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Title: How far can a rubber molecule stretch before breaking? *ab initio* study of tensile elasticity and failure in single-molecule polyisoprene and polybutadiene

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Abstract

We present *ab initio* calculations of the internal C-C bond dissociation curve for single molecules of (*cis*1,4) polyisoprene, polybutadiene, and polyethylene, all of comparable length. We define 'bond rupture' as that point on the reaction coordinate where the unrestricted Kohn-Sham, or diradical, solution falls below the restricted, or closed-shell, solution. Using this well-defined though crude approximation, we find that rupture occurs at a tensile force of 6.8 nN for polyisoprene and 7.2 nN for polybutadiene. Their respective rupture strains are 45% and 42%. Our calculations show that the energy density vs. extension is not sensitive to the length of the molecule, i.e., it is essentially independent of the number of isoprene units contained. These relatively large rupture strains have important implications for understanding the failure mechanism in rubber, and imply that purely enthalpic chain stretching must commence well before tensile failure occurs.

I Introduction

Isoprene and its variant butadiene are rubber elastomers having high commercial importance as well as historical relevance to classical elasticity theory, which had its origins in the 1930's. The classical theory attributes the retractive force in rubber to the change in conformational entropy of the individual polymer chains that comprise the cross-linked network as the rubber is subjected to strain. As the network chains are straightened, their conformational entropy decreases, leading to a change in the free energy. The putative mechanism that produces the retractive force is the tendency for the polymer chains to seek conformations with more probable (higher entropy) end-to-end distances in response to random thermal collisions. The theory is formulated from within the framework of thermodynamics and numerous variations have been derived over the past 70 years for various ideal network models.

Common to all of the theories is the assumption that inter-atomic bond lengths are fixed, i.e, not capable of storing energy or breaking. Recently, Livadaru et al.¹ have extended the classical theory by allowing the interatomic bonds to be elastic. However, none of the classical elasticity theories are able to include a physical failure mechanism. For this reason, the question of how network chain failure develops has been largely ignored.

Recent advances in Atomic Force Microscopy (AFM) technology have enabled the measurement of mechanical bond rupture in single molecules under tensile strain^{2 3 4}. At the same time, increased computational capability has made analogous *ab initio* theoretical studies of the rupture process feasible^{5 6 7 8 9}. AFM experiments and Density Functional Theory (DFT) simulations have been applied to a variety of biomolecules^{5 10 3 9 11}, organic molecules^{7 12}, and inorganic molecules^{6 8 13 4}. *Ab initio* Molecular Dynamics simulations of mechanically induced bond rupture have been carried out for cis-polyacetylene⁷ and polydimethylsiloxane⁸. Theoretical frameworks that take into account the effect of thermal vibrations have been proposed by Beyer⁶, Rohrig et al.⁷ and Neuert et al.¹¹. Experimental values for bond rupture forces^{2,5} of ~2 nN appear to be associated with the attachment region of the polymer rather than an intra-chain C-C bond. Rupture forces for C-C bonds calculated with DFT for propane⁶ and cis-polyacetylene⁷ range between 6 and 9 nN.

In an attempt to elucidate the molecular basis of chain failure in rubber networks, we have performed DFT calculations for single molecules of (cis1,4) polyisoprene and polybutadiene as they are extended from their equilibrium conformation towards the dissociation limit. If one defines a coordinate for extension as the distance between the two terminal carbon atoms of an oligomer of butadiene, then a reaction path can be defined by optimizing all remaining coordinates under the constraint of a fixed extension. One intuitively expects a bond rupture to occur somewhere along that path. If one imagines a simple dissociation of the C-C bond into two radicals, then the reaction coordinate should be a smooth function of the extension coordinate, as in the dissociation of H₂. These radical sites do not have to result in unpaired spin on the atoms involved in bond rupture; in fact we find significant electronic and geometric rearrangement. Other channels are, of course, potentially more energetically favored. For example, it may be that hydrogen transfer from one fragment to another is a favored pathway, and that should be revealed in the subsequent relaxation of other vibrational modes. In any event, the precursor to these events would seem to involve breaking of a C-C bond and the

generation of two weakly coupled fragments. One, admittedly arbitrary, way to define this transition is that point along the extension curve at which an unrestricted Kohn-Sham solution lies lower in energy than the restricted, closed shell, solution. That definition suffers from the fact that the actual extension curve may be continuous, but it has the advantage of pinpointing the 'weakest' bond, of allowing geometric relaxation in other coordinates to accompany extension, and of being well defined. It is the approach we use here in order to understand the internal reorganization and energy storage accompanying extension of a single molecule.

