatures. The primary radicals were found to be more reactive, in the sense that they produced more volatile fragments, than the secondary radicals. The source of the difference in reactivity was that the primary radicals were usually terminated by the \dagger -scission of a C-CH₃ bond, whereas the most common mode of termination for the secondary radicals was \dagger -scission of a C-H bond (see Figure 1), which occurred more frequently at the higher temperatures used in these simulations. This data was used to compute rate constants for the propagation and termination reactions, which are reported in Table 3 and plotted in Arrhenius form in Figures 5 and 6.

Table 2. Zip-Lengths and Termination Times

T(K)	Z(T)	*t _{avg} x 10 ⁻¹² s
	-CH ₂ • End Group	
2000	3.6 1.3	58 30
1750	3.5 1.0	83 35
1500	2.0 1.1	125 72
	-(CH ₃)CH• End Group	
2000	0.1 0.1	7 2
1750	0.4 0.2	18 4
1500	2.0 0.5	156 41

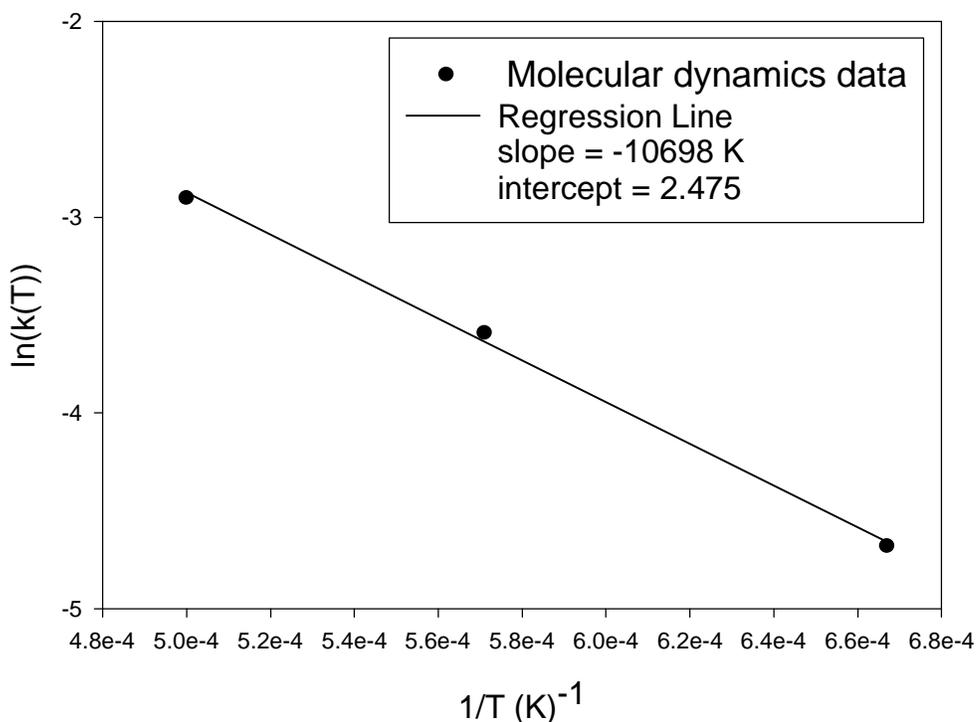


Figure 5. Arrhenius plot of the rate constants for the propagation reactions.

Table 3. Rate constants for the Propagation and Termination Reactions

T(K)	k(T) x 10 ⁻⁹ s ⁻¹	
Propagation (†-scission of a backbone C-C bond)		
2000	55	12
1750	28	7
1500	9	1
Termination (†-scission of a C-H bond)		
2000	153	56
1750	57	12
1500	6	2

The kinetic constants for the β -scission propagation reactions are $E_a = 89 \pm 4$ kJ/mol and $A = 1.2 \times 10^{13} \text{ s}^{-1}$. This activation energy is noticeably different from the value obtained in a

previous study of the rate of β -scission in pentyl radical, where the kinetic constants were reported as $E_a = 113 \pm 17$ kJ/mol and $A = 1.7 \times 10^{13} \text{ s}^{-1}$ [Nyden, 1999]. This difference was anticipated since the $R(\text{CH}_3)\text{CH}-\text{CH}_2\text{R}$ bonds in polypropylene free radicals are weaker than the $\text{RCH}_2-\text{CH}_2\text{R}$ bonds in pentyl radical.

