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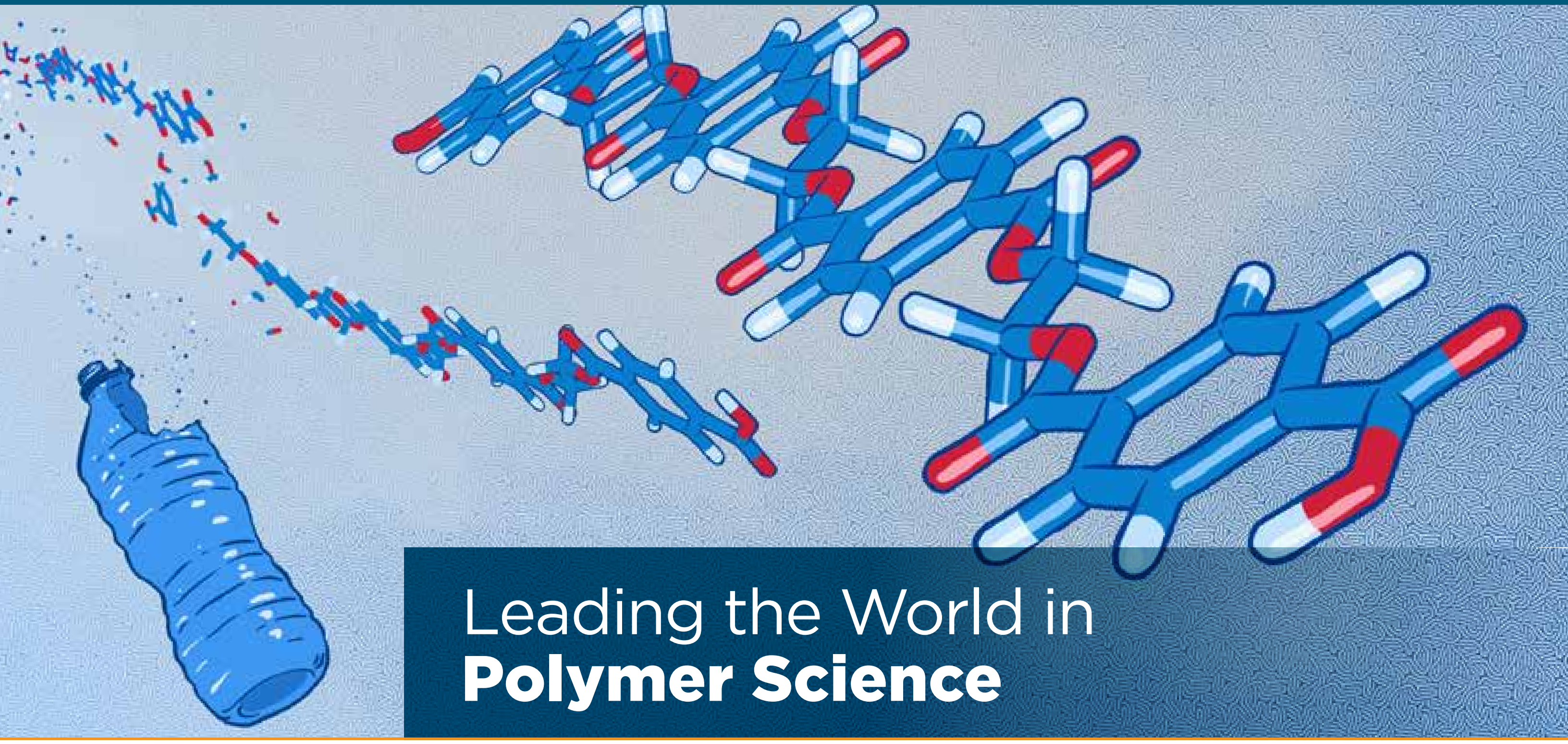
FALL 2022 NEWSLETTER



Leading the World in **Polymer Science**

From your clothing to the fiber-optic cables bringing you high-speed internet, polymers are everywhere, with applications in nearly all fields of science and industry. Polymer science plays a crucial role in providing solutions to global needs including food, clean and abundant water, air, energy, and health.

