Molecular dynamics study of the depolymerization reaction in simple polymers

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A molecular dynamics experiment was designed to follow the sequence of depolymerization reactions occurring when a polymer degrades into its constituent monomers. This simulation addresses internal changes that certain materials undergo at the moment of burning. Polymer fragments were thermally generated from the random scission of longer polymer chains containing 50–950 units. Subsequently, these thermal fragments depolymerized and coiled dramatically, forming incipient "agglomerates". These agglomerates cooled while depolymerizing; the cooling mechanism remarkably inhibits the depolymerization reaction and eventually terminates the degradation process leading behind a sample of cold stable agglomerates. The size distribution of the polymer fragments is given as well as the IR spectrum of a typical sample at 2000 K.

1. Introduction

The combustion of polymeric materials involves a series of complex reactions that begin with thermal degradation. An important step in this process is the formation of volatile monomers from condensed phase fragments. Once formed, these monomers react with oxygen in the gas phase releasing large amounts of heat in the process of forming stable combustion products. Some of these products are particles on the nanometer scale that result form incomplete depolymerization of the degrading materials. Very little is known about the processes leading to the formation of these particles. More understanding on these lines is of great interest for the material fabrication. Examples of polymers with a strong tendency to depolymerize are polystyrene, poly-(methyl methacrylate) and polytetrafluoroethylene.

Computer models based on both kinetic and statistical approaches have been used by other researchers to study aspects of the thermal decomposition of polymers [1–5]. Molecular dynamics has been successfully applied in the past to the study of liquid to glass transitions [6,7] and melting [8] in polymers, as well as to unimolecular decompositions in small molecules [9], and to the structural changes, melting and wetting in clusters [10]. In all of these instances the numerical results were at the basis of further theory development. In this work we present a novel computer model of the effects in polyolefins and related polymers caused by the depolymerization reaction. Our goal is to provide insight into the mechanisms leading to internal energy and conformation changes in the degrading polymer fragments.

Depolymerization is a chain reaction which is initiated with the formation of free radical polymer fragments (FRP) resulting from the random scission of the original polymer molecules. Depolymerization starts when one monomer dissociates from the end of a FRP fragment. The reaction leaves be-

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hind a new FRP fragment which is reduced in size by one monomer unit. Subsequently, the newly formed FRP fragment ejects a second monomer from its end and, in turn, a smaller FRP fragment is left behind. In principle, depolymerization can continue until the initial FRP fragments have completely "unzipped" into their component monomers. The unzipping process also terminates when the fragment internal energy is low enough not to support further bond dissociations.

Depolymerization starts on the onset of the degradation, when the condensed material is at high temperatures, not yet in thermodynamic equilibrium. The products of degradation go into the gas phase where the monomers react with oxygen activating the combustion mechanism. It is unclear though why most burning polyolefins give rise to nanometer particles that mainly degrade into graphitic-like agglomerates that remain suspended in the external atmosphere. It is also unclear why these materials do no volatilize completely, but leave condensed amorphous remnants upon burning. These are some of the many processes that can occur during degradation [1,2]. At temperatures far below the degradation temperature, these materials are disordered with respect to both the conformation of the individual chains and the chain molecular weights. These polymers are not 100% crystalline, rather they contain many coiled chains giving rise to void-like defects. This is because the interactions between polymer chains are weaker than the interactions within each chain. As an initial effort, in this work we concentrate on the effect of the depolymerization reaction on the conformation of each polymeric chain in the material. That is, as a first approximation, chains are long and have large molecular weight but their interaction with the surroundings is not taken into consideration.

Other reaction channels such as hydrogen transfer reactions can occur during the degradation process. The products from these reactions can be stable small molecules that may, or may not, react with oxygen in the course of the combustion. But the activation energy for depolymerization is lower than that for other reactions. Thus, depolymerization dominates in most hydrogen-poor polymers. Specifically, less energy is required to initiate depolymerization of a fragment than to produce further random scission.