II Simulation methodology

All calculations were performed with the Gaussian03¹⁴ suite of electronic structure codes using the hybrid B3LYP/ functional, in conjunction with a standard 6-31g(d) basis set. The spin unrestricted self-consistent-field (SCF) calculation of the ground state at each point along the extension curve is straightforward. At small distances, the solution and energy is identical to the closed shell restricted result; however, at larger distances, a broken symmetry solution emerges corresponding to two diradicals. Since it is possible to find local minima to the SCF equations in the vicinity of the crossing, we performed several tests to more firmly locate the minimum: these include following the UKS solution from longer extension to shorter, generating an initial guess by mixing the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), and generating an initial guess from the orbitals of the triplet ground state.

As a compromise between network chain fidelity and computational feasibility, we chose model systems containing two isoprene or butadiene units. Two extra C atoms were added at the ends, one necessary to include 4 bonds for each isoprene or butadiene unit, and an additional C to enforce symmetry and reduce end effects. A two-dimensional projection of the isoprene molecule is shown in Figure 1. Atom 32C is in a pendant methyl group bonded to atom 2C. The equilibrium conformation was obtained by optimizing the electronic energy, allowing all atoms to move. The equilibrium end-to-end distances for the butadiene and isoprene-based chains were 1.0658988 nm and 0.9632810 nm, respectively. Using this equilibrium as the initial state, a scan of the potential energy was performed by moving the end carbon atoms away from one another in steps of 0.05, 0.1 or 0.15 Å, depending on the number of isoprene or butadiene units in the molecule. The end atoms, 1C and 2C, were kept fixed during optimization at each end-to-end distance. Because of the extra end C atoms, there are two possible definitions for that part of the chain comprising an integral number of butadiene or isoprene units, depending on which end C atom is included, R_{1-19} and R_{2-5} , where the subscripts refer to atom numbers in Fig. 1. The average of these equilibrium lengths for molecules containing two butadiene and isoprene units were 0.884179 nm and 0.8478015 nm, respectively.

III Results and discussion

The potential energy as a function end-to-end extension factor (R/R_o) for the model chains, composed of two butadiene or isoprene units, is shown in Fig. 3. Initial optimization of both molecules results in cis conformations (even if the molecule is initially in a trans configuration) and this conformation does not change, even at high

extension. This behavior has been observed previously⁷ and is attributed to the large cis-trans energy barrier. Apparently the force required to overcome the cis-trans barrier is greater than the tensile strength of the chain. In Fig. 3, we see that bond rupture, as we have defined it, occurs at extension factors (λ) of 1.36 and 1.42 for butadiene and isoprene, respectively, and is accompanied by a decrease in potential energy of \sim 110 kcal/mole. The fragment state immediately after rupture contains two unpaired electrons, which accounts for the plateau energy of \sim 60 kcal/mole. For the isoprene molecule, rupture, occurs at the single bond between atoms 14C and 17C; for the butadiene case, two bonds fail simultaneously, 6C-9C and 14C-17C. Presumably, the pendant methyl groups in the isoprene molecule break the symmetry enough to make one bond slightly weaker. We attempted to find an avoided curve crossing for the rupture transition state by moving the two fragments back toward one another and performing an optimization at each step, but we did not see the C14-C17 bond reestablished. We do not believe that a curve crossing exists in view of the large (\sim 110 kcal/mole) energy barrier at rupture, which is in agreement with Beyer's⁶ conclusion.

