

Spotlights on Recent JACS Publications

 Cite This: *J. Am. Chem. Soc.* 2020, 142, 18279–18280

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■ USING MECHANOCHEMISTRY TO IMPROVE POLYMER STRESS RESPONSE

Polymer-based materials subjected to stress become susceptible to macroscopic failure—a process driven by fracturing of individual polymer chains. In the search for more stress-responsive materials, chemists have looked to polymer hidden length—a portion of a polymer backbone that is contained within a macrocyclic loop, held together by a chemical bond between non-adjacent backbone atoms. Known as “hidden length” because it does not contribute to the end-to-end distance of the polymer, it can be incorporated in a way that allows release under mechanical loads, providing localized strain relief without chain fracture.

To date, hidden length designs have focused mostly on the choice of the sacrificial bond, but Wengui Weng, Wenke Zhang, Roman Boulatov, and co-workers describe a new mechanophore that adds mechanochemical reactivity to the hidden length itself (DOI: [10.1021/jacs.0c09220](https://doi.org/10.1021/jacs.0c09220)). The researchers integrate 2,3-diphenyl-cyclobutene-1,4-dicarboxylate into macrocyclic cinnamate dimers and find that stretching the corresponding polymer more than doubles its length without fracture of the chain. Theoretical calculations, validated with experimental studies, show that breaking the chain by stretching it requires 11 times as much energy as that required for a simple polyester of the same initial length. The study provides evidence of the potential benefits of incorporating mechanochemically active components into polymer hidden length.

Christine Herman Ph.D.

■ DISCOVERY OF MEMBRANE BLEBBING INDUCED BY Zn^{2+} –LIPID BINDING

Like an advanced telecommunications network, our cells are in constant contact. Instead of using emails or text messages, cells communicate with each other via chemical signals. One cell will secrete a chemical messenger which then floats in the extracellular matrix to other cells. Then, other cells open the message and react accordingly. Not only must the chemical messenger travel through the phospholipid membrane of the sending cell, but it must permeate the membrane of the receiving cell. This process may be promoted by divalent metal cations. Research has shown that binding of Ca^{2+} and Mg^{2+} to lipids activates cell-signaling cascades. However, the interaction of other metal cations is less explored.

Remarkably, Paul Cremer and co-workers demonstrate that Zn^{2+} binds to phosphatidylserine lipids in supported lipid bilayers (SLBs) (DOI: [10.1021/jacs.0c09103](https://doi.org/10.1021/jacs.0c09103)). The SLBs, which are useful models of cell membranes, respond to zinc

binding by forming unilamellar blebs, or spherical bulges of the membrane. This exciting finding suggests that Zn^{2+} can alter the physical properties of membranes by replicating the rolling up or blebbing effect induced by membrane proteins. The authors hope that this discovery will open new investigations into the role Zn^{2+} may play as a secondary messenger in the chemical communication system.

Kimberly Bolduc

■ A NEW METHOD CREATES PRECISION POLYMERS

Creating polymers with controlled monomer sequence, molecular weight, and stereochemistry is an area where nature is currently streets ahead of science. But a team of scientists led by Masami Kamigaito has come closer to closing this gap (DOI: [10.1021/jacs.0c09289](https://doi.org/10.1021/jacs.0c09289)). They developed an efficient strategy that allows them to synthesize a new family of sequence-regulated polymer mimics with controlled molecular weight and perfect tacticity from vinyl monomers as starting materials.

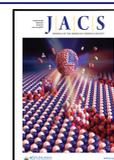
By combining iterative atom transfer radical additions and olefin metathesis reactions with selective recrystallization and later polymerization, their novel method makes it possible to prepare carbon–carbon main-chain sequence-regulated polymers with controlled molecular weights greater than 10^4 , and with stereoregularity. In particular, this same sequence-regulated segment can be introduced into a block polymer with norbornene derivatives in a living C–C bond-forming reaction, such as ring-opening metathesis polymerization. Understanding how to achieve precise and periodic sequences in vinyl polymers will allow chemists to tune polymeric materials for applications in areas like bioengineering, molecular electronics, and catalysis.

Lučka Bibič Ph.D.

■ ENHANCING MOLECULAR CAGES WITH ELECTROSTATICALLY BOUND CAPS

Molecular cages' ability to house guest molecules makes them excellent tools in controlling the transportation of molecular targets. However, which substrates a particular cage can capture depends on its chemical characteristics, such as a

Published: October 28, 2020



positively charged cage struggling to encapsulate a cationic guest due to electrostatic repulsion. Hiroki Takezawa, Makoto Fujita, and co-workers have explored a molecular cage with this issue, where the six Pd(II) ions at its vertices easily allow it to house neutral and anionic guests, but reject cationic substrates (DOI: [10.1021/jacs.0c08835](https://doi.org/10.1021/jacs.0c08835)).

They address this problem by developing an anionic “capping” compound that binds to the cage’s open faces with negatively charged sulfonate groups, providing a more favorable electrostatic environment for cationic substrates. Using both ^1H NMR and XRD, the authors demonstrate not only that the “capped” cage can encapsulate a cationic guest (1-adamantyl ammonium), but also that an “uncapped” cage will exchange a neutral substrate for a cationic substrate when the capping compound is added.

This expansion of molecular cage functionality has been achieved without covalent modification, requiring only the addition of a single small molecule to the solution. Because of this, the authors hope this capping technique can be applied to existing molecular cages, expanding their possible applications.

Charlie Crowe

■ NANOWIRES TAKING ENERGY STORAGE A LONG WAY

The transition from life dependent on fossil fuels to a sustainable energy future relies heavily on the development of next-generation battery technologies to ensure electric vehicles can go farther and homes are powered when the sun goes down or wind stops blowing. Lithium–air batteries (LABs) have attracted significant attention due to their impressive theoretical capacity; however, throughout battery discharge, the growth of insulating lithium peroxide (Li_2O_2) limits the discharge capacity and contributes to a large charging overpotential. Resolving the growth mechanism and resulting structure of Li_2O_2 is critical to realizing the full potential of LABs.

Kohei Uosaki and co-workers have applied electrochemical methods and graphene-coated gold electrodes to grow forests of highly ordered, crystalline Li_2O_2 nanowires (NWs) with 500 times the areal cathode capacity of an unmodified electrode (DOI: [10.1021/jacs.0c05392](https://doi.org/10.1021/jacs.0c05392)). Characterization by XRD, Raman, and other techniques allowed them to elucidate the growth mechanism and resulting structure of these Li_2O_2 NWs. Utilizing $^{18}\text{O}_2$ and $^{16}\text{O}_2$ as compositional markers throughout NW growth, it was possible to clarify that the growth occurs continuously at the Li_2O_2 /substrate interface.

This work not only revolutionizes the synthesis of high aspect ratio Li_2O_2 crystals but provides novel insight that will propel future research to improve the capacity of LABs. Simultaneously, the authors suggest that understanding this growth technique may prove invaluable to other interesting electrochemically grown products, like superoxides.

Peter Rudd