Magnetic tweezers reveal polymers' hidden properties

By David Nutt

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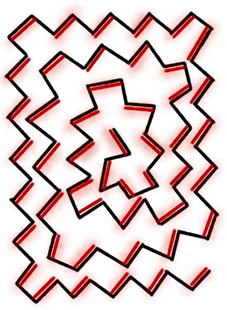
Conjugated polymers are essentially clusters of molecules strung along a backbone that can conduct electrons and absorb light. This makes them a perfect fit for creating soft optoelectronics, such as wearable electronic devices. However, as flexible as they are, these polymers are difficult to study in bulk because they aggregate and fall out from solution.

A group led by Peng Chen, the Peter J.W. Debye Professor of Chemistry and Chemical Biology in the College of Arts and Sciences, circumvented that problem by employing an approach his lab pioneered on other synthetic polymers. This approach, called magnetic tweezers, allowed them to stretch and twist individual molecules of the conjugated polymer polyacetylene and, for the first time, measure its mechanical and kinetic properties during polymerization reaction.

The insights they gained could eventually lead to more flexible and robust soft electronic materials.



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This schematic illustration shows the structure of a conjugated polymer, which is essentially a series of clustered molecules strung along a backbone that can conduct electrons and absorb light.

The team's paper, "Single-Chain Polymerization Dynamics and Conformational Mechanics of Conjugated Polymers," published June 16 in CHEM. The paper's lead author is postdoctoral researcher Susil Baral.

"The conjugated polymer is really a prototype," Chen said. "You always modify it to tailor it for applications. We are hoping everything we measured – the fundamental properties of synthesis kinetics, the mechanical property – become benchmark numbers for people to think about other polymers of the same category."

Previous efforts to address the solubility of conjugated polymers have often relied upon chemical derivatization, in which the structures are modified with functional groups of atoms. However, that approach can affect the polymer's innate properties.

In 2017, Chen's group was the first to use a measurement technique known as magnetic tweezers to study living polymerization, visualizing it at the single-molecule level. The technique had already been used in the biophysics field for studying DNA and proteins, but no one had successfully extended it to the realm of synthetic polymers.

The process works by affixing one end of a polymer strand to a glass coverslip and the other end to a tiny magnetic particle. The researchers then use a magnetic field to manipulate the conjugated polymer, stretching or twisting it, and measuring the response of a single polymer chain that grows. The amounts are so small, they stay soluble in solution, the way bulk amounts normally would not.

Chen and his team were able to measure how long chains of conjugated polymers, which consist of hundreds of thousands of monomer units, grow in real time. They discovered that these polymers add a new monomer per second, a much faster growth than their nonconjugated analogs.

"We found that while growing in real time, this polymer forms conformational entanglements," Chen said. "All polymers we have studied form conformational entanglements, but for this conjugated polymer, this conformational entanglement is looser, allowing it to grow faster."

By pulling and stretching individual conjugated polymers, so-called force extension measurements, the researchers were able to assess their rigidity and better understand how they can bend in different directions while remaining conjugated and retaining electron conductivity.

They also discovered the polymers displayed diverse mechanical behaviors from one individual chain to the next – behaviors that had been predicted by theory but never observed experimentally.

The findings highlight both the uniqueness of conjugated polymers for a range of applications as well as the strength of using a single-molecule manipulation and imaging technique on synthetic materials.

"Now we have a new way to study how these conjugated polymers are made chemically and what is the fundamental mechanical property of this type of material," Chen said. "So we can study how these fundamental properties change when you start tailoring them for application purposes. Maybe you can make it more mechanically flexible and make the polymer longer. Or adjust the synthesis condition to either synthesize the polymer in a faster or slower way."

Co-authors include Geoffrey Coates, the Tisch University Professor in A&S; former postdoctoral researcher Chunming Liu; Kaori Kubo, Ph.D. '17; doctoral student Udit Kumar Chakraborty; and postdoctoral researcher Xianwen Mao.

"Conjugated polymers are a fascinating class of materials due to their inherent optical and electronic properties which are dictated by their polymer structure," said Dawanne Poree, program manager for the Army Research Office, an element of the U.S. Army Combat Capabilities Development Command's Army Research Laboratory, which supported the research.

"These materials are highly relevant to a number of applications of interest to the Army and Department of Defense, including portable electronics, wearable devices, sensors and optical communication systems," Poree said. "To date, unfortunately, it has been difficult to develop conjugated polymers for targeted applications due to a lack of viable tools to study and correlate their structure-property relationships."

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