This is because the double bond in the dissociating monomer forms at the same time as the single bond between the monomer and the FRP fragment breaks. As a consequence, the activation energy for depolymerization is reduced by the energy difference between a double and a single bond along the backbone. In this work we have only taken into account two possible reaction channels – thermal random scission and depolymerization. In section 2 we present the model used to represent simple polymers and describe the computer simulation methods. In section 3 we discuss our results which are mainly qualitative. The picture of degradation that emerges is the following. Polymer fragments that undergo depolymerization result in highly coiled incipient "agglomerates". These agglomerates cool down while depolymerization still takes place. The cooling mechanism competes with depolymerization and eventually terminates the depolymerization process giving rise to long-lived cold agglomerates. This behavior contrasts with the polymer fragments resulting from thermal random scission which are extended (not too coiled) and hot. Various analysis are given to support these observations. Section 4 concludes this Letter.

2. The computer experiment

All of the computer simulations considered in this paper were initiated from independent polymer chains in free space. The molecular weights of the model polymers ranged from $50M$ to $950M$, where M is a unit of the polymer with mass of 14.5 au (i.e. approximately the mass of a CH_2 group). Each polymer chain was modeled by N spherical units interacting through the classical potential:

$$V = \sum_{i=1}^{N-1} V_b(r_{i,i+1}) + \sum_{i=1}^{N-2} V_a(\theta_{i,i+1,i+2})$$

$$+ \sum_{i=1}^{N-2} \sum_{j=i+2}^{N} V_{nb}(r_{i,j}) . \qquad (1)$$

The first term

$$V_b = D\{1 - \exp[-\alpha(r-r_e)]\}^2 , \qquad (2)$$

is a Morse potential representing the covalent bond between pairs of adjacent units. This nearest-neigh-

bor interaction was supplemented by an asymmetric pseudo three-body interaction

$$V_a = \tfrac{1}{2} k_\theta (\cos\theta - \cos\theta_0)^2 . \tag{3}$$

This term accounts for the preferential orientation $\theta_0 = 113.3°$ between any three contiguous units as a result of the sp^3-hybridization. The third term

$$V_{nb} = 2\epsilon [(\sigma/r)^9 - 1.5(\sigma/r)^6] , \tag{4}$$

is a van der Waals interaction between non-bonded units in the chain. The core parameter, σ, takes into account the excluded volume of the units. The value of the six parameters used in this work were introduced in the study of torsional motions in butane [11,12]. These values are in atomic units (hartree for energies): $D=0.1324$, $\alpha=1.018$, $r_e=2.891$, $k_\theta = 4.949 \times 10^{-2}$, $\epsilon = 1.9 \times 10^{-4}$, and $\sigma = 7.559$. The global minimum of the potential energy function corresponds to the planar zigzag configuration depicted in fig. 1 where all dihedral angles Φ are $180°$. The bending force constant k_θ is large enough such that the potential energy hypersurface V presents many local minima corresponding to stable coiled conformations with randomized dihedral angles.

This Hamiltonian is simple and can be improved at the cost of more studies. We think it gives a good starting model for the search of the qualitative aspects of a generic behavior. One possible refinement is to include a cutoff function at large separations in the bonding term V_b and in the asymmetric term V_a. Potentials of this type have been used to model various degrees of hybridization such as in silicon [13,14] or in sulfur [15]. An additional refinement would be to consider pseudo four-body interactions. These contributions have been taken into account to study the solid–liquid transition of polymers and covalent systems [16,17]. However, the major mechanism of melting was first revealed using simpler Hamiltonians which did not contain four-body terms [8,13].

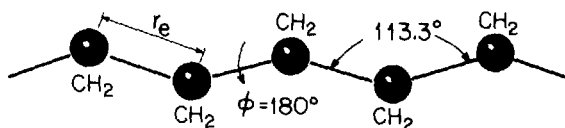The time evolution of each polymer chain was fol-

Fig. 1. The planar zigzag conformation of polyethylene.

lowed using molecular dynamics at constant energy. The Hamiltonian of each chain was considered to be the sum of the kinetic energy of each unit as a whole plus the potential energy given in eq. (1). The Hamilton equations of motion $\partial H / \partial p_i = \dot{q}_i$, $\partial H / \partial q_i = -\dot{p}_i$, $i = 1, 2, ..., 3N$, were solved using ODE [#1]. This computer program uses a variable time step to control the local error in solving the differential equations. However, the maximum time step was set to 0.004 ps which is one order of magnitude smaller than the vibrational period of the covalent bonds. All simulations were started from the planar zigzag geometry (fig. 1), with the initial momenta chosen at random from a uniform distribution. The time evolution of most chains was followed for 10 ps. Temperature was defined as $\tfrac{2}{3} k_B$ times the trajectory averaged kinetic energy per unit, where k_B is Boltzmann's constant.

