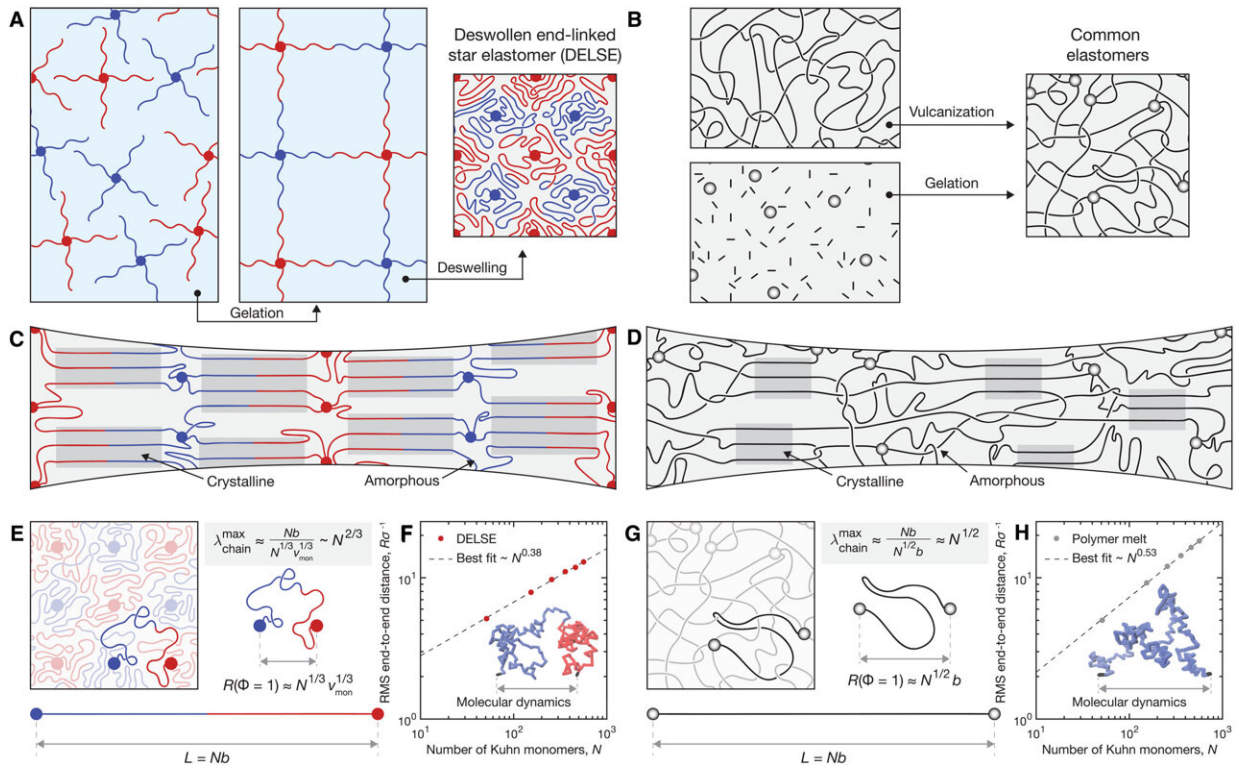
Developing a futuristic elastomer with ultrahigh strain-induced crystallization

December 27 2023, by Thamarasee Jeewandara



Deswollen end-linked star elastomers. (A) The DELSE forms through controlled crosslinking of star macromers followed by solvent evaporation to form a homogeneous crosslinked polymer network (illustrations are exaggerated to highlight architectural differences). (B) Conventional elastomers form through random crosslinking processes such as vulcanization of long polymer chains or gelation from monomers. (C) The more homogeneous architecture supports chain alignment during stretching causing crystalline domain formation in the DELSE. (D) In contrast, physical barriers like trapped entanglements and inhomogeneities limit the effect of SIC in common elastomers. (E) The RMS

end-to-end distance of polymers chains in a DELSE in the undeformed state scales as N1/3, as validated by (F) molecular dynamics simulation (representative simulated chain conformation inset). (G) The RMS end-to-end distance of polymers chains in a conventional elastomer in the undeformed state scales as N1/2, as validated by (H) molecular dynamics simulation (representative simulated chain conformation inset). Credit: *Science Advances* (2023). DOI: 10.1126/sciadv.adj0411

Strain-induced crystallization can strengthen, toughen, and facilitate an elastocaloric effect in elastomers. The resulting crystallinity can be induced by mechanical stretching in common elastomers that are typically below 20%, with a stretchability plateau.

