Polymer dielectrics

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Molecular dampers for high-temperature capacitors

Leonie Braks & Ali Coskun

The macrocycle component of polyrotaxanes is used to dampen the molecular vibrations of polyimide at high temperatures, thereby preserving electronic resistivity and resulting in improved dielectric capacitor efficiency.

Mechanically interlocked molecules and polymers offer chemists and materials scientists a unique combination of the stability of molecular structures with the dynamic nature of supramolecular assemblies. This combination enables researchers to achieve control across multiple length scales, from individual molecules to nanoscopic, microscopic and macroscopic systems. One notable example of a mechanical bond is rotaxanes, composed of ring-shaped molecules threaded onto a linear molecule, a discovery for which Sir Fraser Stoddart was co-awarded the 2016 Nobel Prize in Chemistry[1].

To harness the potential of mechanical bonds in material design, various polyrotaxanes have been developed. The most well-known polyrotaxanes, so-called main-chain polyrotaxanes, comprise three key components: a (polymeric) thread, multiple rings and a capping group that prevents the rings from dethreading (Fig. 1, centre). The common synthetic approach is threading followed by stoppering, where the rings are thermodynamically favoured to form the inclusion complex on the polymer chain followed by the incorporation of bulky end groups as stoppers. Other approaches include threading a ring on a monomer and subsequent polymerization, or clipping, where the ring is closed after association with the polymer chain. By variation of the ring, polymer and synthetic methods, the chemical and topological architecture, as well as the properties, can be finely controlled.

The dynamic nature of the mechanical bond allows for motions such as sliding and rotation, imparting unique properties. For instance, crosslinking the rings creates a 'molecular pulley' effect, which dissipates forces and forms networks with remarkable elasticity and toughness[2,3]. In addition, in a daisy-chain-type alignment, polyrotaxanes can function as molecular machines, such as artificial muscles, by exploiting the sliding motion of the ring along the chain upon environmental triggers[4]. A high threading density of rings on conducting polymer chains can protect the core from external influences, such as solvents and temperature, enabling their use in high-performance molecular electronics[5].

Now, writing in *Nature Materials*, Qi Li and colleagues present the use of the mechanical bond to modulate the dielectric properties of the resulting polymeric material[6]. A key challenge in designing dielectric polymers for capacitors is ensuring their stability in high-temperature environments. Capacitors rely on extremely low electronic conductivity to store charges with minimal losses. However, the dielectric properties of commercially available dielectric polymers typically degrade above 100 °C, where electron conduction increases exponentially[7].

Current strategies for developing heat-resistant dielectric polymers often focus on broadening the bandgap and increasing the glass transition temperature. However, these approaches have shown limited success beyond 200 °C. A major obstacle is phonon-assisted charge transfer, which becomes more likely as molecular chain vibrations intensify with increasing temperatures (Fig. 2a).

To address this issue, Li and colleagues incorporated crown ethers onto a polyimide backbone (Fig. 2b), by threading dibenzo-18-crown-6 (C_{18}) onto a diamine monomer based on supramolecular self-assembly. Upon addition of the anhydride, initial polymerization occurs at room temperature, followed by acylation at increasing temperatures (up to 200 °C). Despite the absence of a traditional capping group, the authors have shown using NMR spectroscopy that C_{18} does not dethread, most likely due to the presence of bulky CF_3 groups on the polymer chain. Using molecular dynamics simulations, it was found that at an optimal ring loading of 0.5 wt%, the vibrational amplitude of the polymer chain can be reduced by 12.3% due to the presence of mechanical bonds (Fig. 2c). Fluorescence emission spectroscopy confirmed that charge transfer between chains was suppressed, and even at a high temperature of 250 °C, the minimum distance for phonon-assisted transfer is not reached. Furthermore, density functional theory simulation showed that the C_{18} is preferentially located at the inflection points during the vibration, where charge transfer is most likely.

