



Insight into the implication of high-loading mechanical force on the mechanical bond

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Mechanical bonds are good candidates for functional materials due to their inherent flexible mobility. Nevertheless, the mechanical properties of these systems need to be evaluated before any plausible applications. It's well known that interlocked structures can efficiently absorb energy under low tension owing to the 'pulley effect' between the rings. But the mechanical bond will eventually rupture if mechanical energy is strong enough and little is known about this process. Recent advancements in the study of polymer mechanochemistry alongside mechanical bonds have unveiled promising progress. In this perspective, we discuss the mechanical susceptibility of these mechanical bonds, specifically focusing on the rupture of covalent bonds within the interlocked structures when subjected to high-loading forces and the underlying mechanisms. Furthermore, we outline the forthcoming challenges in the development of hybrid force-stimulated functional materials utilizing mechanical bonds.

INTRODUCTION

Mechanical bonds, featuring entanglement(s) in space between two or more components, have emerged as a booming field.¹ Generally, mechanical bonds refer to rotaxanes, catenanes, and molecular knots. They consist of two or more components that are bound together by mechanical interlocking, incapable of separation without breaking covalent chemical bond(s). These mechanically interlocked structures are known for the creation of molecular machines, underscored by their recognition in the 2016 Nobel Prize in Chemistry. On the other hand, benefiting from their large amplitude intramolecular mobility, mechanical bonds are able to absorb energy by undergoing mechanical sliding, thereby fostering the rapid evolution of slide-ring functional materials. Despite extensive research over decades, a fundamental question remains in the field: How strong is a mechanical bond? The search for answers to this question may lead to a deeper understanding of mechanical bonds and will have important implications for the designation of mechanical bonds incorporated mechanoresponsive motifs. It may also shed some light on the effect of entanglements in polymeric materials under tension. Empirically, the mechanical strength of a mechanical bond equals the weakest covalent bond within its structure. This may be the case under zero-force conditions. However, the application of external force prompts the mechanical bond to slide and undergo structural deformation, significantly altering the force transmission and tensile stress distribution from its initial state. Studies of the mechanical properties of mechanical bonds have been done using single-molecule force spectroscopy such as AFM and optical tweezers.² These advanced techniques can offer detailed information on the non-covalent interactions under low-loading rates (within piconewton force ranges, pNs). The breaking of covalent bonds can also be achieved using a modified AFM tip. However, such investigations are yet to be conducted on mechanically interlocked molecules. Tensile tests on bulk materials including slide-ring gels have been investigated as well at the macroscopic level.

Polymer mechanochemistry studies the mechanical reactions of mechanical active units (colloquially referred to as mechanophores) in polymers in solutions.³ Upon ultrasonication, an intense shear force can be generated through the cavitation effect. The solvodynamic force is predicted to be greatest in the middle of the polymer chain, leading to the scission of the polymer primarily near the center of the chain (Figure 1A). The force generated by ultrasonication typically reaches nNs, facilitating the breaking of covalent bond(s). This technique has been used to construct force related functional materials at the macroscopic level and study the fundamental mechanisms of mechano-reactions at the molecular level. Introducing poly-

mer mechanochemistry strategy to mechanical bond systems offers a pathway to explore the mechanical strength of these interlocked structures. In this perspective, we discuss the hybridization of these two fields and highlight some recent examples, aiming to address the question and some potential future applications.