Researchers at the University of Tennessee, Knoxville, in fields including chemistry, physics, chemical engineering, biosystems engineering, and forestry are investigating polymers through a variety of fundamental scientific problems with real-world impact—from designing and creating new advanced materials to improving industrial processes to creating sustainable biofuels.

As an indication of the significance of their work, UT has been ranked the top global university for polymer science in U.S. News and World Report's *Best Global Universities*. The ranking is based on research performance from 2015 through 2019 as well as citations from publications through April 29, 2021.

Polymer science research within UT's College of Arts and Sciences includes work being conducted by the research group of UT-ORNL Governor's Chair for Polymer Science Alexei Sokolov. The team is advancing fundamental understanding and design of novel polymeric materials for various current and future technologies—from gas separations and carbon capture to 3D printing.

Sokolov's group also works on polymer electrolytes for use in new generations of solid-state batteries and other energy storage technologies.

"We are working on polymers with dynamic bonds that are recyclable and have self-healing ability," said Sokolov.

> "These polymers might replace current plastics and drastically reduce pollution."

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Another area of focus, led by the research group of Associate Professor of Chemistry **Brian Long**, is creating new synthetic materials to separate greenhouse gases such as carbon dioxide from nonharmful gases in a more energy-efficient and cost-effective manner. This research has shown tremendous promise, with implications for reducing industrial greenhouse gas emissions.

"Think about what your body is touching right now—your clothing, your chair, your phone or computer. What are you touching that's not a polymer or that doesn't contain polymers? Polymers have provided solutions to almost every societal need in modern human history—even the DNA, RNA, and proteins in our body are polymers," said Long.

Researchers at UT are even tackling one of the most pressing global needs today—how to minimize or eliminate waste plastics in the environment. For example, research efforts led by Professor Mark Dadmun and Assistant Professor Johnathan Brantley seek to develop new chemical methods to aid recycling of waste plastics, improve the properties of new products and materials made from mixed plastic waste streams, and create a circular plastics economy.

Commenting on the announcement of the ranking, Vice Chancellor for Research Deborah Crawford said, "Our researchers deserve this recognition for their work advancing our understanding of polymers and how they can contribute to making life and lives better. At UT, our commitment is to contribute to the creation of a more just, prosperous, and sustainable future through world-class research and scholarship. Our polymer scientists and engineers are doing just that!"

GRADUATE STUDENT SPOTLIGHT

Miranda Limbach, third year PhD student, recently earned an Outstanding Student Poster award at the fall meeting of the American Chemical Society (ACS). Limbach's poster, titled "Atomic View of Aqueous Cyclosporine A: Unpacking a Decades-Old Mystery," was one of eight student posters in the division of physical chemistry to be honored at the meeting.

"This was my first time at the ACS Conference," said Limbach. "Presenting the poster was lots of fun. Everyone who stopped seemed really interested and the judges were anonymous so you didn't know who was or wasn't a judge."

Limbach's presentation and poster were based on a collaborative effort between the department, the neutron scattering division at Oak Ridge National Laboratory (ORNL), and the University of Vanderbilt.

Limbach's work investigates cyclosporine A, a macrocyclic immunosuppressant. Macrocycles are a class of molecules with the ability to permeate the cell membrane and bind to a number of target proteins. Macrocycles have important applications in the pharmaceutical industry and can contribute to both the development of new drugs, including antibiotics, and the successful delivery of those drugs in the human body.

Earlier in 2022, this work was published in the *Journal of the American Chemical Society*, with a number of UT chemistry co-authors, including graduate students Aleksandra Antevska, Damilola Oluwatob, and Amber Gray, Assistant Professor Thanh Do, and Director of Nuclear Magnetic Resonance (NMR) Core Facilities Carlos Stern.

Limbach credits her experience in the Department of Chemistry and time in Thanh Do's research group with preparing her for a successful presentation.

"The nice thing about Dr. Do's lab is we use a lot of techniques so we get to learn a little bit of everything," said Limbach. "I've been learning a little bit of mass spectrometry and x-ray diffraction and I learned a lot about 2D NMR. The department has been great. Everyone's really open to making sure you learn everything you need."