This effect led to a reduction of the leakage current at an electric field of 125 MV m^{-1} and 250 °C from 3.3×10^{-4} A cm^{-2} to 6.7×10^{-5} A cm^{-2} for the unthreaded and C_{18}-threaded polyimide, respectively. Finally, a larger crown-ether (C_{34}) was found to have the most desirable properties for inhibiting charge transfer and further reduced the d.c. conductivity compared with commercial polyimides. The devices prepared with this ring could achieve an efficiency of 90% at 250 °C with a discharged energy density of 4.1 J cm^{-3}. Furthermore, more than 100,000 charge–discharge cycles could be stably run at a high field of 300 MV m^{-1}.

The choice of the ring component and its loading density has a crucial role in determining the material's properties. For example, a recent study using polyimides with a high threading density of β-cyclodextrin rings achieved the opposite effect: a decrease in the dielectric constant due to increased free volume between chains[8]. In this work, slight decreases in electrical resistivity were also observed when the ring loading was increased to more than 1 wt%, highlighting the importance of optimizing the free volume and the chemical structure of the ring component.

Transforming existing dielectric polymers into polyrotaxanes represents a promising strategy for designing high-temperature dielectric materials. As the choice of ring type, polymer thread and ring density all substantially influence performance, future research on the chemical structure of the ring component beyond the crown ethers explored in this study, and ring density, as well as new polymeric backbones can provide deeper insights into these mechanisms, paving the way for