In a new report now published in *Science Advances*, Chase M. Hartquist and a team of scientists in mechanical engineering and materials sciences at MIT and Duke University in the U.S. used a class of elastomers formed by end-linking to achieve a percentage of strain-induced crystallinity.

The deswollen and end-linked star elastomer abbreviated as DELSE reached an ultrahigh stretchability to scale, beyond the saturated limit of common elastomers, to promote a high elastocaloric effect with an adiabatic temperature change.

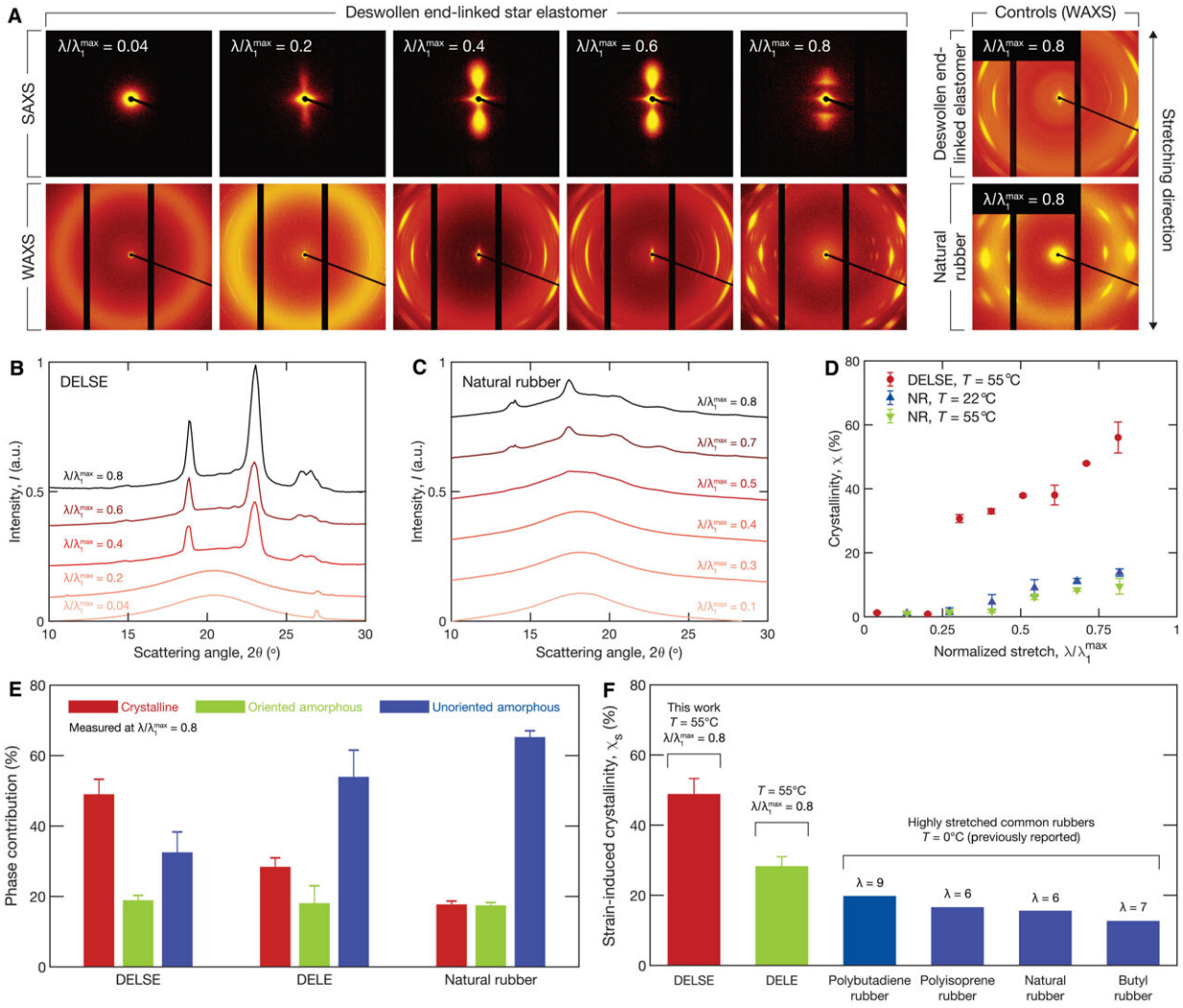
Strain-induced crystallization

The process of strain-induced crystallization is common in elastomers and gels where amorphous polymer chains can transform into highly oriented and aligned domains due to an applied mechanical strain. Since the oriented and aligned crystalline domains can resist crack extension and blunting to facilitate crack deflection, the process of strain-induced

crystallization preserved the network integrity, while achieving close to 100% recovery in seconds.

