Tight Knots in Polymers

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Introduction

Since polymer strands are analogous to macroscopic ropes it is natural to ask if a polymer can be pulled into a tightly knotted structure that is difficult to untie. To be specific, is it possible to create stable, long-lived knots in polymers by stretching? DeGennes[1] has speculated that stable tight knots might account for certain long memory effects in polymer melts.

This note reports molecular dynamics studies on the stability of tight knots in polymers. These studies indicate that tight knots are unstable. Loosely knotted, model strands of polyethylene, atactic polypropylene, and atactic poly(1-butene) were constructed. The knots were tightened by stretching the strands, and then the strands were permitted to relax. In every case, 300 K thermal noise sufficed to loosen the knots in times around 10 or 20 ps. Morse potentials were used to model each carbon−carbon bond, which renders it breakable. The strands were stretched almost to the breaking point before they were relaxed. Therefore, these calculations indicate that at room temperature, a knotted polymer strand breaks under tension before it can form a stable tight knot.

Computational Details and Results

Strands of polyethylene, atactic polypropylene, and atactic poly(1-butene) were modeled with 78 main-chain carbon atoms and, in the case of polypropylene and poly(1-butene), with 38 methyl or ethyl sidegroups, respectively. Hydrogen atoms were modeled explicitly.

The intramolecular force-field, except for the carbon−carbon stretching potential, was adapted from the work of Sorensen et al.[2] Since it would make no sense to stretch chains beyond their natural breaking point, a Morse potential was used to model the carbon−carbon bonds. The Morse potential was selected to have the same minimum and the same curvature at the minimum as the corresponding harmonic potential of ref 2, and to have a dissociation energy of 82.6 kcal/mol.[3] Table 1 summarizes the force-field employed in this study.

Each chain was stretched by the application of external potentials. The potential

$$V_1 = (72\ \text{kcal/mol})(x - b_1)^2 \quad \text{if } x > b_1 \qquad (1a)$$

$$V_1 = (72\ \text{kcal/mol})(x + b_1)^2 \quad \text{if } x < -b_1 \qquad (1b)$$

$$V_1 = 0 \quad \text{if } -b_1 \le x \le b_1 \qquad (1c)$$

where x represents the x-coordinate of an atom, confines the atom to a slice of space bounded by $x = \pm b_1$. Likewise, the potential

Table 1. Force-Field Parameters[a]

C−C bonds	$V = 82.6\{\exp[-1.934(R - 1.53)] - 1\}^2$
C−H (primary) bonds	$V = 338(R - 1.09)^2$
C−H (scondary-tertiary) bonds	$V = 328(R - 1.09)^2$
C−C−C angles	$V = 53.8(\theta - 1.9373)^2$
C−C−H angles	$V = 42.9(\theta - 1.9106)^2$
H−C−H angles	$V = 38.5(\theta - 1.8832)^2$
X−C−C−Y torsions	$V = 0.139(1 + \cos 3\phi)$
C···C nonbonded	$V = 15000 \exp(-3.09R) - 641/R^6$
C···H nonbonded	$V = 4320 \exp(-3.415R) - 138/R^6$
H···H nonbonded	$V = 2650 \exp(-3.74R) - 27.4/R^6$

[a] Length, angle, and energy units are Å, radians, and kcal/mol, respectively. Nonbonded interactions act between all four-center or higher pairs out to a cutoff of 10 Å.

$$V_2 = 0 \quad \text{if } x > b_2 \qquad (2a)$$

$$V_2 = (72\ \text{kcal/mol})(x - b_2)^2 \quad \text{if } 0 \le x \le b_2 \qquad (2b)$$

$$V_2 = (72\ \text{kcal/mol})(x + b_2)^2 \quad \text{if } -b_2 \le x < 0 \qquad (2c)$$

$$V_2 = 0 \quad \text{if } x < -b_2 \qquad (2d)$$

excludes the atom from the region bounded by $x = \pm b_2$. The two values b_1 and b_2 were constrained to move in concert: $b_1 = b - 0.375$ Å; $b_2 = b + 0.375$ Å. Figure 1 displays the positive branches of these two functions. A few main-chain atoms on each end of the chain were subjected to V_2, thereby pulling simultaneously one end into the region $x < -b$, the other into the region $x > b$. Adjacent to these, one carbon atom at each end was "neutral," experiencing neither external potential and hovering, therefore, near $x = \pm b$, respectively. All other main-chain carbons, including those in the knotted region of the chain, experienced V_1. The chain is stretched by increasing b, and the chain is unable to untie, even when the knot is loose. No hydrogens nor carbons in side groups experienced these potentials.