MECHANICAL PROPERTIES OF THE MECHANICAL BOND

In 2018, De Bo summarized the progress on the mechanical strength of the mechanical bond.⁴ The minireview focused mainly on non-covalent interactions using single-molecule force spectroscopy, as limited information existed at the time about the covalent rupture of a mechanical bond. This is not because their rupture process is unimportant, but on the contrary there is a lack of suitable methods and techniques. Stoddart and coworkers first introduced ultrasound to study the mechanical property of a [2]rotaxane-centered poly(methyl acrylate) (Figure 1E).⁵ The [2]rotaxane has a macrocycle threaded into an axle with two stoppers, and two polymer tails extending from one end of the axle and the macrocycle. After sonication, the mechanical degradation of the rotaxane can be confirmed by the change of charge-transfer UV-vis absorption initiated by the interaction between the electron-defect macrocycle and the electron-rich unit along the axle. This nice piece of work successfully demonstrated the dissociation of a rotaxane under force. However, it's unclear whether the disassembly was caused by the dethreading of the macrocycle or by the cleavage of covalent bond(s) within the interlocked structure (see Figure 1E for possible cleavage pathways). To facilitate the study, we attached a force sensitive Diels-Alder adduct (a known mechanophore that undergoes the retro-DA reaction under tension, depending on its geometry) to the axle of a [2]rotaxane and examined the effects of the rotaxane on the activation of the DA adduct (Figure 1F, the cyan color dot represents the DA adduct).⁶ The activities of this mechanophore were investigated both thermally and mechanically. It was shown that the DA adduct on the rotaxane is cleaved faster than its linear counterpart under identical heating conditions. Mechanically, however, the rDA rate of the rotaxane is notably slower. This suggests that the rotaxane structure may weaken the mechanical activation of the DA adduct. Further computational calculations of the rotaxane revealed there are two high strain regions developed concomitantly in the rotaxane, compared to only one in the linear control. The additional competing high strain region is located at the stopper junction of the rotaxane, which could effectively diminish the mechanochemical coupling around the DA adduct. This unprecedented strain distribution is caused by the deformation of the macrocycle and the bending and distortion of the stopper under external tension. In a follow-up study,⁷ the mechano-active DA adduct was simply replaced by a mechano-inert DA adduct isomer, to depict the mechanical strength of the intrinsic rotaxane, as there's no weak chemical bond within the system (Figure 1G). Results showed that the rotaxane was cleaved faster than its linear control, and analysis of the fragments confirmed that the rupture occurred in the region of the stopper junction. These studies indicate that the intrigued rotaxanes have varied mechanical stabilities. At high-loading rates, a rotaxane is more active due to the high-stress region generated by the distortion and bending of the structure. However, the activity can be modulated if a mechanophore is involved. Although slide rings can improve the elasticity and flexibility of materials, it's important to investigate their mechanical strength if the material is to be subjected to high stress during its lifetime.

When cyclizing the axle of a rotaxane into a loop, it turns into a catenane. Unlike rotaxanes, the rings in catenanes can rotate along each other, giving the system additional mobility. Craig group pioneered the study of the