The method plays a key role in a variety of applications, including elastocaloric cooling, and strain-based actuation.

The typical process of strain-induced crystallinity in common elastomers is below 20%, while natural rubber only achieves about 15% crystallinity when stretched to six times its initial length at room temperature. In this new work, Hartquist and a team of researchers described a class of deswollen, end-linked star elastomers to achieve up to 50% strain-induced crystallinity. The scientists credited the ultrahigh strain-induced crystallization to a uniform network structure and a high stretchability to obtain the expected outcomes.



Ultrahigh SIC of the DELSE. (A) WAXS and SAXS patterns show structural development of the DELSE at 55°C compared to the DELE at 55°C and NR at 22°C when mechanically stretched. The WAXS intensity profile develops crystalline peaks for (B) the DELSE and (C) NR during stretching. (D) The crystallinity index increases more dramatically for the DELSE compared to NR. (E) Deconvolution of WAXS scans gives the distribution of oriented and unoriented phases. (F) Strain-induced crystallinity of the DELSE measured from WAXS pattern deconvolution is compared to the DELE and reported values for various common rubbers with SIC. Error bars denote standard deviations. Credit: *Science Advances* (2023). DOI: 10.1126/sciadv.adj0411

To study the additional features of the elastomer, the team used X-ray analysis to show how the structure and strain-induced deswollen and end-linked star elastomer promoted crystallinity when compared to common elastomers. The research team further analyzed the crystal structure formed using detailed X-ray analysis, where the deswollen and end-linked star elastomers displayed a diffraction spot to mark the formation of poly(ethylene dioxide) crystals in a helical structure. This elastomer promoted higher strain-induced crystallinity, when compared to common elastomers.

Mechanical performance and elastocaloric cooling

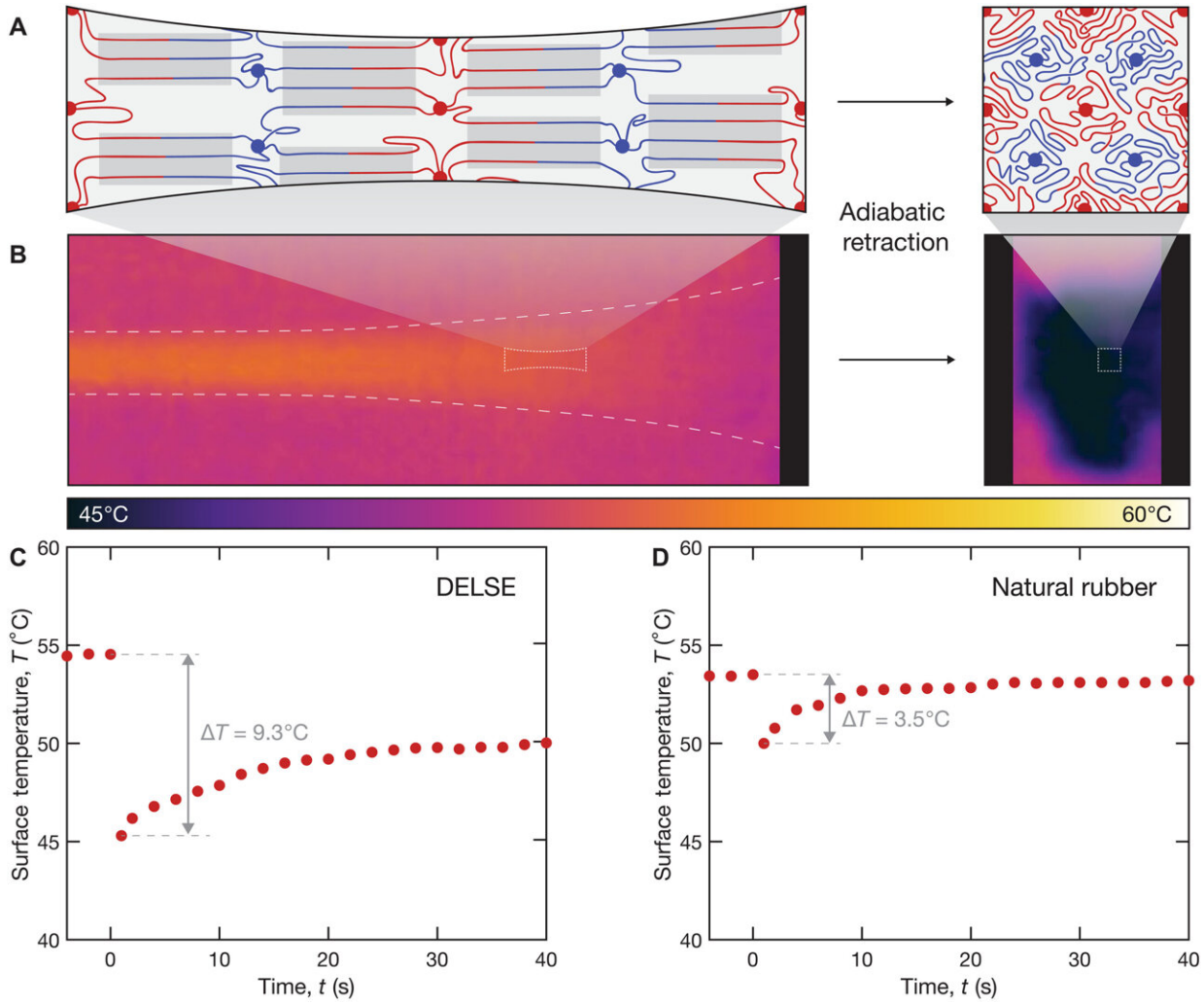
The research team conducted mechanical characterization at 60°C to investigate ultrahigh strain-induced crystallization in deswollen end-linked elastomers, which effectively promoted high toughness, with low stress-stretch hysteresis. Hartquist and the team reinforced the softest materials by introducing reversible bonds to induce large stress-stretch hysteresis.