The computer experiments were performed as follows: Each polymer chain in the zigzag configuration was heated instantaneously by an external energy of the order of 0.019 hartree/unit. This energy was rapidly distributed among all degrees of freedom resulting in a Boltzmann distribution of speeds in less than 0.1 ps [19]. The chains equilibrated to temperatures in the range of 2500 K. Free radical polymer fragments began to form after approximately 1 ps by random scission of the original chains. A fragment was considered to form whenever the distance between any two neighboring units exceeded a dissociation distance $r_d = 18$ au. When any two fragments were that far apart from each other, the only significant interaction was the eventual repulsion due to the asymmetric factor V_a. This artifact introduced a nonphysical directional bias because the fragments dissociated preferentially at angles close to θ_0. We do not believe that this has a significant effect on the internal properties of the individual polymer fragments described in section 3.

The monomers in our model consisted of two units connected by a double bond. This double bond was represented by the Morse potential in eq. (3), where D was replaced by $D' = 1.759D$. The sequential depolymerization reactions were simulated by introducing a switching function that modified the pair potential terms V_b on either side of the dissociating bond. The prescription was as follows: the two bonds

[#1] Based on the corrector predictor algorithm, see ref. [18].

N = 42
time = 11.8 ps
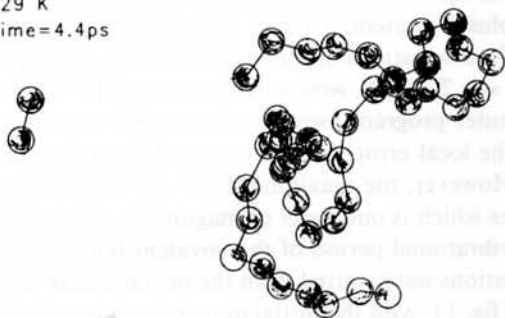T = 2229 K
life time = 4.4 ps

Fig. 2. A coiled polymer fragment in the process of depolymerizing.

adjacent to the dissociating bond were strengthened by the amount $D' - D$, whereas the two next-nearest bonds were weaken by the same amount of energy. A depolymerizing fragment is depicted in fig. 2. On the average monomers were ejected approximately every 2 ps. Therefore, at the end of an experiment *both* FRP fragments and monomers were present. These species were still interacting among themselves.

3. The qualitative picture of polymer degradation

The thermal random scission of the polymer chains resulted in the formation of an initial number of FRP fragments. Three or four fragments were produced in a typical simulation. The fractional size (ratio of the fragment size to the initial size of the polymer chain) distribution of the fragments is depicted in fig. 3. This figure is based on the data collected from 25 independent simulations started from polymers with an average chain length of 478 units from which a total of 72 fragments were produced by thermal random scission. The distribution is not simple because the number of random scission varied between experiments. There is, however, a noticeable bias towards small fractional sizes. This observation is consistent with statistical predictions based on discrete breakage models [20], but it disagrees with the log–normal distribution function resulting from the model of liquid-like coalescence of particles [21].
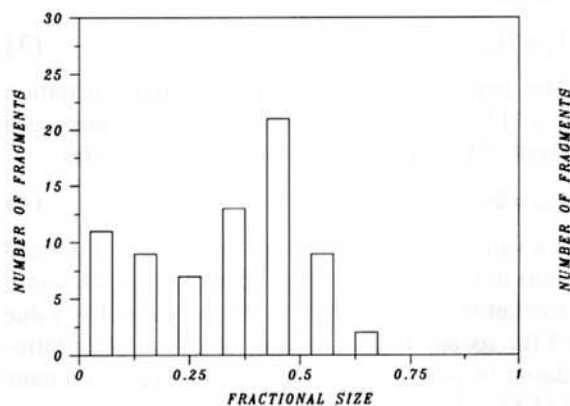
FRACTIONAL SIZE DISTRIBUTION

Fig. 3. Distribution of the fractional sizes of 72 polymer fragments. The fractional sizes were computed as the ratio of the number of units in the fragment to the number of units in the original polymer.

