

# Evolution of Fragments Formed at the Rupture of a Knotted Alkane Molecule

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**Abstract:** Common experience tells us that a knot significantly weakens the polymer strand in which it is tied, which, in turn, leads to more facile chain rupture under tensile loading. Using first-principles molecular dynamics calculations we describe the dynamical evolution of the radicals that form after chain rupture of a single knotted alkane molecule in its very early stages of life. They are able to recombine, to form cyclic alkanes, and to undergo disproportionation phenomena with nearby chain segments. The breaking of a single knotted polymer chain under mechanical loading is thus predicted to reveal phenomena falling in the domain of ultrafast spectroscopy.

## Introduction

The topological properties of knots,<sup>1</sup> their occurrence in organic and biopolymers,<sup>2</sup> and the modifications to physical and chemical properties induced by the presence of knots<sup>3</sup> are well-established fields of research.<sup>4</sup> Simple single-chain knots are consistently observed in real polymers,<sup>5</sup> including DNA<sup>2</sup> and other bio-polymers,<sup>6</sup> and are widely studied with computer simulations.<sup>7</sup> In particular, the “trefoil” knot, familiarly referred to as the “overhand knot”, is the simplest and most commonly occurring kind of single-rope knot.<sup>8</sup> Even so, relatively little is known about knots in polymer strands at the atomic level.<sup>9</sup> The response of knotted polymers to mechanical deformations, such as stretching (tensile loading), has a major impact on polymer technology. In fact, techniques, such as atomic-force microscopy (AFM)<sup>10</sup> or optical tweezers,<sup>11</sup> can now manipulate single molecules and thus apply tensile load at a molecular level. Recent first-principles quantum mechanical calculations<sup>12</sup> have

shown that the properties of a “trefoil” knot in a polyethylene chain, subjected to tensile loading, closely follow the well-known behavior of macroscopic ropes.<sup>8</sup> Indeed, analysis of the strain energy distribution along the knotted polymer chain, in terms of a classical force field model,<sup>13</sup> shows that the bonds at the entrance and exit points are far more stressed than the others and that the bonds near the center of the knot are still reasonably close to their ground-state geometry. First principles calculations also confirm our common experience that the presence of the knot significantly reduces the tensile strain that can be stored in the strand before breaking. Moreover, the break point in a microscopic polymer strand occurs at either the entrance or exit point of the knot,<sup>12</sup> exactly as in a macroscopic rope,<sup>8</sup> and as recently observed in optical tweezers experiments.<sup>6</sup>

The focus in the present article is not directed at the behavior of the stress distribution and the nature of the break point in a knotted polymer but rather on what happens to the resulting chain fragments *after* the break occurs. Since the rupture of a polymer strand necessarily generates fragments that are radicals, one would anticipate interesting chemical phenomena, e.g., radical recombination, which have no obvious corresponding counterpart with a macroscopic rope. Accordingly, we have investigated the breaking of an individual alkane molecule that contains a simple trefoil knot focusing on the dynamical evolution of the radicals that form after the break. Although this is an idealized system, studying the nature of chemical processes characterizing individual molecules is a necessary first step in understanding polymer properties at the macroscopic level.

## Computational Details

We have shown elsewhere<sup>12</sup> that an *n*-alkane containing 28 carbon atoms and, accordingly, 58 hydrogens is large enough to be knotted into a trefoil. In that work, as in the present case, tension was applied by constraining the end-to-end length of

