Molecular Dynamics

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Knots “Choke Off” Polymers upon Stretching

*Tim Stauch and Andreas Dreuw**

Abstract: *Long polymer chains inevitably get tangled into knots. Like macroscopic ropes, polymer chains are substantially weakened by knots and the rupture point is always located at the “entry” or “exit” of the knot. However, these phenomena are only poorly understood at a molecular level. Here we show that when a knotted polyethylene chain is tightened, most of the stress energy is stored in torsions around the curved part of the chain. The torsions act as “work funnels” that effectively localize mechanical stress in the immediate vicinity of the knot. As a result, the knot “chokes” the chain at its entry or exit, thus leading to bond rupture at much lower forces than those needed to break a linear, unknotted chain. Our work not only explains the weakening of the polymer chain and the position of the rupture point, but more generally demonstrates that chemical bonds do not have to be extensively stretched to be broken.*

Knots are ubiquitous topological features of polymers.[1–10] The probability that a polymer gets tangled into a knot rises exponentially with its length: As soon as a chain reaches the length of a few hundred repeating units, it is practically certain that the chain is knotted.[2,3,5,8,9] The most common knot that occurs in polymers is the overhand knot, which is well-known from macroscopic ropes commonly used in sailing and rigging. Although the overhand knot is the simplest and smallest knot and consumes the least material, it is known to reduce the strength of the rope by approximately 50 percent.[11] Interestingly, the rope ruptures at the “entry” or “exit” of the knot. Both effects—the weakening of the rope and the rupture in the vicinity of the knot—can also be observed at the molecular level.[12–14] In polymers, the rupture results in the formation of two radicals, which is attributed to mechanical stress mostly localized in the carbon–carbon bonds at the entry or exit of the knot.[13–15]

However, most previous work was based on constrained molecular dynamics (MD) simulations and the “united atom scheme”,[16,17] in which, for example, methylene bridges are described as pseudo-atoms. These methods have a number of drawbacks in the investigation of mechanical bond rupture in a polymer knot, since electronic degrees of freedom are not included explicitly and not all internal modes of the molecule that potentially play a role in the mechanochemical processes (e.g. torsions involving hydrogen atoms) are included in the united atom scheme. Due to the neglect of these important factors, the questions why polymers are weakened by a knot and why they break in its immediate vicinity have not been answered. Here we present a first-principles study in which we use both static EFEI (External Force is Explicitly Included)[18] calculations, which constitute quantum chemical geometry optimizations under an external force, and Born–Oppenheimer molecular dynamics (BOMD) simulations under constant tensile stress to investigate the mechanical properties of an overhand knot in a polyethylene chain under tensile stress. To quantify the various energy contributions that play a role in the rupture of the overhand knot, we use the JEDI (Judgement of Energy DIstribution) analysis, which we have reported recently.[19] The JEDI analysis is a quantum chemical analysis tool for the distribution of strain energy among all degrees of freedom in a molecule. Based on the harmonic approximation, an energy value is assigned to every bond length, bond angle, and dihedral angle of a mechanically strained molecule. In contrast to previous work, this procedure ensures that electronic effects are treated explicitly and that all relevant degrees of freedom are included in the analysis of the distribution of strain energy in a polymer knot. Further details on the computational methods can be found in the Supporting Information.

When a knotted polyethylene chain is stretched, most of the strain energy is stored in the torsions (Figure 1 A). The bond angles also store crucial parts of the energy and the significance of the bonds as energy reservoirs increases with increasing force. However, the percentage of strain energy in the carbon–carbon bond that ultimately breaks remains very low throughout the entire coordinate. In our calculations, the bond rupture occurs at a pulling force of 2.6 nN in opposite directions in the immediate vicinity of the knot (in comparison to 5.6 nN in a linear, unknotted chain), demonstrating that an overhand knot indeed substantially weakens the strength of a polyethylene chain.

To investigate the reason for this remarkable decrease in resistance to tensile stress, a more detailed analysis of the distribution of mechanical stress in the overhand knot that is stretched by 2 nN in opposite directions is helpful (Figure 2). Most of the strain energy in the bond lengths is stored by those bonds at the entry or exit of the knot. This proportion, however, is much smaller than the energy stored by the torsions around the curved part of the knot. This effect can also be observed when the total strain is considered (panel “Total” in Figure 2). While mechanical stress is evident in the bonds in the vicinity of the knot, much more strain is distributed around the curved part of the knot. This observation leads us to the physical picture that the curved part of the structure essentially “chokes” the chain and cuts it at the entry or exit of the knot. The mechanism of the choking becomes clear upon comparison to a linear, unknotted polymer, where all bonds are stretched and all angles are