We investigated the extent of coiling as measured by the average radius

$$\langle r \rangle = \sum_{i=1}^{n} |r_i - r_0| / N, \qquad (5)$$

of the free radical fragments generated in random scission reactions. In eq. (5) r_i is the position vector of the ith atom and r_0 is the position vector of the center of mass of the fragment. The degree of coiling in a fragment is inversely related to the average radius [22]. That is, the average radius of a coiled fragment is small compared to a planar zigzag chain having the same number of units. This data is plotted in figs. 4a (for fragments that *did not* depolymerize) and 4b (for fragments that *did* depolymerize) as a function of the number of units in the free radical fragments. Whenever possible, the averages were computed from trajectories that lasted 10 ps. In the case of the depolymerizing fragments, however, new fragments formed by ejection of monomers in considerably less than 10 ps. In this cases the averages were computed over the time interval between successive monomer ejections (approximately 2 ps). The straight lines in both figures correspond to perfect planar zigzag polymers. In all of the observed simulations, the ejection of monomers was followed by a recoil which, after many such reactions, resulted in a compression of the depolymerizing fragments.
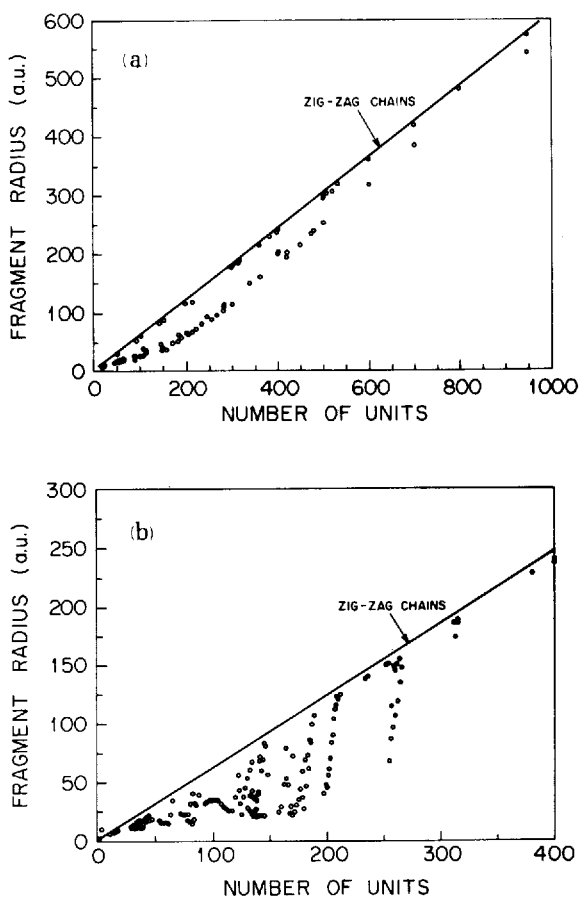
Fig. 4. Average radii of free radical fragments as a function of the number of units. (a) Fragments that did not depolymerize; (b) fragments that depolymerized. The straight line corresponds to perfect planar zigzag polymers.

The dihedral angles (Φ) in the fragments randomized in the process producing coiled fragments. A comparison of figs. 4a and 4b indicates that the extent of coiling was greater in the depolymerizing fragments. The average radii of the fragments that did not depolymerize decreased by about 20% from their planar zigzag values, whereas the radii of depolymerizing fragments typically decreased by more than 50%. These highly coiled, depolymerizing fragments looked like agglomerates. The dramatic shrinkage in size is clearly visible in computer movies based on the trajectories of the degrading polymer fragments [23] [2].

[2] Copies of these videotapes are available from the authors.

The agglomerates were also observed to cool in the process of depolymerizing, as a consequence of the rapid succession of bond dissociations to eject the monomers. This effect is evident in fig. 5 which is a plot of the internal temperature of a particular depolymerizing fragment as a function of the number of its remaining units. This cooling mechanism tended to inhibit further depolymerization, thus increasing the lifetime of the coiled fragments. *The fragments self quenched in melted-like conformations.* Similar cooling mechanisms were observed in atomic clusters at temperatures above the melting point. When atoms started to evaporate from these clusters, the clusters cooled [24,25]. In contrast, the stretched FRP fragments that did not depolymerize tended to maintain their original temperature.