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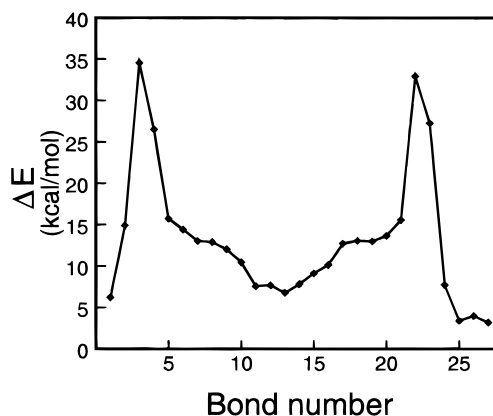
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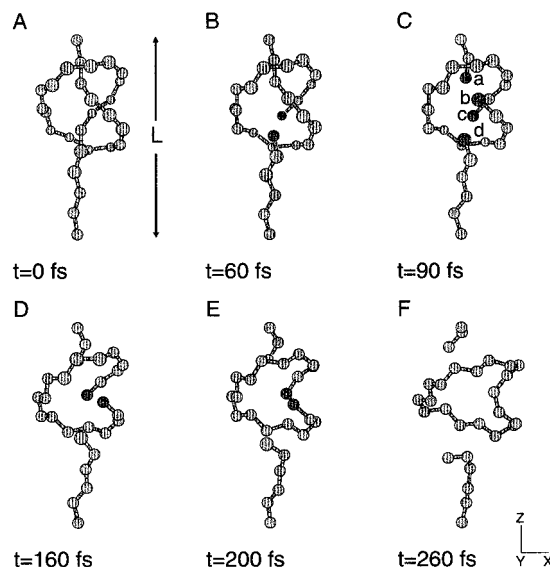
the molecule, i.e., the  $C_1-C_{28}$  distance  $L$ , to a series of fixed values. Calculations with gradually increasing  $L$  were performed until chain rupture occurred. Classical molecular dynamics (MD) simulations were used to preequilibrate the system for about 250 ps at any new value of  $L$ , thus bridging any two successive quantum-mechanical calculations. The minimum end-to-end distance between the terminal methyl group carbon atoms,  $L$ , required to produce chain rupture on the time scale of the calculations in the knotted  $C_{28}H_{58}$  alkane was 13.5 Å. This corresponds to a contour length of the chain of ca. 41 Å, as compared to an equilibrium chain length of  $\sim 35$  Å.

The knotted polymer chain was studied using Car-Parrinello<sup>14</sup> molecular dynamics<sup>15</sup> based on density-functional theory (DFT) with Becke and Lee-Yang-Parr (BLYP)<sup>16</sup> for the exchange and correlation functionals. A valence-electron pseudopotential/plane-wave scheme was employed, with a kinetic-energy cutoff of 60 Ry, a  $\Gamma$ -point sampling of the Brillouin zone. Since chain rupture yields unpaired electrons, the spin variables were handled through the so-called local spin-density approximation.<sup>17</sup> Periodic boundary conditions were used with the aim of extending the present single-chain results to liquid-crystal systems at the same level of accuracy and without any loss of consistency.

First-principles MD is particularly useful in the study of molecular processes involving breaking and formation of chemical bonds. Even though DFT-based estimates of transition-state energetics have only limited accuracy,<sup>18</sup> the qualitative estimates of relative values of barriers between different reaction paths are generally more satisfactory.<sup>19</sup> In addition, we have shown elsewhere<sup>12</sup> that the methodology employed yields bond energies accurate to better than 2%. In the present case, as it will be shown in the following, the chemistry of gas-phase-like chain radicals in their earliest stages of life is dominated by barrierless reactions such as recombination and disproportionation. Even though the latter process is energetically less favorable than the former, the ratio of the respective reaction rate constants is about 0.4–0.6 for ethyl radicals and even larger for longer fragments. This is due to an activation barrier that, for both reactions, is zero within experimental error.<sup>20</sup> The occurrence of one of them, rather than the other, appears to be purely driven by dynamical factors, such as steric effects and topological constraints. The CPMD approach allows one to follow the dynamical evolution of systems with as many as a few hundred atoms. Interatomic forces are determined by the instantaneous electronic structure. Unlike classical force fields, this feature ensures an accurate description of very different situations such as, in the present case, changes in hybridization status and coordination.<sup>21</sup> To follow the dynamical evolution of the system at room temperature ( $T = 300$  K), we employed a time step of 6.0 a.u. (= 0.145 fs). The starting configuration



**Figure 1.** Strain energy distribution for a  $C_{28}$  *n*-alkane molecule that has been tied into a trefoil knot. The actual configuration, which has an end-to-end separation  $L = 14.0$  Å, is shown in Figure 2a. This representative configuration was obtained from a classical MD simulation using a force field model.<sup>13</sup> The system was evolved for 200 ps and then annealed for 50 ps.