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[*] M. Sc. T. Stauch, Prof. Dr. A. Dreuw
Interdisziplinäres Zentrum für Wissenschaftliches Rechnen
Ruprecht-Karls-Universität Heidelberg
Im Neuenheimer Feld 368, 69120 Heidelberg (Germany)
E-mail: dreuw@uni-heidelberg.de

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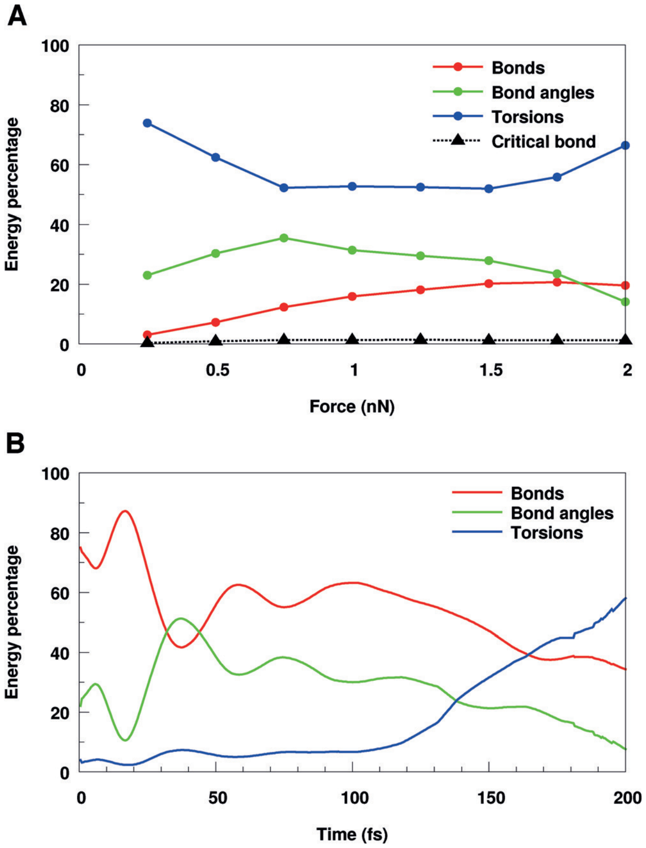

Figure 1. Distribution of the stress energy among the degrees of freedom in a polyethylene chain that includes an overhand knot. A) Static EFEI calculations. B) BOMD trajectory under the effect of an external force of 2 nN stretching the molecule in opposite directions.

displaced, so that mechanical stress is distributed relatively evenly over the entire chain. Hence, it takes strong forces to accumulate enough energy to break a bond in the chain, because all other bonds are also stretched significantly. If, on the other hand, a knotted chain is stretched, the torsions in the curved part of the knot act as "work funnels" that efficiently pass on the strain energy to the bonds that ultimately break, thus localizing the mechanical stress at the entry or exit of the knot and preconditioning the bonds in this region for bond rupture. As a result, the rupture of the chain occurs at much lower forces than in the case of the unknotted chain, since the other bonds remain relatively relaxed and mechanical stress is not "wasted" on them. It should be noted that this effect is clearly a result of the tightening of the knot: If the stretching force is too weak (see the right panel in Figure 2), mechanical stress is mostly localized in the linear part of the chain and the torsions are not strained enough to act as work funnels.

The conclusions drawn from the static EFEI calculations are supported by dynamic BOMD simulations of the overhand knot under a constant external force. At 0 K, a force of 2.05 nN ruptures the chain in the immediate vicinity of the knot after 932 fs. During the first 200 fs of the trajectory in which the knot is tightened by a force of 2 nN in opposite directions, the build-up of strain in the torsions is observable (Figure 1 B): The strain energy rapidly propagates from the terminal bonds, where the force is applied, to the center of the knot and then accumulates in the dihedral angles around its curved part. Color-coded movies of the trajectory shown in Figure 1 B can be found in the Supporting Information. BOMD trajectories carried out at 100 K, 200 K, and 300 K with different stretching forces show that thermal oscillations resulting from a higher temperature have a destabilizing effect on the knot. For example, at 300 K the time until bond rupture decreases from 795 fs upon application of 2 nN to 679 fs (2.05 nN) and 550 fs (2.1 nN), a result that is consistent with literature.[20] Further details can be found in the Supporting Information.