The equations of motion were integrated by the velocity Verlet algorithm[4] with a time step of 1 fs. Interaction with an external heat bath was simulated by rescaling all velocities after each time step to enforce a kinetic temperature of 300 K.[4] Constant temperature simulation is essential to this problem, because as the chain stretches its total potential energy increases and at constant total energy, the chain would grow progressively colder. Velocity rescaling at each time step is usually considered to be a rather crude constant temperature technique, but is nevertheless adequate for this problem. Furthermore, at intervals of 1 ps, the atomic velocities were completely randomized and selected anew from the appropriate Boltzmann distribution.

Loosely knotted initial structures were prepared on the diamond lattice and subjected to the potentials of eqs 1 and 2, as described above, and annealed at relatively low b values for a period of 10 ps. Then each chain was stretched through a series of stages, each of duration 1 ps, during which the value of b was set 0.25 Å greater than its previous value. At the end of each stage, the atomic coordinates were written to hard disk and the velocities were newly randomized. This continued until chain fracture. The last unfractured chain

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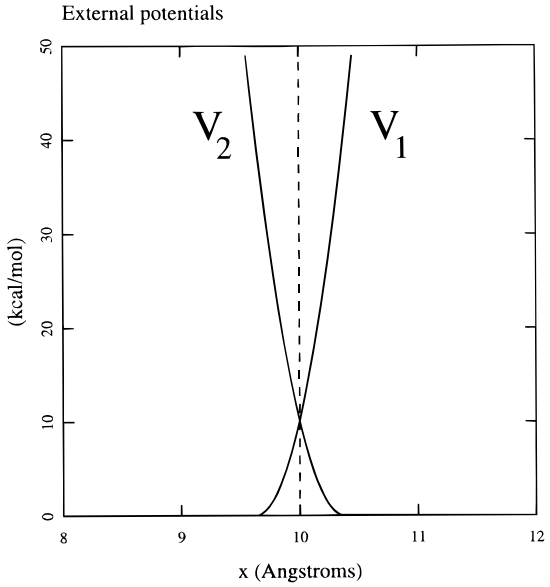

Figure 1. The two external potentials, V_1 and V_2, employed to stretch the chain and to keep it from coming unknotted when still loose, plotted for $b = 10$ Å. Only the positive branch is displayed; both V_1 and V_2 are symmetric about $x = 0$. Respectively, they confine atoms to regions $|x| < b$ and $|x| > b$.

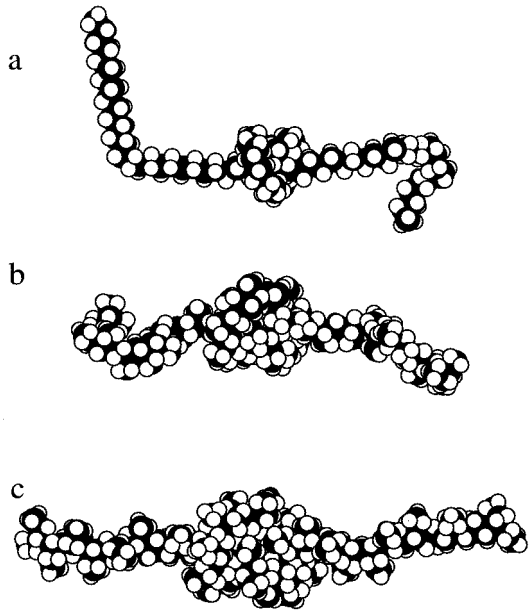

Figure 2. Planar projections of tight knots in models of (a) polyethylene, (b) atactic polypropylene, and (c) atactic poly(1-butene).

in each sequence was then annealed for 10 ps with the stretching potentials still present. Figure 2 displays planar projections of the resultant structures.

