On the Distribution of Fragment Sizes in the Fragmentation of Polymer Chains.

B.C. Hathorn,[a] B.G. Sumpter[b] and D.W. Noid[b]

[a] Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

[b] Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

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Abstract

The fragmentation pattern of a single step cleavage of a polymer is calculated using a simple model based on Transition State Theory to describe the distribution of fragment sizes. Subsequent molecular fragmentations can be simulated by repeated application of the model. The results for the fragmentation pattern are compared to those observed for molecular dynamics calculations performed at high temperatures.

I. INTRODUCTION

Polymers are subject to fragmentation under a wide variety of experimental conditions, including thermal degradation and chemical oxidation processes. The sequence of chemical reactions involved is quite complex. The initial step, however, in the series of chemical reactions is the same–the cleavage of one of the bonds in the polymer after some initiation process.

A number of authors have offered mathematical descriptions for following the time evolution of the mass or population.[1] The population dynamics are followed in a continuum approximation by watching the evolution under the influence of a fragmentation kernel. A common application is to employ a kernel which promotes completely random scission, with equal probability distribution for all possible fragment sizes.[1] Such an approximation considerably simplifies the mathematical model.[2]

A number of researchers have simulated the cracking of the polymer *via* molecular dynamics simulations[3–8]. In order to have a rate of bond cleavage for the polymers which is sufficiently fast to be modeled on the short timescales of MD simulations, however, the temperature of the simulation must be very high–substantially higher than the conditions under which the thermal fractionation typically takes place.

Here, we describe a simple method by which the relative rates of the fragmentation at the individual bonds can be estimated using a Transition State Theory (TST) approach and using a one-dimensional polymer as a guide. As the probability of forming a given fragment size is dependent on the branching ratio into the possible fragment channels, the cancellation of a number of parameters in the TST approach gives a probability distribution for fragment sizes in a single fragmentation step. The estimation of the branching ratios should be excellent in cases where the daughter fragments have chemical properties (dissociation energies and bond force constants) very similar in nature to the parent. We note that the distribution we find is different from the commonly employed purely random scission distribution. In this case, the distribution of fragments is derived by a consideration of the chemistry involved.

Subsequent fragmentations can be accounted for by repeated application of the model on each of the newly formed fragments. In Section II we describe the simple model for the unimolecular fragmentation, and calculate the fragmentation pattern which results. The repeated application of the fragmentation formula yields the distribution of molecular fragment sizes following a number of successive fragmentations. In Section III, we compare the fragmentation pattern to that which is observed in the molecular dynamics calculations.

II. THEORY

In order to simplify the discussion here, we treat the reaction with a canonical (fixed temperature) TST formalism.[9–14] The rate for a reaction, whether it is the fragmentation at the end of a chain, or somewhere in the middle, is given by

$$k = \frac{k_B T}{h} \frac{Q^\dagger}{Q} \tag{1}$$

where $Q^\dagger$ and Q are partition functions for the transition state and reactants, respectively, h is Planck's constant, T is the absolute temperature, and k_B is Boltzmann's constant. One could, instead, use a Rice-Ramsperger-Kassel-Marcus (RRKM) type expression,[10–14] which treats the conservation of energy and angular momentum microcanonically, however, in the present case, where the reactions are thermalized, such additional complication is unnecessary.

Recalling that the vibrational partition function is given by $Q = \prod_i k_B T/h\nu_i$ for the reactant[9–14] (with a similar expression for the transition state, where there is one fewer degree of freedom), we have for the rate of fragmentation at bond j,

$$k_j = \nu_{eff,j} \frac{B}{B^\dagger} e^{-E_{a,j}/k_B T} \tag{2}$$

where $E_{a,j}$ is the activation energy of the reaction, and $\nu_{eff,j}$ is the ratio of the product of the reactant and transition state frequencies. The factor $B/B^\dagger$ is the ratio of rotational constants in the molecule and the transition state, obtained by treating the separating fragments as a pseudo-diatomic molecule.[9–14] Implicit in the pseudo-diatomic assumption is that the molecular fragments do not rotate freely about their respective molecule-fixed axes, and as such the moments of inertia of the fragments do not appear in the expressions for the partition function.