To further investigate why an overhand knot weakens a polymer, a model system was developed, in which a closed

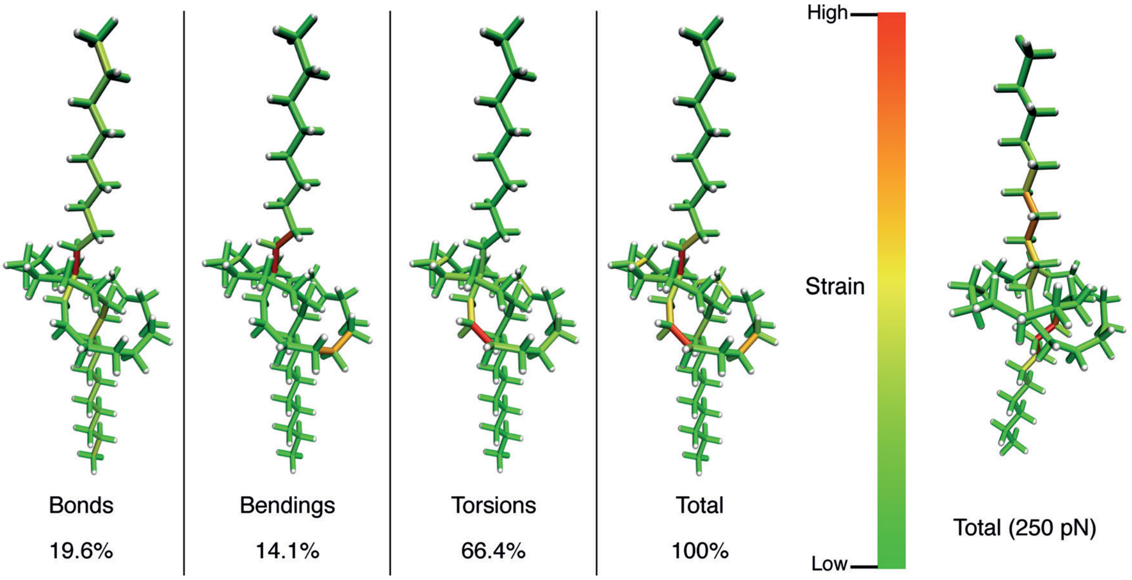

Figure 2. Distribution of stress energy among the degrees of freedom in a polyethylene chain in which an overhand knot is stretched by an external force of 2 nN. On the right, the total stress distribution is shown for a pulling force of 250 pN.

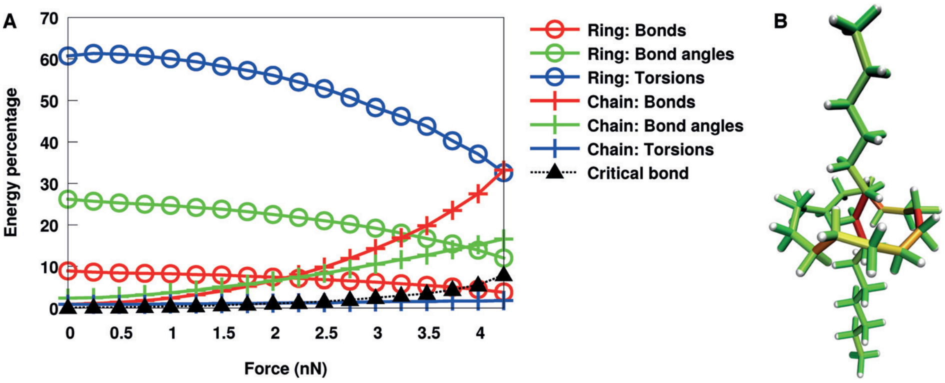

Figure 3. Distribution of stress energy in the model system with a 14-membered ring A) as a function of the external force and B) at an external force of 3.5 nN.

hydrocarbon ring was placed around a polyethylene chain. The tightness of the knot then simply corresponds to the size of the ring, with smaller rings signifying a tighter knot. As an example, the distribution of strain energy in the model system with a 14-membered ring, in which the chain is stretched by different forces, is considered (Figure 3 A). At the beginning of the stretching coordinate, by far the highest amount of energy is located in the torsions of the ring. Stretching the chain further leads to a transfer of strain energy from the ring to the chain. The bonds of the chain are particularly susceptible to this energy transfer and bond rupture ultimately occurs in the middle of the chain. This effect can also be observed in Figure 3 B, in which the model system with a 14-membered ring and an external stretching force of 3.5 nN is shown. The region closest to the ring stores by far most of the strain energy that is attributed to the chain. On the other hand, the amount of strain energy stored in the chain amounts to only one-third of the total strain of the system, while the rest is mostly localized in torsions of the ring.

