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•HIGHLIGHTS•

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Increasing polymer scission rate by tying an overhand knot

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Similar to the phenomenon of knotted ropes in life, knotted climbing ropes will reduce their strength due to knots. Although computer simulations [1], theoretical speculation [2,3], and intuition [3] suggest that similar processes may occur at the nanoscale, this hypothesis has not been experimentally proven before. With the increasing maturity of molecular recognition and self-assembly, a research communication by Leigh *et al*. [4] published in *Nature Chemistry* introduced a molecular overhand knot into a polymer to study its effect on the scission rate of the polymer chain under tension.

Because the mechanical properties in the macroscopic world are not applicable to the nanoscopic world, the research project integrates a collar into the polymer to investigate the effect of the structure on the polymer's rupture velocity and the specific breaking bonds under tensile conditions [5,6]. The force in the central region of the polymer is the greatest under the conditions of ultrasound, and was, therefore, the most suitable position for embedding in the knot. In order to maintain the closed structure of the knot, the authors added a mechanically vulnerable unit — a mechanophore built around a furan/maleimide Diels-Alder adduct (Figure 1). When the tension accumulates along the backbone to a certain value, the mechanophore breaks, opening the collar and causing the knot to tighten under tension and then break [7]. The experimental result shows that the presence of molecular junction increases the cutting rate by more than 2.6 times and reduces the cutting force. This indicates that the presence of molecular-level knots may adversely affect the mechanical strength of polymers and other analogs [8].

The mechanical strength of the polymer was evaluated through a comparative analysis of the chain center knot **1**, gating unit **2**, and linear ligand **3**. Results revealed comparable cleavage rates between knot **1** and gate **2**, while the cleavage rate of linear ligand **3** was notably slower, indicating superior mechanical strength of the linear ligand. In seeking to pinpoint opportunities for enhanced reactivity, the authors sought to identify the breaking point. Proton nuclear magnetic resonance (^{1}H NMR) spectroscopic analysis confirmed that the position of the breakage is located at the Diels-Alder gate fracture. The investigations unveiled that the C–O bond adjacent to the naphthalene group experienced chain breakage, with cleavage observed solely for the oxynaphthalene linked to ethylene glycol, leading to contraction primarily around the central pyridine unit. The fracture location was further demonstrated by applying constrained geometries to simulate external force (CoGEF). The authors first used molecular mechanics to simulate the extension of the model knot lacking gate elements, in addition to the density functional theory (DFT), to simulate the elongation shortening of this model with the CoGEF curve, demonstrating bond cleavage at peak energy levels. Notably, the twisting angle of C–O–C bonds exceeded 30°, accompanied by a 35° bending of the oxynaphthalene unit, culminating in cleavage along the C–O bond.

When the polymer strand is in the collapsed cavitation bubble, the chain stretches until the gating unit opens, forming an overhand knot that is capable of diffusing along the polymer chain. Within the cavitation field environment,

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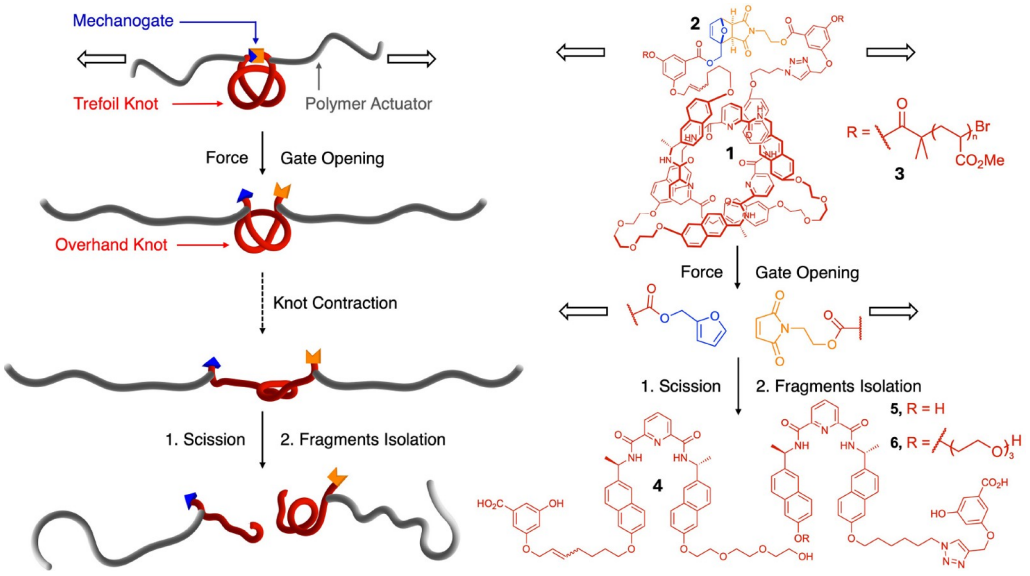