The researchers further studied the stretchability of elastomers to show how the materials stretched beyond the limits of entangled networks for broader applications. They then studied the potential to use a caloric material for solid state cooling applications by investigating the elastocaloric effect in deswollen end-linked star elastomers, and compared the outcomes with conventional elastomers.

The scientists investigated the potential to use a caloric material for solid state cooling applications by studying elastocaloric effects in deswollen end-linked star elastomers when compared with natural rubber. An ideal elastocaloric cooling cycle can harness the decrease in conformation of entropy to increase thermal entropy and heat the bulk material.

In elastomers with strain-induced crystallization, additional latent heat

contributed to crystallite formation to heighten the effect. The increased stretchability and uniform chain length distribution of the material increased the theoretical elastocaloric effect, when compared to conventional elastomers. Such elastomers formed strong candidates with suitability for advanced solid-state cooling technologies.



Elastocaloric effect of the DELSE. (A) Schematics indicate the destruction of crystalline domains and disruption of polymer chain alignment during adiabatic retraction. (B) Thermal images of the DELSE during the retraction. The applied mechanical loading and measured surface temperature are recorded for the (C) DELSE and (D) NR during the retraction process. Credit: *Science Advances*

(2023). DOI: 10.1126/sciadv.adj0411

Outlook

In this way, materials scientists Chase M. Hartquist and colleagues compared the deswollen and end-linked star elastomer with natural rubber to show their increased stability, different polymer chemistry, and well-formed structure that combinatorically increased strain-induced crystallization and elastocaloric effect in elastomeric materials. The comparison between the materials revealed their stretchability and chemistry, as well as the significance of the relatively homogenous structure.

Since the early discovery of the rubber band by J.R. Katz in 1924 due to strain-induced crystallization, this biomaterial has played a significant role in society from household goods to car tires. In this report, the team described the next-generation elastomers developed with profound strain-induced crystallization that exceeded the dimensions of natural rubber and other common materials.

The materials developed showed the capacity to outperform conventional counterparts, suggesting the ability to engineer soft materials by regulating their network architecture. These materials play a crucial role to construct futuristic aerospace structures, medical devices and for applications of elastocaloric refrigeration.

More information: Chase M. Hartquist et al, An elastomer with ultrahigh strain-induced crystallization, *Science Advances* (2023). DOI: 10.1126/sciadv.adj0411