The transfer of strain energy from the ring to the chain proceeds in a very similar fashion for all ring sizes (Figure 4 A). Only the rupture forces are different. The smaller the ring (signifying a tighter knot), the less force is needed to break the chain. Accordingly, the strain energies in the bond lengths, obtained via the JEDI analysis, as well as the maximum bond lengths before bond breaking decrease with decreasing ring size (Figure 4 B). We use a 14-membered chain without a ring, in which two bonds in the middle of the chain are stretched, as a reference and observe that, with increasing ring size, the maximum bond energies and bond lengths approach the values for the reference system. It is important to note that the energies shown in Figure 4 B are used exclusively for the stretching of the bonds that ultimately break. Despite the decrease of these energies with decreasing ring size, the total energy needed to break a carbon–carbon bond (typically between 1.5 and 2 eV) of course does not change when rings of different sizes are placed around a hydrocarbon chain (see also the Supporting Information). The torsions of the ring contribute the rest of the energy needed to break the bonds in the chain. As can be seen in Figures 3 A and 4 A, these two kinds of modes are coupled and transfers of energy from the torsions of the ring to the bonds in the chain are possible. In other words, the deformation of the ring preconditions the critical bonds in the chain for facilitated rupture. Mechanistically, the transfer of energy from the ring to the chain is a result of the angle bendings in the chain, since, as the angles gradually approach linearity upon stretching, the torsions of the ring can relax and the ring gets "smaller" and less strained. Hence, the bond rupture is a combined effect of bond stretching, angle bending, and torsional motions and it is not enough to consider only the mechanochemistry of the scissile bonds in pulling experiments. These observations support our view that the curved part of the overhand knot, for which the ring is a model, chokes the chain in its immediate vicinity due to the capability of the torsions to act as work funnels that localize the mechanical stress.

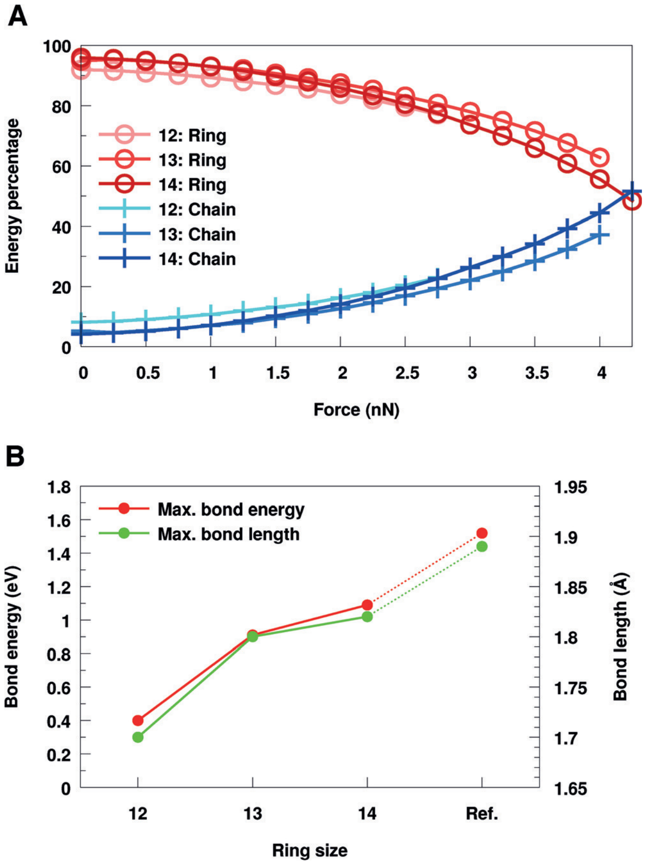

Figure 4. Comparison of the model systems with different ring sizes. A) Force dependence of the proportions of strain stored in the ring and the chain. B) Dependence of maximum bond energy and maximum bond length of the scissile bond on the ring size. A 14-membered chain without a ring, in which two bonds in the middle of the chain are exposed to a force, is taken as the reference (Ref.). Lines are included to guide the eye.

We have presented a first-principles study in which we have investigated the mechanochemical behavior of a polyethylene chain that is tangled into an overhand knot. Using the JEDI analysis, we found that when the polymer is stretched, most mechanical stress is localized in torsions around the curved part of the knot. The bonds at the entry or exit of the knot, one of which ultimately breaks, somewhat surprisingly do not store particularly large amounts of strain energy. Pulling at the ends of the chain rather tightens the knot, which in turn causes the curved structure to choke the chain in the immediate vicinity of the knot. This effect can be explained by the capability of the torsions in the knot to act as work funnels by effectively localizing the mechanical stress at the entry or exit of the knot and predissociating the bonds in this region. This is the reason why an overhand knot leads to a substantial weakening of the strength of a polymer chain. To what extent this observation can be transferred to macroscopic ropes remains unclear. Nevertheless, it is surprising that both kinds of ropes—macroscopic and microscopic—are weakened by an overhand knot by around 50 percent and rupture occurs at the same position. Moreover, our study demonstrates that bonds do not have to be excessively stretched to be broken in mechanochemical reactions. Investigating this effect further could lead to new perspectives in mechanochemical synthesis.

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