Figure 1 Graphical representations (left) and chemical structural formulas (right) of the breakage and separation of an overhand knot within a polymer through the cavitation-induced elongational flow. In this process, a gated overhand knot — which is equivalent to a trefoil knot — is stretched through a cavitation elongational flow modified through activating polymer chains (color online).

there is insufficient time for the overhand knot to untie. As the overhand knot progresses into its final stage of contraction, numerous skeletal deformations emerge, ultimately leading to the rupture of the C–O bond, stabilized by the hydrogen bonding of amide and pyridine lone pairs of electrons.

Matter exhibits different behavior at varying scales; while macroscopic knots are stabilized by friction and inertia, these forces do not apply at the nanoscale. Despite this, overhand knots show similar stress distribution and breaking points whether in molecular, microscopic, or macroscopic strands. Knotting in polymers drastically reduces the mechanical strength, decreasing the force required for scission from ≥5.6 to 2.9 nN, and increasing the scission rate by at least 2.6 times compared to unknotted polymers. Such knots alter which chemical bonds break in a polymer chain compared with those in unknotted polymers.

Knots are common in biomacromolecules and spontaneously form in many synthetic polymers, though the likelihood of random knot formation is significant only in polymers with molecular weights greater than 1 MDa. Understanding how knots affect the mechanical integrity of polymers can be extended to various applications, from developing more durable synthetic fibers to designing new materials with tailored mechanical properties. Future research could also investigate the effects of different knot types and densities on polymer behavior and the application of these principles in natural systems where knotting and entanglement naturally occur. Particularly in biomaterials and medical devices, these studies might lead to breakthroughs that enhance durability and functionality. Furthermore, the fields of nanotechnology and molecular machines will greatly benefit from this research. By introducing and controling molecular knots, scientists can design more complex and efficient nanostructures and molecular devices, which will further promote the field. Ultimately, integrating knot mechanics into material sciences opens new pathways for innovation in applications of both natural and synthetic polymers, providing a broad horizon for the development of future materials.

Conflict of interest The authors declare no conflict of interest.

1 Saitta AM, Soper PD, Wasserman E, Klein ML. *Nature*, 1999, 399: 46–48
2 Stauch T, Dreuw A. *Angew Chem Int Ed*, 2016, 55: 811–814
3 Beyer MK, Clausen-Schaumann H. *Chem Rev*, 2005, 105: 2921–2948
4 Zhang M, Nixon R, Schaufelberger F, Pirvu L, De Bo G, Leigh DA. *Nat Chem*, 2024, https://doi.org/10.1038/s41557-024-01510-3
5 Tubiana L, Rosa A, Fragiacomo F, Micheletti C. *Macromolecules*, 2013, 46: 3669–3678
6 Virnau P, Kantor Y, Kardar M. *J Am Chem Soc*, 2005, 127: 15102–15106
7 Zhang M, De Bo G. *J Am Chem Soc*, 2020, 142: 5029–5033
8 Chen Y, Mellot G, van Luijk D, Creton C, Sijbesma RP. *Chem Soc Rev*, 2021, 50: 4100–4140