We next consider the branching ratio under some simple conditions. We assume that the force constant for the bond being broken is independent of the location, and that the activation energy is approximately the same. This would be close to that which would be expected in the case of a one-dimensional polymer, where each of the monomer units have similar chemical reactivity. In this case, we can write the effective frequency as[15]

$$\nu_{eff,j} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_j}} \tag{3}$$

where μ_j is the reduced mass of the effective vibration, and k is the effective force constant. If the chain consists of an N-mer with monomer units of mass M, the reduced mass for fragmentation is that of the center of mass separation of the fragments after the bond breakage,

$$\mu_j = \frac{M(N-j) \times Mj}{MN} \tag{4}$$

We find that the effective frequency for fragmentation of bond j is given by

$$\nu_{eff,j} = \left(\frac{\sqrt{kN}}{2\pi\sqrt{M}}\right)(N-j)^{-1/2}j^{-1/2}. \tag{5}$$

We also estimate that the transition state distance, defined by the center of mass separation, $r^\dagger$ for the fragments are similar, from which we obtain the result

$$B_j^\dagger = \frac{h}{8\pi^2\mu_j}r^{\dagger 2}. \tag{6}$$

The rate for the fragmentation at position j is now given by

$$k_j = Cj^{1/2}(N-j)^{1/2}e^{-E_{a,j}/k_BT}, \tag{7}$$

where C is a collection of constants which are independent of the position in the chain where fragmentation occurs,

$$C = \frac{8\pi^2}{hr^{\dagger 2}}B\left(\frac{\sqrt{kN}}{2\pi\sqrt{M}}\right). \tag{8}$$

We note that the reactant molecule has been treated as a pseudo-diatomic molecule, and hence only has one rotational constant. A more accurate representation might be that of an asymmetric top, in which case the dependence would be on $\sqrt{ABC}$ where A, B, and C are the rotational constants, rather than on the single rotational constant, B. In the following discussion, we note that we are only concerned with effective branching ratios (relative rates) and the normalization constant appearing in Eq. (7) cancels.

In the linear chain approximation, we can now calculate the total rate of all fragmentations,

$$k_T = C\sum_{j=0}^{N}(N-j)^{1/2}j^{1/2}e^{-E_{a,j}/k_BT}, \tag{9}$$

Where we have extended the range of the summation to include the $j=0$ and $j=N$ terms, both of which are zero.

The probability of fragmentation at a particular position, j, in a polymer of length N is given by the ratio of the rate of fragmentation at position j to the total rate of fragmentation,

$$P_N(j) = \frac{(N-j)^{1/2}j^{1/2}}{\sum_{n=0}^{N}(N-n)^{1/2}n^{1/2}}. \tag{10}$$

In this expression, we have made the approximation that the activation energies of the individual reactions, $E_{a,j}$ are identical. While technically incorrect, due to the varying zero-point energies of the channels, the approximation should be good, particularly at the high energies of a thermal decomposition, $k_BT \gg E_a$, and when the chemical reactivity of the monomer units is substantially identical. If the sum in the denominator is replaced by an integral,

$$\sum_{n=0}^{N}(N-n)^{1/2}n^{1/2} \approx \int_0^N x^{1/2}(N-x)^{1/2}dx = \frac{\pi}{2}\left(\frac{N}{2}\right)^2, \tag{11}$$

we obtain a closed form solution for the probability of a fractionation at any given location,

$$P_N(j) = \frac{8}{\pi N^2}j^{1/2}(N-j)^{1/2}. \tag{12}$$

In particular, we note that the probability spectrum is peaked towards fragmentation in the middle, rather than fragmentation at the end of the linear chain. A more accurate expression than (12) could be obtained by forgoing the step of replacing the sum with the integral in (11) and performing the summation exactly, however this step provides a transparent analytic form of the probability distribution. The difference in the sum *vs.*

integral involves a small error introduced in the normalization constant. The main feature of this probability distribution is that it is independent of such features as the mass of the monomer units and the vibrational frequencies of the parent molecule and transition state.

The fragmentation pattern predicted is, however, for a single step fractionation. In modeling the real system, however, there will be a number of successive fractionation processes. As a simple approximation, each of these fractionation processes can be modeled using using Eq. (12). If the population of fragments of size k at time t is represented by $g_k(t)$ the population at the next time step will be given by

$$g_k(t+1) = (1-f)g_k(t) + \sum_{i>k} f g_i(t) P_i(k) \tag{13}$$

where f is the fraction of the fragments which decompose in any particular timestep, $P_i(k)$ is the probability of a polymer of size i producing a fragment of size k. If fragments show different stabilities, one could modify the effective amount of fragmentation f and replace it by a mass specific fragmentation rate, f_k, however we have not done so here, in the interest of simplicity. We note that to conserve the total population of molecules, fragments consisting of a single monomer unit are not allowed to undergo additional fragmentation,

$$g_0(t+1) = g_0(t) + \sum_{i>k} f g_i(t) P_i(0). \tag{14}$$

The fragmentation process can now be fitted with two parameters, the total number of fragmentation timesteps, and the fraction of molecules which fragment in each timestep. We note that this crude model does not include the possibility of recombination to produce large fragments from smaller ones, as is apparent in the MD simulation, however, it is seen that even without including such features in the model, we can successfully reproduce the general features of the fragmentation pattern.