The tensile forces as a function of extension for polyisoprene and polybutadiene, shown in Fig. 4, were calculated by numerically differentiating the energy profiles. Due to the extra end carbon atom in our models, there is some ambiguity in the end-to-end length for the double butadiene or isoprene units. There is also some uncertainty in the fraction of the total potential energy associated with their energy. Since the extra bond is a double bond, it tends to stretch less and store less energy than the single bonds in the chain, and we estimate that the energy error introduced by the extra carbon atom is less than 5%. Rupture occurs at a tensile force/ strain of 6.8 nN/ 45% for isoprene and 7.2 nN/ 42% for butadiene and these values are consistent with previous calculations^{6, 7}. The discontinuity in the forces, near an extension ratio of 1.18, is associated with a conformational change due to a rotation about the single bond between carbon atoms 9 and 11. The least squares quadratic fit to the energy vs. strain profile for isoprene ($E(\epsilon) = k\epsilon^2$, $k = 874.37$ /extension factor), where $\epsilon = \lambda - 1$, is shown with the dashed line. The quadratic fit is in disagreement with the computed energy by more than a factor of two at low extension. We investigated both the singlet and triplet state for the 2-unit isoprene system. The triplet state for the unstretched equilibrium conformation lies 61.89 kcal/mole above the singlet state. The stored energy vs. extension for the triplet is compared to the singlet in Fig. 5

To establish that our results are relevant to longer chains representative of a rubber network, we also performed extension scans for isoprene molecules containing 1 and 3 isoprene units. In Fig. 6, we compare the energy stored per isoprene unit as a function of extension factor. The failure behavior (rupture energy density and maximum extension) is similar for all three cases.

The vibrational entropy was computed at each end-to-end distance as the The vibrational entropy as a function end-to-end extension is shown in Fig. 7. We find that the entropy decreases slightly from the initial state to an extension approximately half way to the rupture strain, and then increases back to nearly the original value. At 300 K, the change in free energy due to the change in vibrational entropy at the mid point is 2.4 kcal/mole, which is less than 12% of the change in potential energy. At rupture, the net change in vibrational entropy is slightly positive by 0.003 kcal mole⁻¹ °K⁻¹. It does not appear that vibrational entropy plays a significant role in chain stretching.

IV Phenomenological discussion of relevant experiments

The relatively large rupture strains and forces that we calculate for rubber molecules has an important implication with regard to rubber elasticity: Because isoprene molecules must be stretched by a factor of 1.45 to achieve rupture, at moderate to high strains, rubber elasticity must include a substantial enthalpic component. In this section, we examine how chain stretching and rupture might affect three types of experiments: 1) tensile stress/ strain, 2) sample heating accompanying rapid tensile strain and 3) the snap-back velocity of stretched rubber. Our goal is to see if the rupture strains and forces that we have calculated can provide a consistent estimate for the network density (number of chains per unit volume) in tension for all three types of experiments.

The tensile failure of rubber is usually evidenced by a clean fracture, clearly due to the rupture of covalent bonds at some narrow region along the sample. Presumably, near the failure strain, network chains have ruptured throughout the sample, weakening the network. Catastrophic fracture then occurs at the weakest point in the network. A typical tensile stress/ strain curve for isoprene rubber is shown in Fig. 8. If an isoprene sample fails at an extension ratio of 7, then the last chains that ruptured before must have commenced stretching at an extension factor of 4.8 (7/1.45). Since the cross links of a rubber network each nominally contain four chains, the network remains intact for a single chain failures. Consequently, at least two chains emanating from a cross link must rupture before the last chain can fail. This suggests that enthalpic stretching, accompanied by rupture, must begin at strains 45% below the failure strain, $\lambda \sim 3.3$. A reasonable assumption is that the elastic response of rubber at moderate to high strains is dominated by purely enthalpic chain stretching. One might expect that the bond-rupture force can be related to the breaking stress of a rubber sample under tensile strain. A typical value for the stress at break¹⁵ is ~ 6 MPa for isoprene rubber and it occurs at an extension factor of ~ 7 . Unfortunately, the cross link density is not easily measured and it is not reported for this experiment. We can make an estimate for the nominal cross link density in isoprene rubber from a recent paper by Mott and Roland¹⁶ which reports the concentration of crosslinker as 1 phr (part per hundred) yielding a cross link density of ~ 33 mole/m³. Assuming one tetravalent crosslink for each dicumylperoxide (two network chains per crosslink), this corresponds to a chain density of 66 moles/m³ (4×10^{19} cm⁻³), with an average chain length of 170 isoprene units (75 nm). If we make the additional assumption that all of the tensile stress at failure is due to chains being stretched and that the average stretching force about $\frac{1}{2}$ the rupture force, F_{rupture} (3.4 nN), then the density of chains required for a stress of 6 MPa is 2.4×10^{16} cm⁻³, or $\sim 0.06\%$ of the nominal network chain density. The mechanism requires that only a small fraction of the network chains are in a stretched state at sample failure.