The model described by Eq.(10) can be simplified further by assuming that the rate of termination by intermolecular hydrogen transfer is much greater than the rate of termination by the dissociation of a hydrogen atom or methyl group from the β -bond. The justification for this assumption is that the maximum rate of mass-loss that can occur if the chains terminate prior to undergoing intermolecular hydrogen transfer, in which case only 2 frpfs are created per random scission, is

$$\frac{1}{m(t)} \frac{dm(t)}{dt} = -2nk_i(T). \quad (18)$$

The rate of mass-loss obtained from this equation, after substituting reasonable values for the thermal degradation temperature ($T_d = 673$ K) and average degree of polymerization ($n \sim 10^4$), is much too slow to account for the experimental data on polypropylene [Madorsky, 1964]. In contrast, the assumption that $k_t(T)d_0/m_0 \gg k_i(T)$ leads to

$$Z(T) \approx \frac{k_p(T)m_0}{k_t(T)d_0}. \quad (19)$$

Substituting Eqs.(11) and (19) into Eq.(10) gives

$$\frac{1}{m(t)} \frac{dm(t)}{dt} = -2k_i(T) \left[Z(T) + \frac{k_p(T)}{k_t(T)} \right], \quad (20)$$

which, for short zip-lengths, reduces to

$$\frac{1}{m(t)} \frac{dm(t)}{dt} = -2k_i(T) \frac{k_p(T)}{k_t(T)}. \quad (21)$$

The right hand side of Eq.(21) is the fraction of the polymer sample, as determined by the ratio of the number of volatile fragments produced in the propagation reactions to the total number of repeat units, that is volatilized in the time span of a random scission reaction. Although the ratio of k_p to k_t is analogous to zip-length, it can attain values far in excess of the average degree of polymerization because it corresponds to the volatile fragments produced from many generations of frpfs that are spawned, via hydrogen transfer reactions, from parent frpfs created in a single random scission event.

The most common modes of termination observed in the computer simulations were β -scission of $\text{C}-\text{CH}_3$ and $\text{C}-\text{H}$ bonds. Cyclization reactions, whereby a radical site reacts with a carbon on the same chain, were observed less frequently. It is well known that the relative

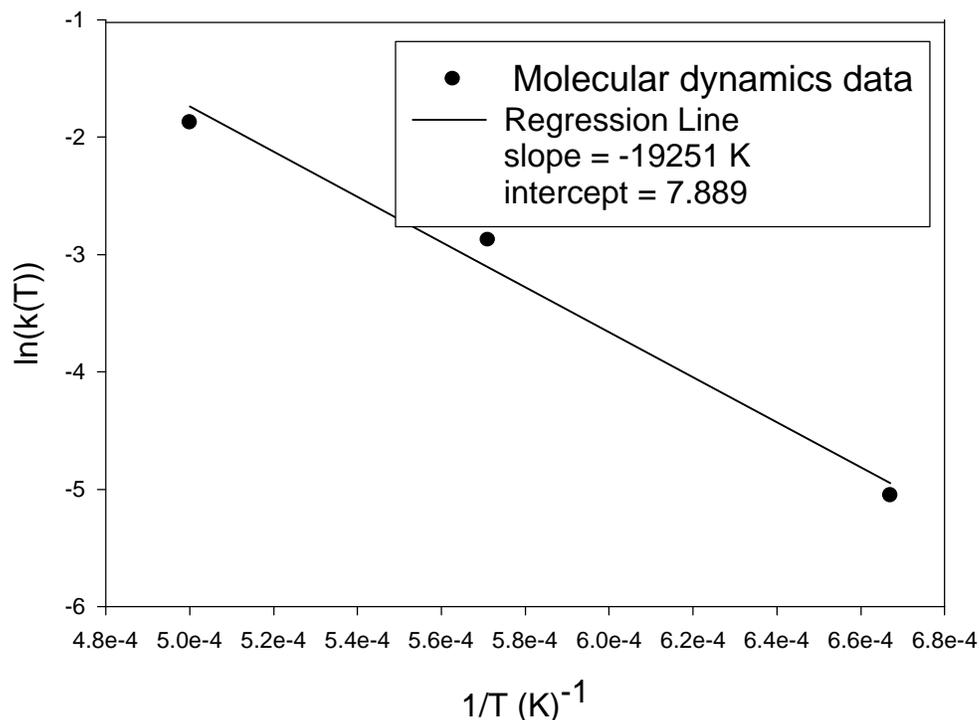


Figure 6. Arrhenius plot of the rate constants for the termination reactions.

stabilities of radicals follow the trend: primary < secondary < tertiary [Solomons, 1976]. This suggests that the distribution of frpfs will be skewed in favor of secondary and tertiary radicals, which are formed when a hydrogen is transferred from a methine to a methylene carbon as illustrated in Figure 1. The tertiary (or secondary, if the free radical site is on a chain end) radicals which result can be terminated by β -scissions of C-H bonds, but not by the dissociation of a methyl group, which is in the ρ position relative to the location of the free radical. On this basis, it was concluded that the former reaction should be the predominant mode of termination even though it has a much higher activation energy than β -scission of CH-CH₃ bonds.

The kinetic constants obtained for the C-H β -scission reactions are $E_a = 160 \pm 20$ kJ/mol and $A = 2.7 \times 10^{15} \text{ s}^{-1}$. The activation energy, which is about 71 kJ/mol greater than the value obtained for the propagation reactions (which correspond to β -scissions of C-C bonds), is consistent with expectations based on the observation that the C-H bonds ($D = 410$ kJ/mol) are considerably stronger than the C-C bonds ($D = 322$ kJ/mol) that comprise the backbone of the polymer. The pre-exponential factor, however, seems to be about an order of magnitude too big, even after taking into account the higher vibrational frequency of the C-H bonds (~ 3 times the vibrational frequency of a C-C bond) and the fact that there are 5 (if it is a secondary radical on

a chain end) - 7 (if it is a tertiary radical in the interior of the chain) C-H bonds (2 on each of the adjacent methylenes and 3 on the methyl) that are β to the site of the radical.