A sample fragmentation spectrum is shown in Fig 1 after 15 time steps with 15% of the individual units undergoing fragmentation at each step. The fragmentation spectrum is schematic in nature, not representing any particular polymer species, as Eq. (12) is independent of the particular vibrational frequencies, force constants, and molecular weights within the context of the present model. At each time step the only additional required input is the branching ratio for the fragmentation of a polymer species into species of lower molecular weight, represented by Eq. (12). Of particular interest is the asymmetry of the molecular weight distribution after a number of fractionations, where the molecular weight distribution for a single fractionation represented by (12) is clearly symmetric with respect to $N/2$.

III. DISCUSSION

We first note several approximations we have made in the present theory. First, we have assumed that the activation energy is the same for the fragmentation of each of the bonds in question. This approximation is obviously not exact, but at high temperatures, the difference in the activation energies for the rate constants, $\exp(-\Delta E_a/k_B T)$ becomes less important. In addition, in large polymer systems, the daughter fragments have similar chemical reactivity to the parent. In addition, we have assumed a straight bond fission, rather than the a more collective motion for a flexible polymer strand.

In the present calculation, we have used a canonical TST rate constant for the branching ratios, which amounts to taking a thermal average over the individual microcanonical branching ratios. One might argue that it is more appropriate to use a microcanonical approach,[10–14] however, in the present case, where the activation energies for the possible reaction pathways are presumed to be identical, the results are the same for thermal reactions. As a result, we have chosen to apply the more straightforward canonical TST approach, using partition functions instead of densities of states. In this simplified approach, we find that the branching ratio is independent of the mass of the individual monomer units.

We have also assumed that after each fragmentation step the populations of fragments are allowed to rethermalize. This is necessary because at modest temperatures a single fractionation will require nearly all of the energy available in the thermalized molecule, leaving insufficient energy for further fractionation in the microcanonical system.[10–14] We have also assumed similar timescales for the fractionation of the different polymer pieces. In practice, however, one would observe differences in fragmentation rates for different molecules, with those which have unusual stability having longer lifetimes. This consequences of this effect are well known, and evident in a more traditional mass spectrum, where characteristic peaks are enhanced. In the present case, however, where we are interested in the fragmentation of a polymer strand, we can assume that each of the smaller fragments has similar chemical properties to the parent, at least when the fragments are sufficiently large, as opposed to smaller molecules with a number of different functional groups.

We now compare our results to that of the molecular dynamics simulations.[3] The molecular dynamics simulations are performed in thin films, as opposed to single polymer strands, and show a propensity to fragment into fragments of low molecular weight. This trend is in agreement with the present theory, although not in a single fragmentation step. In order to obtain a similar distribution of fragments, subsequent refragmentation must be allowed. In addition, the results in the present theoretical treatment are continuous, as opposed to the more discrete nature of the molecular dynamics simulation. Part of this is due to the fact that the molecular dynamics simulation is performed by averaging over a small number of trajectories.[3]

The present theory also does not incorporate the possibility of recombination of fragments to form higher molecular weight species from lower molecular weight species. Such a possibility, if included, would indeed lead to production of masses with higher molecular weight than the parent peak, as is observed in the molecular dynamics simulation.[3]

We do see, however, that our assumption of a rethermalization step between fragmentation steps is justified in the asymmetry of the mass spectrum. If such a step did not occur, we would expect each polymer to undergo a single fragmentation, producing fragments of size $N-j$ and j, and thus the spectrum would be symmetric about $N/2$, as is the probability distribution given by Eq. (12). The asymmetry of the spectrum is clearly evident in the numerical experiment.[3]

A more detailed calculation of the fragmentation pattern of the polymer could be obtained through a detailed kinetic analysis using a master equation[1,2] to study the time evolution of the population under the influence of the derived fragmentation kernel. To be compared directly to experimental behavior, however, such an analysis should also involve both the fragmentation of the parent and the reassociation of the daughter populations of the polymer. Such a calculation is beyond the scope of the present study.

In summary, we have shown that a fragment distribution for thermal polymer fragmentation can be obtained with a simple model in a minimal amount of computation time. In addition to the considerable savings in computer time, the simulations can be done at lower temperatures than the comparable molecular dynamics simulations, which are more appropriate to the typical conditions for the reaction. Since the model is based on a statistical treatment, and does not require detailed potential information, the simulations can be performed on very large systems, where MD simulations are impractical.

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FIG. 1. Calculated fragmentation pattern for a polymer with 100 units after 15 timesteps with a 15% fragmentation rate at each timestep. The point at 100 monomer units represents the residual of the parent peak after 15 successive fractionations.