Discovery challenges 30-year-old dogma in associative polymers research

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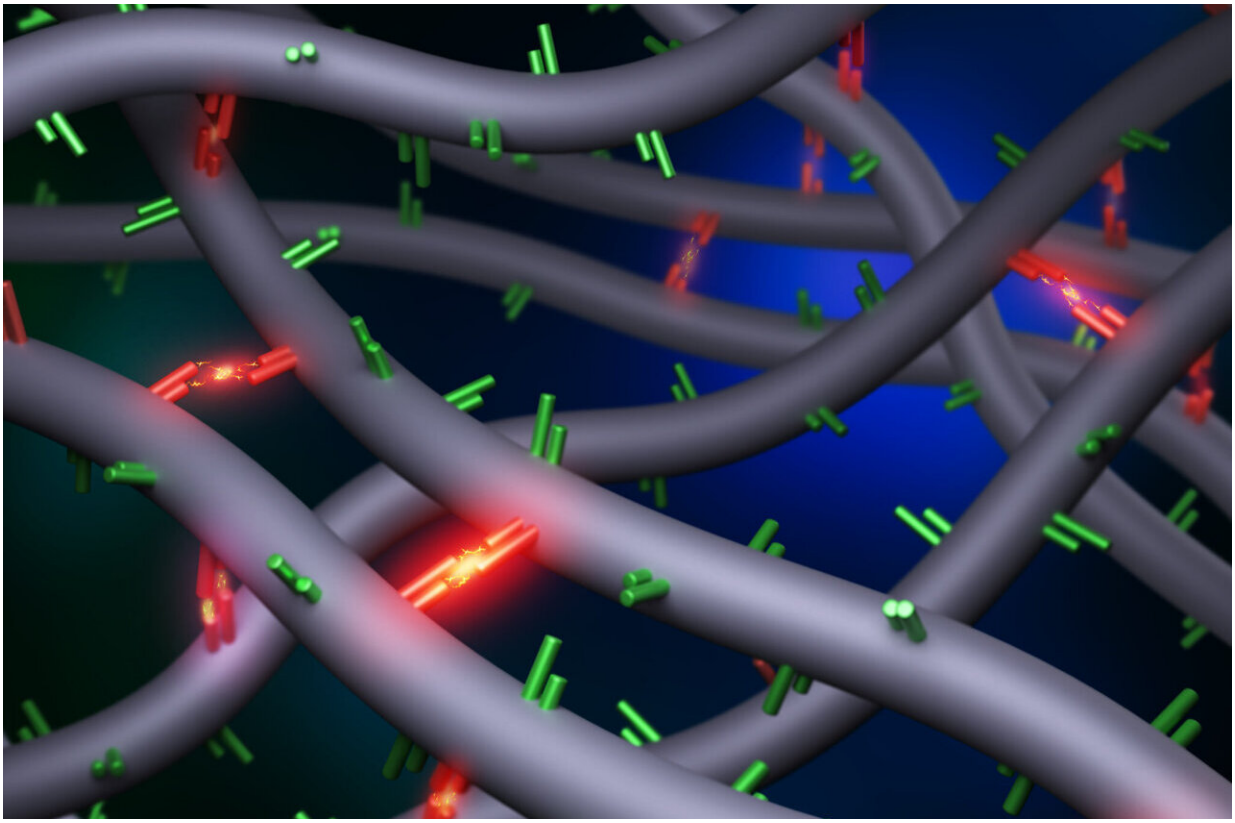

A 3D rendering illustrating two monomers forming a reversible double-hydrogen bond that slows down polymer movement without creating an elastic network. Selected for a Synopsis in Physics and an Editors' Suggestion, and highlighted as the front cover in Physical Review Letters. Credit: S. Nian et al., *Phys. Rev. Lett.* 130, 228101 (2023)

A University of Virginia-led study about a class of materials called associative polymers appears to challenge a long-held understanding of how the materials, which have unique self-healing and flow properties, function at the molecular level.

Liheng Cai, an assistant professor of materials science and engineering and chemical engineering at UVA, who led the study, said the new discovery has important implications for the countless ways these materials are used every day, from engineering recyclable plastics to human tissue engineering to controlling the consistency of paint so it doesn't drip.

The discovery, which has been published in the journal *Physical Review Letters*, was enabled by new associative polymers developed in Cai's lab at the UVA School of Engineering and Applied Science by his postdoctoral researcher Shifeng Nian and Ph.D. student Myoeum Kim. The breakthrough evolved from a theory Cai had co-developed before arriving at UVA in 2018.