One way of quantifying the stresses in the chain is to plot average carbon−carbon bond lengths. Figure 3 displays lengths of the main-chain carbon bonds averaged over the 10 ps anneal described above. The most prominent features are the two maxima in each curve. These occur along the chain at the boundaries of the tight knot and of course indicate that the stress accumulates at these two points. One of the two peaks always corresponds to the bond which eventually breaks. The separation between the two peaks, 23, 28, and 36,

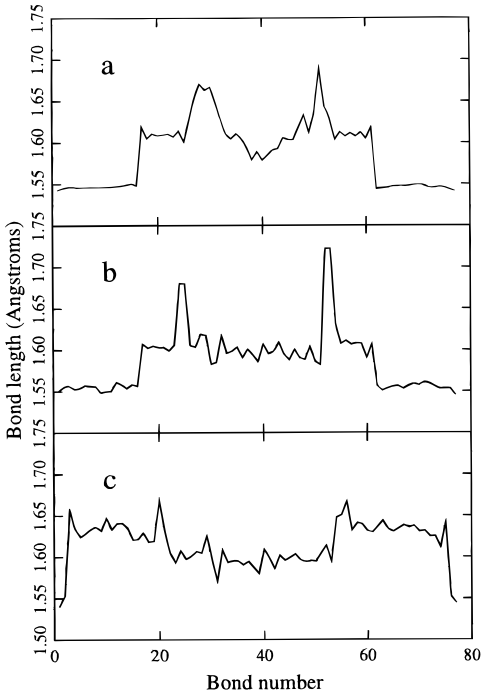

Figure 3. Mean bond lengths of backbone carbon−carbon bonds in the maximally tightened chains of (a) polyethylene, (b) atactic polypropylene, and (c) atactic poly(1-butene). The two peaks mark the boundaries of the knotted part of the chains and indicate that the stress is accumulated at these bonds.

respectively, measures the chain length required to form a tight knot in each of the three polymers. The extreme right and left parts of the curves correspond to the ends of the chain that are confined by V_2. These bonds assume unstrained lengths of about 1.54 Å. The strain in each of the side groups of both polypropylene and poly(1-butene) was also measured, although not plotted here. There was no appreciable strain in any of the side groups.

The stability of these knots is determined, of course, by the time required for them to loosen following removal of the stretching potentials. In all likelihood, this is an activated process. Because of the possibility that the recoil of the chains upon removal of the tension would facilitate traversal of the activation barrier and cause us to underestimate the lifetime of the tight knot, I felt it prudent not to remove the tension all at once. Rather, the tension was relaxed gradually by stepping the system back through the 1 ps stages, decreasing b by 0.25 Å in each stage. Then the chains were annealed at 300 K in the absence of any external potentials. This annealing continued, with observations taken at intervals of 10 ps, until the knot had come loose. The knot was determined to be loose based on direct observation of chain projections, and through measurement of the carbon-bond strain. In the case of poly(1-butene), the knot had already come loose prior to this annealing. In the other two cases, total annealing times of 20 ps or less were adequate to loosen the knot.

Discussion and Conclusions

Unless the traditional molecular mechanics potentials such as those given in Table 1 are unable to adequately represent such highly strained chain molecules, the results of these calculations indicate that thermal

fluctuations at room temperature are able to loosen tight knots in chains in times of around 10 ps. Furthermore, the knots in question were maximally tight, since in each case they were strained almost to the point of breaking. The loosening of the tight knot is undoubtedly an activated process, in which case, these calculations indicate that the activation energy is not large. One might expect the activation energy to be higher in chains with side groups, but on the other hand, the side groups might also interfere with knot tightening. These calculations probed the effects of side groups by comparing both polypropylene and poly(1-butene) with polyethylene. They indicate that the side groups have no effect on knot stability.

References and Notes

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