Our simulations show that the total potential energy stored in a chain just before rupture can be quite large, ~ 80 kcal/mole per isoprene unit. For long chains, representative of a rubber network, we are justified in ignoring the final state energy (the plateau in Fig. 3) of ~ 60 kcal/mole, since it is independent of the chain length and small compared to the total stored energy. When a network chain fails, all of its stored energy will be converted to heat. Using our estimate above for network chain length, about 170 isoprene units¹⁶ suggests that a chain can store $\sim 14,000$ kcal/mole (9.7×10^{17} J/chain) at rupture. We would expect two things to happen if network chains are ruptured during

tensile strain: 1) The temperature should increase and, 2) the sample should experience damage, i.e., permanent set. While we do not have enough detailed information about rubber networks to make a quantitative prediction for how much the temperature should increase as it is strained, experiments clearly show that the temperature does increase. Measurements by Dart et al.¹⁷ show an abrupt, 10 C increase in temperature at extension factors in the range of 3 to 6. Using the specific heat for rubber of 1.95 J/g¹⁸, this temperature increase corresponds to an energy density of 19.5 J/g or 17.7 J/cm³ for the nominal rubber density of 0.91 g/cm³. We can obtain an estimate of the density of chain ruptures by dividing this energy density by the average energy stored in a chain at rupture (9.7×10^{-17} J/chain), or 1.8×10^{-17} . This corresponds to ~0.5% of nominal network chain density of 4×10^{19} cm⁻³, obtained above.

Finally, we can estimate the active network fraction that would be required to explain the high retraction velocities observed in snap-back experiments¹⁹. In these experiments, the tip and midpoint velocity were recorded after one end of a stretched rubber sample was abruptly released. From an initial extension factor of 5.5, the tip retraction velocity was observed to be as high as 100 m/s and constant over the retraction event. We can estimate the fraction of chains in a stretched state to the total number of chains, by equating the average stored energy in the chain to the final kinetic energy of the chain and associated material.

$$1/2Mv^2 = E_{chain} \quad (1)$$

The mass associated with each chain is then given by:

$$M = 2E_{chain} / v^2. \quad (2)$$

Assuming that the stored energy in the stretched chains is ~½ of the energy at rupture, we estimate the stored potential energy, E_{chain} , to be 4.4×10^{-17} J. Using the observed velocity value of 100 m/s, the mass associated with each active chain, M , is 8.9×10^{-19} g. For the nominal chain length and network density that we calculated above, this corresponds to a ratio of 1 active chain for every 392 network chains, or ~0.25 % of all network chains.