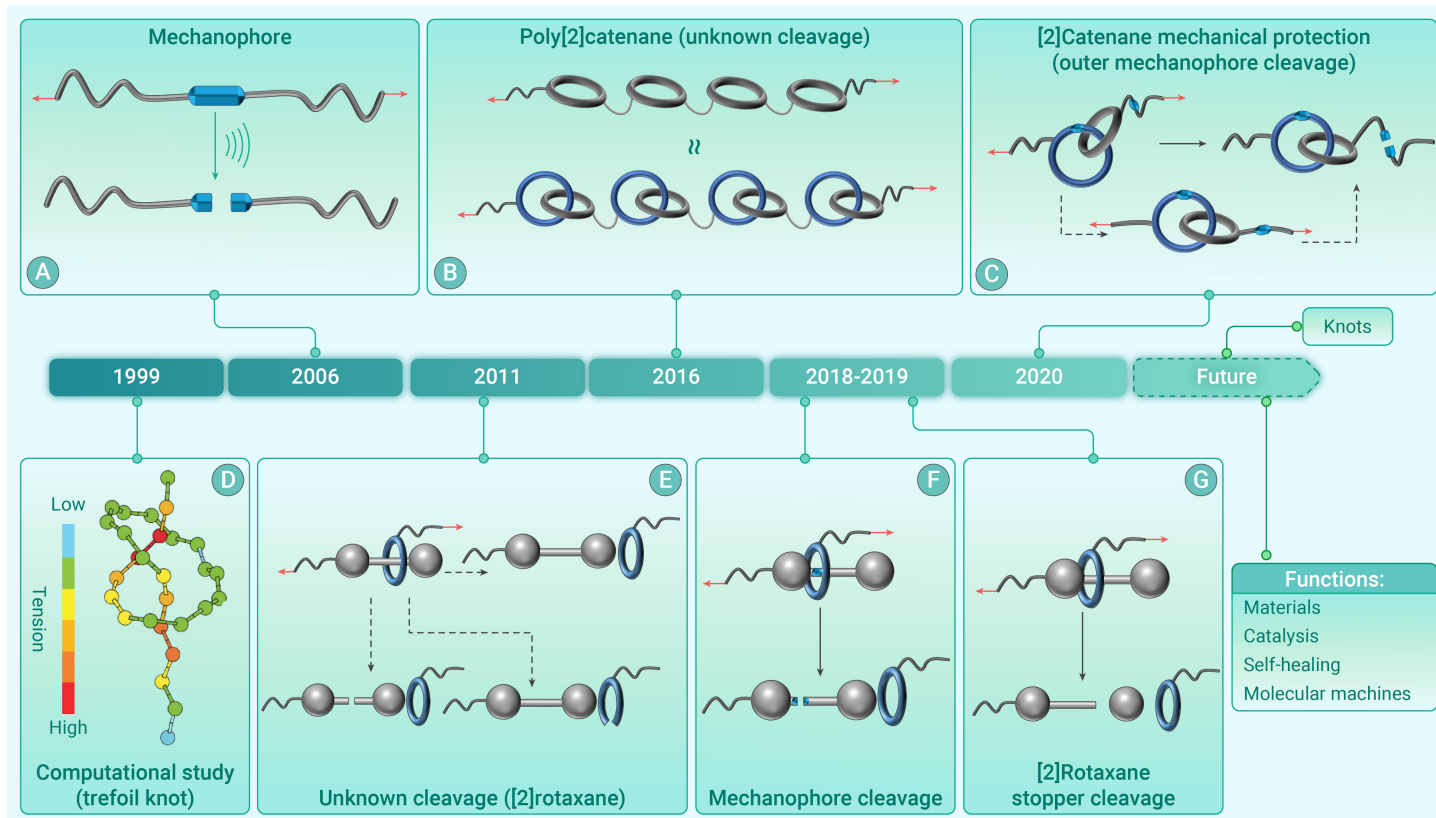


Figure 1. Mechanical strength of the mechanical bond. Red arrows indicate the direction of the force.

mechanical behavior of a poly[2]catenane using ultrasound (Figure 1B).⁸ Different from the mentioned rotaxanes, the poly[2]catenane showed at least similar strength under high strain compared to its macrocyclic or linear counterparts. This is surprising and yet promising, as it shows that the hybridization of catenanes in materials does not reduce the strength of the materials even under high tension, and imparts new dynamic functions to the materials. Inspired by these discoveries, De Bo incorporated two identical mechanophores into a [2]catenane-centered linear polymer, with one located within a macrocycle (inner mechanophore), and the other along the main polymer chain adjacent to the catenane (outer mechanophore) (Figure 1C, the cyan dots represent the mechanophores).⁹ Both experimental and computational results indicated the outer mechanophore was activated while the inner one remained intact. The authors attribute this to the mechanical rotation of the two macrocycles until the tension is equalized over the entire structure, thus successively diverting tensile forces away from the mechanical active group embedded within the catenated macrocycle.

Knots widely exist in both the macroscopic and microscopic world, in biomolecules such as proteins and DNAs, and in any synthetic polymers of sufficient chain length. Knots are believed to strongly influence the properties of polymeric matter, especially its mechanical properties. Early computational studies indicated a trefoil knot in a polymer weakens the chain at the entrance of the entangled structure (Figure 1D).¹⁰ The computational result was exciting, but little progress has been achieved since then, especially on the nano-scale. Compared to rotaxanes and catenanes, molecular knots are more complex structures and enormous efforts have been put into their synthesis in the past decades. Only in recent years, have some advanced synthetic methods been established that allow people to explore their physical and chemical properties. There's a good chance that we will witness the unveiling of the mechanical strength of a molecular knot shortly.

CONCLUSION AND PERSPECTIVE

Current research has unveiled initial but intricate insights into the mechanical strength of mechanical bonds, showing their complex behaviors stemming from internal flexibilities and entangled topologies. Despite significant progress, uncertainties persist in understanding the full scope of the

mechanical bond strength. For instance, only the simplest [2]rotaxane has been studied, the examination hasn't extended to scenarios where multiple rings are threaded into an axle or higher-order rotaxanes like rotaxane dendrimers. Questions remain about how the force conduction along these complex structures and the additional properties they may impart. Similarly, trefoil knot as the simplest knot in the knot family, is yet fully studied and understood. Trefoil knot has been proven to be the weakest of all knots in the macroscopic world, mainly owing to friction and inertia when suffering external force. Does it hold its truth in the microscopic world? Since there's no friction between the atoms, instead dominated by electronic repulsion and Brownian motion. In a typical process, the entire structure contracts and the chemical bonds locked in it distort and rotate according to the direction of the coupled force, these mainly involve entropic variations, followed by enthalpic changes as the bond(s) stretch/bend with accumulated tensile stresses until finally the rupture of certain covalent bond(s). With increasing complexity and crossing links, the geometry of a knot varies drastically. How does force conduct along these knotted structures? The inherent dynamic nature of knots, which can expand and contract or translocate along the polymer chain, further complicates the investigation. Moreover, exploring how to leverage the mechanical behaviors of these structures is a promising area. Mechanical bonds have demonstrated the ability to modulate mechanophores' activities without altering their structures. This capability opens new ways for designing novel force-stimulated materials. Other applications, including force-driven molecular machines, force-controlled switchable catalysts and force-induced self-healing materials are all hinging on the remarkable mechanical properties of mechanically interlocked structures.

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DECLARATION OF INTERESTS

The author declares no competing interests.