The expression obtained for the global rate of mass-loss which results from substitution of the rate constants for random scission, propagation, and termination (*i.e.*, β -scission of C-H) observed in the MD simulations is given in Eq.(22).

$$\frac{1}{m(t)} \frac{dm(t)}{dt} = -1.3 \times 10^{14} \exp\left(-\frac{30318}{T}\right) \quad (22)$$

The corresponding activation energy, $E_a = 252 \pm 32$ kJ/mol (which is obtained by multiplying the numerator and denominator of the exponent by R to put Eq.(22) into Arrhenius form), and pre-exponential factor, $A = (1.3 \pm 0.2) \times 10^{14} \text{ s}^{-1}$, may be compared to the experimental values, obtained from TGA measurements on polypropylene, which are 243 kJ/mol and $7.7 \times 10^{15} \text{ s}^{-1}$, respectively [Madorsky, 1964]. The computer simulations slightly overestimate the activation energy. This is understandable in view of the fact that no attempt was made to represent bond defects, which are almost certainly present in the samples used in the experimental TGA measurements, in the model polymers. There is no equally satisfying explanation for the unrealistically low value of the pre-exponential factor, other than deficiencies in the model. The computed value of the rate constant for the termination reaction, in particular, seems suspicious.

Summary and Conclusions

Molecular dynamics computer simulations were used to investigate the thermal degradation of polypropylene. The predominant degradation pathway deduced on the basis of these simulations was chain transfer scission, via the transfer of a hydrogen from parent free radical polymer fragments created by random scission initiation. It was further concluded that the propagation reactions, which are responsible for the formation of volatile fragments, are terminated by β -scissions of C-H bonds. The relevant rate constants were evaluated from the number of reactions observed in the computer simulations and substituted into a simple kinetic model to obtain an expression for the global rate of mass-loss for the thermal degradation of polypropylene. The global activation energy derived in this way is in reasonable agreement with the experimental value obtained from thermogravimetric measurements, but the pre-exponential factor is about an order of magnitude too small. This may be a result of ignoring the contributions from second order and other modes of termination, which will be examined further in subsequent investigations.

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References

1. Benson, S.W., *The Foundations of Chemical Kinetics*, McGraw-Hill, New York, NY, 1960, pp. 211-266.
2. Boyd, R.H., *The Relationship Between the Kinetics and Mechanism of Thermal Depolymerization*, In: *Thermal Stability of Polymers*, Marcel Dekker, New York, NY, 1970, pp. 47-89.
3. Curtiss, L.A., Raghavachari, K., Trucks, G.W. and Pople, J.A., Gaussian-2 Theory for Molecular Energies of First- and Second- Row Compounds. *J. Chem. Phys.* 94: 7221-7230, 1991.
4. Cullis, C.F. and Hirschler, M.M., *The Combustion of Organic Polymers*, Clarendon Press, Oxford, England, 1981, pp. 93-228.
5. Dauber-Osguthorpe, P., Roberts, V.A., Osguthorpe, D.J., Wolff, J., Genest, M., Hagler, A.T., *Structure and Energetics of Ligand Binding to Proteins: E. Coli Dihydrofolate Reductase-trimethoprim, a Drug-receptor System*. *Proteins: Structure, Function and Genetics* 4:31-47, 1988.
6. Madorsky, S.L., *Thermal Degradation of Organic Polymers*, Interscience Publishers, New York, NY, 1964, p 124.
7. Nyden, M.R. and Noid, D.W., *J. Phys. Chem.* 95: 940-945, 1991.
8. Nyden, M.R., Forney, G.P. and Brown, J.E., *Macromolecules* 25: 1658-1666, 1992.
9. Nyden, M.R., Brown, J.E. and Lomakin, S.M., *Mat. Res. Soc. Symp. Proc.* 278: 47-53, 1992.
10. Nyden, M.R., Coley, T.R. and Mumby, S., *Polym. Eng. Sci.* 37, No. 9:1496-1500, 1997.
11. Nyden, M.R. and Gilman, J.W., *Comp. and Theor. Polym. Sci.*, 7, 191-198 (1997).
12. Nyden, M. R. "The Molecular Level Design of Fire Retardants and Suppressants," In: *Fire Retardancy of Polymeric Materials*, Grand, A.F. and Wilke, C.A., Ed., Marcel Dekker Publishing Company, 1999, **in press**.

13. Solomons, T.W.G., Organic Chemistry, Secon Edition, John Wiley and Sons, New York, NY, 1976, p 132.
14. Tsang, W. and Kiefer, J.H., "Unimolecular Reactions of Large Polyatomic Molecules over Wide Ranges of Temperature," In: The Chemical Dynamics and Kinetics of Small Radicals, Part I, Liu, K. and Wagner, A., Eds., World Scientific, 1995, 58-119.