"Shifeng and Myoeum essentially created a novel experimental platform to study the dynamics of associative polymers in ways that weren't possible before," Cai said.

"This gave us a new perspective on the polymers' behavior and provides opportunities to improve our understanding of particularly challenging areas of study in polymer science. And from a technology standpoint, the research contributes to the development of self-healing materials with tailored properties."

Polymers are macromolecules composed of repeating units, or monomers. By rearranging or combining these units and tinkering with their bonds, scientists can design polymeric materials with specific characteristics.

Polymers also can change states, from hard and rigid, like glass, to rubbery or even fluid depending on factors such as temperature or force—for example, pushing a solid gel through a hypodermic needle.

Associative polymers are especially distinctive: Their moieties—a general term for molecular subunits with customizable physical properties—are held together by reversible bonds, meaning they can break apart and re-form.

This process enables macroscopic properties inaccessible by conventional polymers. As a result, associative polymers provide solutions to some of the most pressing challenges in sustainability and health. For example, associative polymers are used as viscosity modifiers in fuels, to create tough self-healing polymers, and to engineer biomaterials with physical properties critical to tissue engineering and regeneration.

One key to the UVA team's work was overcoming a material feature that has stymied researchers for years. In the lab, scientists work with materials whose bonds can break and re-form at "laboratory time scales," meaning within time frames they can observe through experiments. However, in nearly all existing experimental systems, the moieties aggregate into small clusters, which prevents precise study of the relationship between reversible bonds and polymer behavior.

Cai's collaborators at the National Synchrotron Light Source II conducted experiments using a sophisticated X-ray tool — the soft matter interfaces beamline shown here — to reveal the inner makeup of the polymers without damaging the samples. Credit: University of Virginia

Cai's team developed new types of associative polymers where the bonds are evenly distributed throughout the material and at a wide range of densities. To confirm that their materials do not form clusters, the researchers collaborated with Mikhail Zhernenkov, a scientist at the U.S. Department of Energy's Brookhaven National Laboratory. They conducted experiments using a sophisticated X-ray tool—the soft matter interfaces beamline—at the National Synchrotron Light Source II to reveal the inner makeup of the polymers without damaging the samples.

These new associative polymers allowed Cai's team to precisely study

the effects of reversible interactions on the dynamics of associative polymers.

Dynamics and behavior refer to traits such as the temperature at which molecule movement slows to a rigid "glassy" state, viscosity (how freely a material flows) and elasticity (its ability to snap back after being deformed). A mix of these traits is often desirable to design, for example, a biomaterial compatible with human tissue that can reconstitute itself after injection.

For 30 years, it had been accepted that when the reversible bonds remain intact, they act as crosslinkers, resulting in a rubbery material. But that's not what the UVA-led team found.

Collaborating with Shiwang Cheng, an assistant professor in Michigan State University's chemical engineering and materials science department and an expert in flow dynamics, the team precisely measured the flow behavior of their polymers in a wide range of time scales.

"This requires careful control over the local environment, such as temperature and humidity of the polymers," Cheng said. "Over the years, my lab has developed a set of methods and systems for doing so."

The team found that the bonds can slow down polymer movement and dissipate energy without creating a rubbery network. Unexpectedly, the research showed that reversible interactions influence the polymers' glassy qualities rather than their viscoelastic range.

"Our associative polymers provide a system that allows for investigating separately the effects of reversible interactions on [polymer] movement and glassy behavior," Cai said. "This may offer opportunities to improve the understanding of the challenging physics of glassy polymers like plastics."

From their experiments, Cai's team also developed a new molecular theory that explains the behavior of associative polymers, which could shift thinking about how to engineer them with optimized properties such as high stiffness and rapid self-healing ability.

In addition to Nian, Kim, Cheng and Zhernenkov, Cai collaborated with Ting Ge, a computational simulations expert and assistant professor of chemistry and biochemistry at the University of South Carolina, and Quan Chen from the State Key Lab of Polymer Physics and Chemistry at the Changchun Institute of Applied Chemistry, who provided the initial code for analyzing the flow behavior of polymers.

The paper, "Dynamics of Associative Polymers with High Density of Reversible Bonds," appears in the June 2 issue of *Physical Review Letters*, and is featured as an Editors' Suggestion.

More information: Shifeng Nian et al, Dynamics of Associative Polymers with High Density of Reversible Bonds, *Physical Review Letters* (2023). DOI: 10.1103/PhysRevLett.130.228101

Evgeny B. Stukalin et al, Self-Healing of Unentangled Polymer Networks with Reversible Bonds, *Macromolecules* (2013). DOI: 10.1021/ma401111n

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