**Figure 2.** The snapshots show the first 260 fs of dynamical evolution of the system. Only the carbon-atom backbone is drawn. Panel A gives the definition of  $L$  as the fixed end-to-end distance. In panels B–E the “interesting” carbon atoms are enlightened and labeled with letters in panel C (see text). The axis orientation is given in panel F.

employed in the CPMD calculations was obtained from a series of classical MD simulations with an empirical force field model.<sup>13</sup> We discuss in detail the situation shown in Figure 1, which corresponds to a large tensile load at the entrance and exit points of the trefoil.<sup>22</sup>

## Results

**Double Chain Rupture and Cycloalkane Formation.** The corresponding configuration is shown in panel A of Figure 2. Panels B–F depict the initial dynamical evolution of the carbon backbone of the knotted polymer. In less than 100 fs, the long chain molecule breaks at both the entrance and exit of the trefoil (panels B and C), thereby generating a large diradical **b–c**

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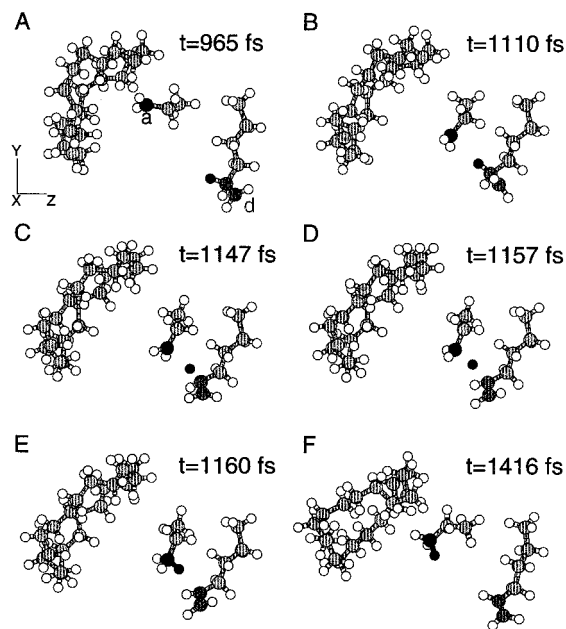
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(22) An estimate of the stretching force applied to the ends of the chain is about 1 nN, which is likely to be soon attainable in experiments with optical tweezers<sup>11</sup> or atomic force microscope (AFM)<sup>10</sup> techniques. As pointed out in ref 23, the typical loading rate of MD simulations ( $\sim 10^{12}$  pN/s) is, however, well beyond the reach of experiments, around 1–10 pN/s for the laser tweezers and  $10^4$ – $10^5$  pN/s for AFM.

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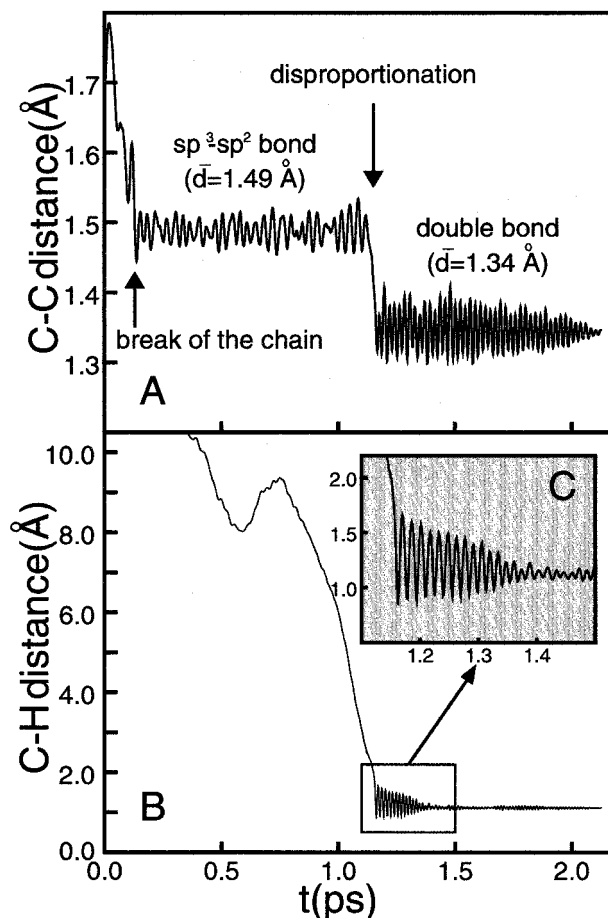