V Conclusions

Using *ab initio* methods, we have calculated the force-extension curves for single molecules containing two butadiene or up to three isoprene units. The consistent rupture strains and forces over a range of chain lengths establishes that our results are representative of longer chains, i.e., polybutadiene and polyisoprene. Bond rupture occurs at a tensile force and strain of 6.8 nN/ 45% for polyisoprene and 7.2 nN/ 42% for polybutadiene. These relatively large rupture strains imply that purely enthalpic chain stretching must commence well before tensile failure occurs. For example, if a sample fails in tension at an extension factor of 7, the rupturing chains must have commenced stretching at an extension factor of 4.8. And if enthalpic stretching is the dominant process at failure, then the large rupture forces imply that only a small fraction (~0.1%) of the network chains are in a load bearing, stretched state. We have estimated this value by inferring a nominal network chain density from a lightly cross linked rubber described by Mott et al.¹⁶. Estimates of the active fraction of network chains from temperature increase and snap-back velocity experiments yields similar low values. Since the network density was undoubtably different in the failure stress, temperature increase and snap-back experiments that we used for comparison, factors of five or more inconsistency are

not surprising. To make quantitative comparisons with experiment will require a consistent set of experiments all using the same, well-characterized material.

Acknowledgments

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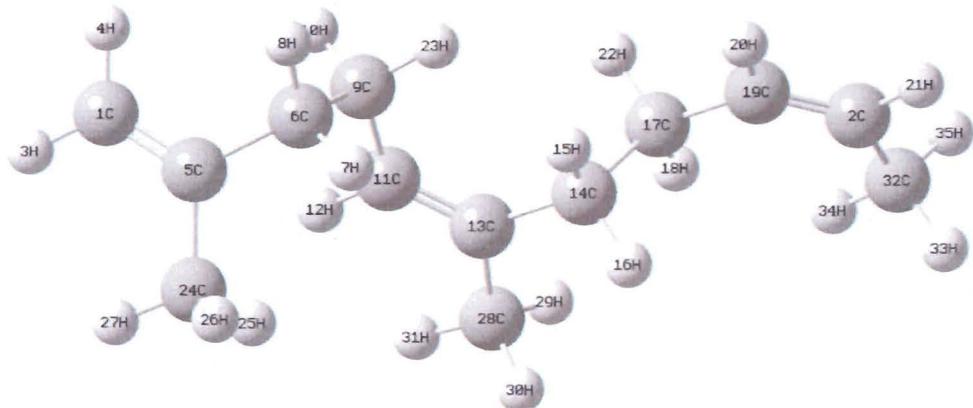


Fig. 1 Initial conformation of double isoprene molecule with additional end carbon atoms. Atoms 24C, 28C and 32C are in pendant methyl groups.

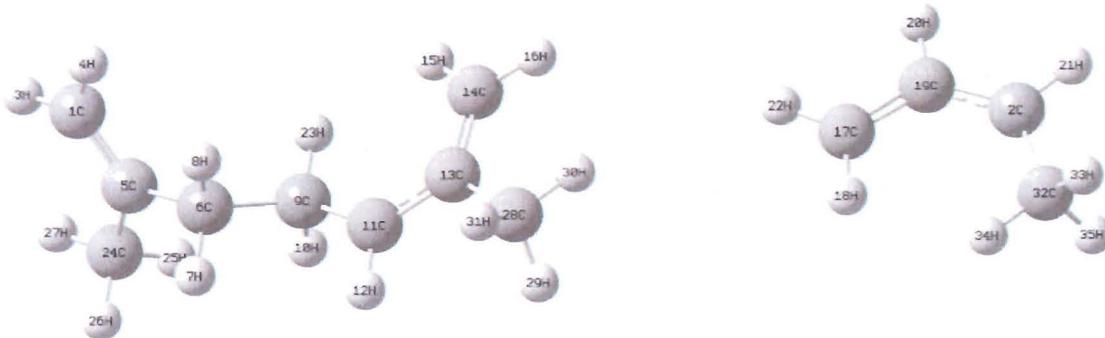


Fig. 2 Conformation just after rupture of covalent bond between atoms C14 and C17.