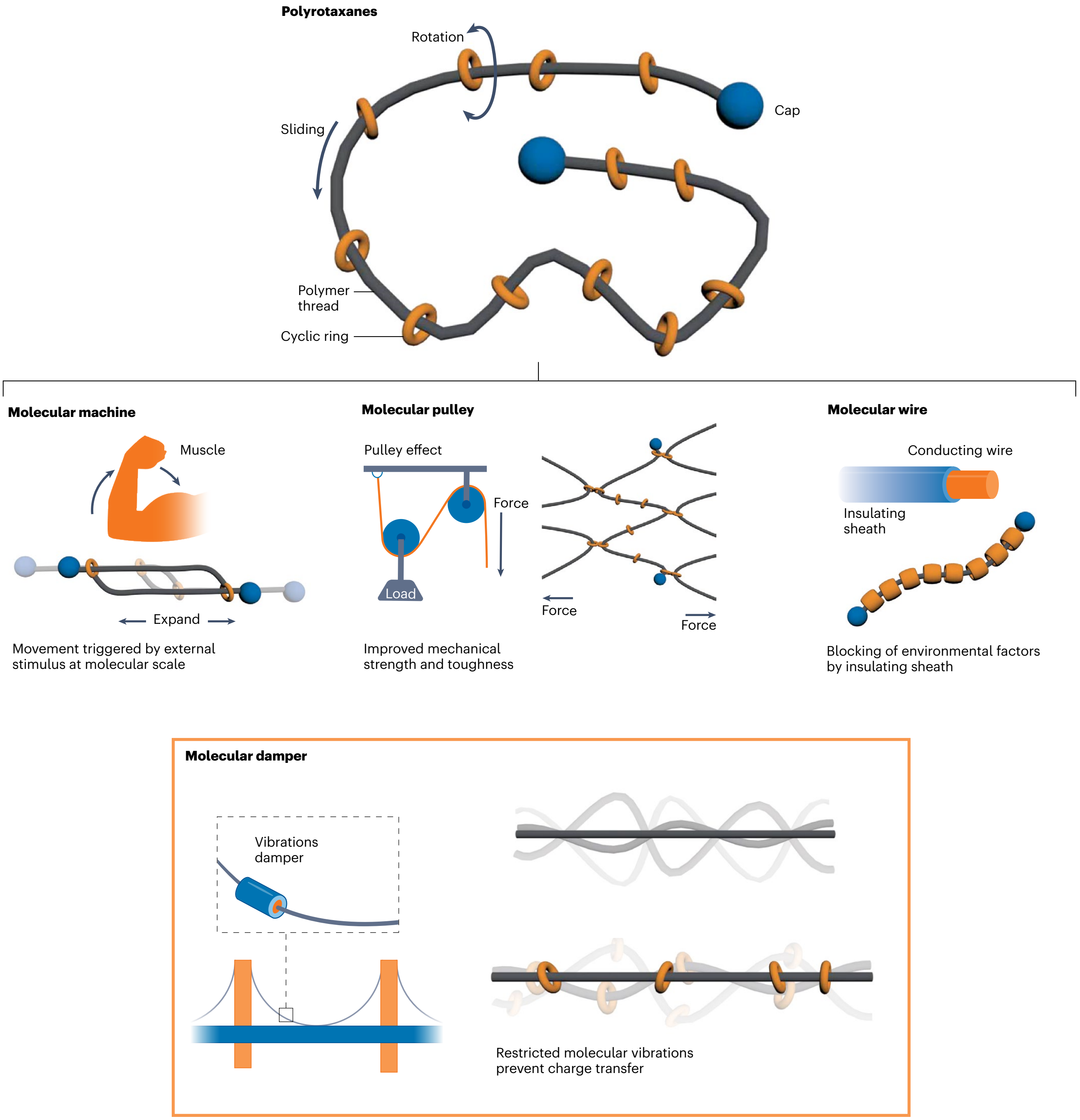

Fig. 1 | Polyrotaxanes and their applications in different fields. A polyrotaxane consisting of a polymer thread with rings and caps is shown at the top. The possible movements of the rings are indicated. In addition, applications exploiting polyrotaxanes and their real-world analogues are shown.

further optimization. Furthermore, exploring polymers with a high threading density, where the rings act as a second insulation layer, further preventing charge hopping, could also provide new research directions. In addition, controlling chain dynamics in polymers on a molecular scale is also key in different fields, such as electromechanical transduction or dipole switching as well as antivibration systems.

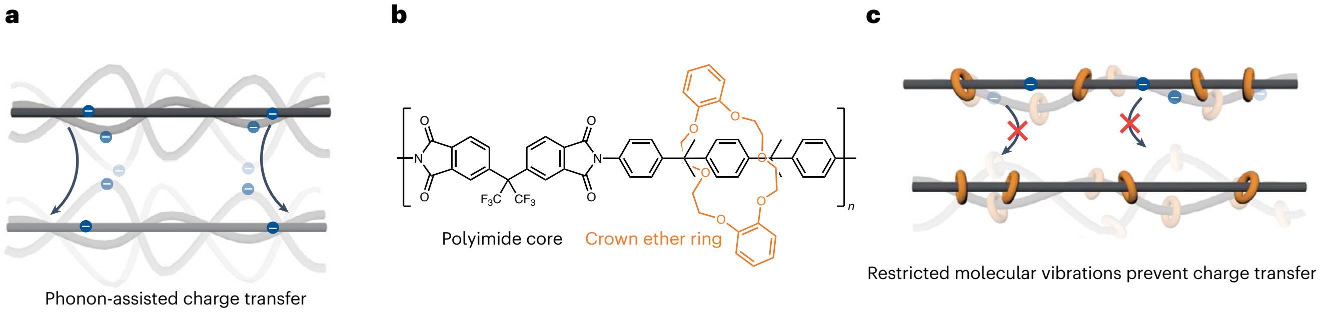

Fig. 2 | The suppression of phonon-assisted charge transfer by incorporation of mechanical bond. a, Increased molecular chain vibrations at high temperatures promote phonon-assisted charge transfer leading to a loss of electronic resistivity of the material. **b**, Molecular structure of the polyrotaxane used in the study by Li and colleagues. **c**, Strategic placement of rings suppresses charge conduction by restricting molecular chain vibrations.

The work by Li and colleagues underscores the versatility of mechanically interlocked polymers in imparting otherwise inaccessible properties to conventional materials.

Leonie Braks & Ali Coskun
Department of Chemistry, University of Fribourg, Fribourg, Switzerland.
e-mail: ali.coskun@unifr.ch

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Competing interests

The authors declare no competing interests.