**Figure 3.** Snapshots of the dynamical evolution of the system after the formation of the cyclic alkane. Carbon atoms are displayed in gray and hydrogens in white. One of the two active carbons and the hydrogen atom that is to be abstracted are shown in black. The other unsaturated carbon and its bonded C atom are displayed in dark gray. In panel A the two active carbons are labeled according to the notation of Figure 2c, and the axis orientation is given.

(following the labeling scheme of panel C) and two smaller radicals **a** and **d**. The system is simply unable to redistribute the imposed tensile stress (see Figure 1) quickly enough to avoid a second bond dissociation.<sup>24</sup> Slightly more than half of the total strain energy ( $\sim 300$  kcal/mol) is released into radical formation energy ( $2 \times 83$  kcal/mol). The remaining part is transformed into kinetic energy of the radicals, that strongly recoil after the chain actually “snaps”.

After the generation of the three radicals, one might have expected to observe the radical recombinations a–c and b–d, thus creating an unknotted strand from the knotted one. However, instead, the radicals are so strongly reactive that, within about 150 fs after the chain rupture, the carbon atoms labeled as b and c form a chemical bond (panel E). This phenomenon is favored by the previously mentioned recoiling of the b and c fragments after the rupture that come very close to each other and thus recombine. This reaction results in the formation of a  $C_{19}H_{38}$  cyclic alkane, still leaving two active radical fragments, one  $C_3H_7^*$  (a) and the other  $C_6H_{13}^*$  (d), whose terminal methyls remain anchored to their initial positions, separated by  $L = 14.0$  Å. The “constraint” on the terminal methyls, thus, inhibits the direct a–d recombination (panel F). This is precisely the situation that is obtained if a knotted polymer is broken using a laser tweezers technique.<sup>6</sup>

**Disproportionation.** In the case of an isolated knot, to have a reaction between the fragments a and d, it will be necessary to remove the constraint on the terminal methyls. However, due to periodic boundary conditions, the simulation system we employ is not completely isolated; it is surrounded by its periodic images. In the present case, the box length in the  $z$  direction, i.e., the direction along which the linear ends of the knotted chain are aligned, is short enough to allow the two broken radicals to interact with their periodic images *after the*



**Figure 4.** Panel A: time evolution of the bond length of the atoms highlighted in dark gray in Figure 3. Panel B: time evolution of the distance between the carbon and the hydrogen atoms displayed in black in Figure 3. The inset (panel C) shows an enlargement of the large-amplitude C–H vibrations following the abstraction reaction.

*knot breaks*. This happens because, after the trefoil ruptures, the fragments recoil strongly along the  $z$  direction and the  $-z$  direction, respectively. In particular, as shown in panels C–F, the  $z$  coordinate of the atom labeled as a tends to increase, while the opposite is true for the d atom.

Figure 3 illustrates the subsequent dynamical evolution of the system, starting about 700 fs after the ring closure that generated the cyclic alkane. It is noteworthy that the longest of the two fragments (whose unsaturated carbon atom is labeled as d) is actually the periodic image, in the  $z$  direction, of the bottom radical of Figure 2 (panels C–F).