Other qualitative observations worth noting concern the infrared spectrum as obtained from the Fourier transform of the velocity autocorrelation function which is depicted in fig. 6. This spectrum corresponds to a sample of four FRP fragments that started to depolymerize at a temperature of 2100 K. The main spectral features are two broad bands centered at about 1000 and 150 cm^{-1} and an intense peak close to the origin. The high frequency band that corresponds to the stretching vibrations of the individual unit–unit bonds is very broad. Indirectly this observation shows that the neighborhood of dihedral angles near each unit–unit bond is different resulting
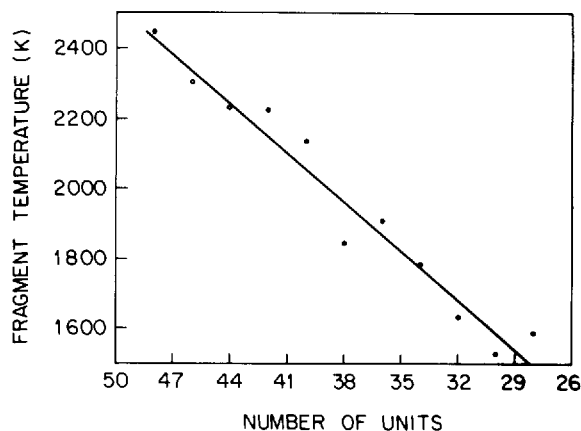

Fig. 5. Temperature of a depolymerizing free radical polymer fragment plotted as a function of the number of remaining units in the main fragment. A total of 10 monomers were ejected from the original fragment.
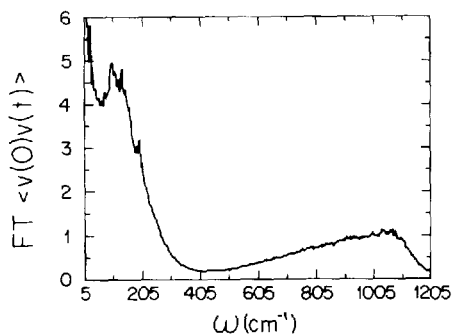
Fig. 6. The Fourier transform of the velocity autocorrelation function (×component) computed from the trajectory of a 400 unit polymer undergoing depolymerization. Four major FRP fragments and 22 monomers were present in the sample at the end of 10 ps.

in a strong inhomogeneous band broadening. The second band corresponds mainly to vibrations of coiled portions of the polymer against other coiled portions in the same polymer fragment. In general these are acoustic-like vibrations in which many units move in phase along the polymer backbone. We observed that the intensity of this band tended to increase as time progressed and the depolymerizing fragments became more compact (agglomerates). This would suggest that the ability for coiling that the fragments acquired upon depolymerizing might be predicted from IR spectra measured as a function of time. Finally, the peak at very low frequencies is due to the rotation of the independent fragments as a whole, to the rotation of the individual monomers, to the vibrations between the dissociated monomers, to the vibrations between the dissociated monomers and the polymer fragments, and to the vibrations between different polymer fragments. It is not surprising to find the low frequency modes [26] because the dispersive interactions V_{nb} are present at the moment of monomer dissociation.

4. Conclusion

This study gives a pictorial, qualitative, description of the process of degradation of polymers in the course of burning. The numerical results are accurate enough to promote a theoretical description which is badly needed in the field. Computer sim-

ulations based on molecular dynamics were used t study changes in the energetics and conformation o free radical polymer fragments undergoing depoly merization reactions. The free radical polymer frag ments were thermally generated by random scissio of model polymers consisting of between 50 and 95 units. The degrading mechanism showed that tw types of byproducts could result from thermal deg radation of simple polymers. One of these byprod ucts are rather cold incipient agglomerates on the na nometer scale made up from polymer fragments i highly coiled conformations. These agglomerates re sulted from the self quenching mechanism produce by the sequence of depolymerization reactions. Th other byproducts are hot polymer fragments in rathe stretched out conformations. The later are good can didates to continue degradation by chemical reac tions other than depolymerization.

Our observations help to understand why com plete depolymerization is hard to achieve and ho complex particles might be formed along with mon omers at the moment of the combustion.

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