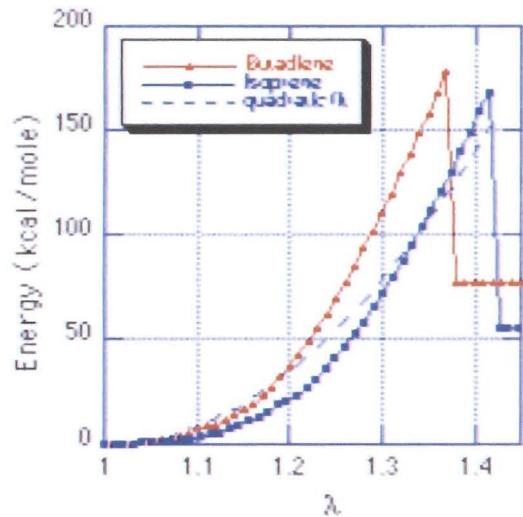


Fig. 3 Electronic energy following optimization as a function of extension factor for butadiene (dashed curve) and isoprene (solid curve). Dashed blue line is least squares quadratic fit of isoprene energy. The abrupt drop in energy is due to bond rupture.

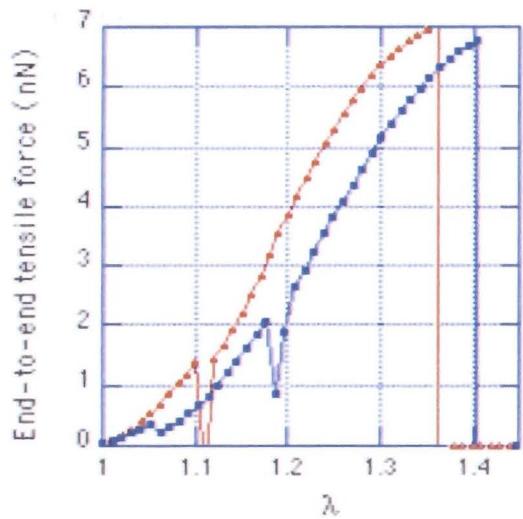


Fig. 4 Tensile force as a function of extension factor for butadiene (dashed curve) and isoprene (solid curve) obtained by numerically differentiating the energy vs. distance.

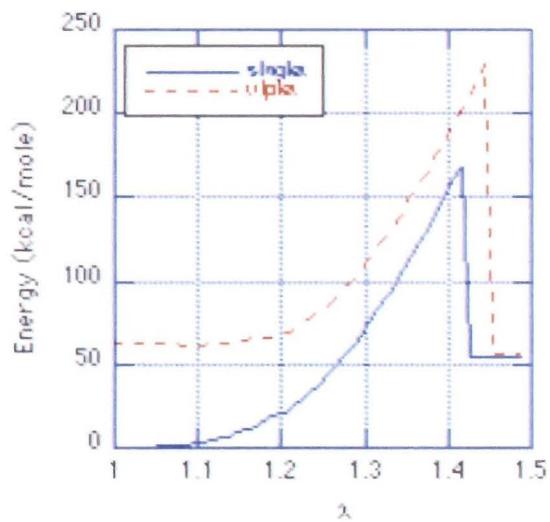


Fig. 5 Comparison of stored energy vs. extension factor (2-unit isoprene chain) for singlet (blue) and triplet (red) states.

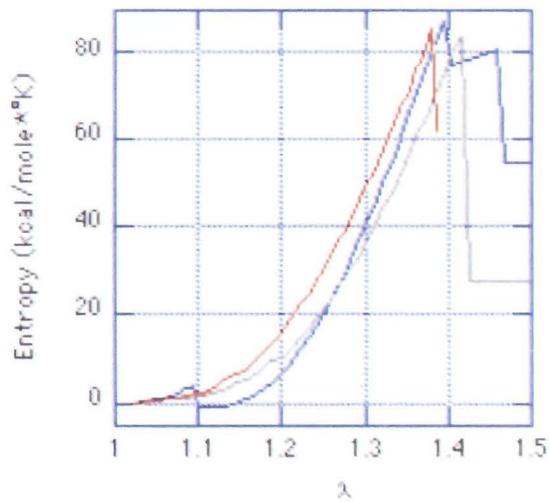


Fig. 6 Comparison of stored energy per isoprene unit vs. extension factor for isoprene chains containing 1 (blue), 2 (red) and 3 (green) isoprene units.