A simple reaction that was expected to occur was the saturation of the dangling bonds through the recombination of the a carbon with the periodic image of the d atom. Instead, the shorter radical attacks the carbon bonded to the d atom (panel B), rather than the d carbon itself, “stealing” one of its hydrogens (panels C–D) and then recoiling away (panels E–F), in a typical disproportionation reaction.

This reaction takes place in a very short time ( $\sim 50$  fs), leaving the two terminal atoms of the longer fragment (displayed in dark gray) to form a double bond, thus saturating all the unpaired electrons. In panel F, the  $sp^2$  hybridization status of these two carbons is clearly observable from their coplanarity with the hydrogens to which they are bonded. The energy gain due to the disproportionation is  $\sim 55$  kcal/mol, which compares favorably with the experimental enthalpy of the analogous reaction between two ethyl radicals (60 kcal/mol). Because of the high

(24) A rough estimate of the time necessary for a longitudinal phonon to travel along the knot is  $\sim 200$  fs.

computational demand of first-principles calculations, we could only follow a few other trajectories. However, in each case we observed the same phenomena. Even though the results may not be meaningful in a strict statistical sense, the energetics of the activation barriers of the competing processes suggest that, on an ultrafast time scale, the occurrence of such reactions is dominated by steric effects, which, in the present case, tend to favor disproportionation against recombination. As expected, the cyclic alkane ring is stable and does not take part in any of these subsequent reactions.

The nature of the relevant bonds can be actually monitored throughout the simulation. In Figure 4 we show two meaningful atom–atom distances as a function of time. In panel A the bond length between the two carbon atoms colored in dark gray in Figure 2 is displayed. The three distinct situations that the system experiences can be clearly identified in this picture. In the very first part of the dynamical evolution ( $\sim 100$  fs), the C–C distance is larger than the single bond equilibrium length (1.54 Å). Here, although all the carbon atoms of the chain are still bonded, the whole system is highly distorted and all the bonds quite stretched. After  $\sim 200$  fs the knot breaks, and the C–C distance then oscillates around an average value of 1.49 Å, which is the typical bond length between  $sp^3$ - and  $sp^2$ -hybridized carbons. Shortly after 1100 fs of dynamics, the “black” hydrogen of Figure 2 is abstracted by the unsaturated carbon atom of the shorter radical (panel B), forming a stable bond with a large-amplitude vibration that relaxes in a time of about 200 fs. In this case, part of the rototranslational kinetic energy of the radicals is converted into molecular vibrations of the shorter a fragment, mainly the C–H bonds of the methyl group involved in the reaction.

Concomitant with the disproportionation reaction, the “dark gray” C–C bond length shortens and begins to oscillate around an average distance of 1.34 Å and at a higher frequency. This behavior, observable in the right part of panel A of the picture, is characterized by a shorter period vibration.

## Summary

In conclusion, we report herein a first-principles MD study of the dynamical evolution of hydrocarbon radicals generated by the breaking of a single polyethylene-like chain containing a simple trefoil knot. The present work suggests that the early stages of evolution are likely to generate interesting chemistry, due to the resulting unsaturated alkane fragments. The 1.5-ps time evolution we monitor is characterized by barrierless reactions that are biased by steric effects. The velocity distribution of the recoiling radicals at the rupture is a key factor and is intrinsically related to the topological constraints imposed by the presence of a trefoil knot. The most logical chemical reaction, namely chain recombination, is totally bypassed in favor of ultrafast phenomena including the formation of a diradical<sup>25</sup> that generates a cyclic alkane, followed by disproportionation and simultaneous carbon–carbon double bond formation. Observation of the phenomena reported herein is likely to present a challenge for experimentalists, particularly because the reactions occur in the femtosecond range.<sup>26</sup> The results we currently report do not include the effects of surrounding neighboring chains on the chemistry of the fragments. However, preliminary calculations on a knotted alkane embedded in a nematic liquid crystal of like molecules show that the environment does not seem to significantly modify the observed chemical reactions.

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