Limbach plans to continue exploring the significance of cyclosporine analogues during her academic career and, after graduation, is considering a future working with NMR facilities or industry.

Solutions to "Forever Chemicals"

Collaborative research conducted by Shawn Campagna, professor of chemistry, and Frank Loeffler, governor's chair professor in microbiology, have made a discovery that could lead to new capabilities for managing environmental contamination.

Commercially used per- and polyfluoroalkyl substances (PFAS) were developed in the 1940's and made their way into a variety of common household products. Today, PFAS are used for plastic and rubber manufacturing and in food wrappers, umbrellas, firefighting foam and more.

PFAS have also been called "forever chemicals" due to their resistance to breaking down in both the environment and the human body. PFAS have been discovered lingering in rivers, Arctic sea ice, human breast milk and in the blood of 97% of Americans. Most troublesome is their potential impact on human health and PFAS have been linked to metabolic disruption, obesity, diabetes, immune suppression, and cancer.

Campagna and Loeffler's work, recently published in *Environmental Science and Technology*, explores a potential avenue for decreasing broad contamination with these chemicals. Their team found that a naturally occurring soil bacterium, *Pseudomonas* sp. strain 273, was capable of degrading and detoxifying 1,10-difluorodecane, a fluorinated compound that could be a model for dealing with PFAS. Surprisingly, this bacterium was also able to use the fluorine containing byproducts to build lipid bilayers, or cellular membranes, which indicates that we don't yet know all that we should about the fate of this type of compounds in biological systems.

"This research is important since fluorinated organic chemicals are emerging contaminants, and we do not yet know how and if they enter the food web," said Campagna. "The fact that bacteria can incorporate breakdown products of these molecules into their biomass indicates that we don't fully understand the environmental impact of these contaminants."

This discovery developed from a long-standing series of collaborations between Campagna and Loeffler and leverages the capabilities of both the Center for Environmental Biotechnology and the Biological and Small Molecule Mass Spectrometry Core.

"There is a pressing need to demonstrate that natural degradation processes for PFAS exist – that they are not forever chemicals," said Loeffler. "The new findings emerged through collaborative efforts at the interface of disciplines, specifically environmental microbiology and analytical chemistry. My group obtained and characterized the unique microorganism, and Dr. Campagna's group had the instrumentation and expertise to perform the analytical procedures."

The team hopes their work can lead to further discoveries of bacteria capable of degrading the entire range of fluorinated pollutants, which could lead to removing PFAS from contaminated areas like drinking water. Campagna's collaboration with Loeffler is just one example of the impactful interdisciplinary work occurring in the Department of Chemistry and across campus.

Eastman Innovation Center Dedicated on UT Campus

The two institutions will work toward a “green corridor” through sustainability partnership.

A longstanding relationship between Eastman and the University of Tennessee, Knoxville, took a leap forward Thursday as leaders dedicated the Eastman Innovation Center on the UT campus and outlined joint initiatives that could have far-reaching economic and environmental impact.

“Connecting our faculty experts with industry leaders, supplying them with the resources and the collaborative environment they need to solve pressing global problems is what a modern land-grant university is meant to do,” said Chancellor Donde Plowman. “The discoveries made through this partnership with Eastman will positively impact communities across the United States and world.”

Plowman and Deborah Crawford, vice chancellor for research, joined Steve Crawford, Eastman executive vice president, technology and chief manufacturing, engineering, and sustainability officer, and Chris Killian, Eastman senior vice president and chief technology officer, in dedicating the new center. Eastman’s center is in the UT Business Incubator, which provides a central location for technology firms to collaborate with UT on research and economic development projects that can benefit Tennessee.

“Our two institutions have decades of shared history,” said Eastman’s Crawford. “Today is a significant new chapter in that history.”

Research Amplification

The center expands an existing research relationship, as the university has been a member of the Eastman Innovation Network of higher education partners since 2015. Eastman will maintain a consistent campus presence, with scientists rotating through its Knoxville space to focus on research proposals from UT research teams of faculty and students.

“Our relationship with Eastman leverages unique intellectual and infrastructure resources and future workforce development in these critical areas of national need,” said Dayakar Penumadu, Fred N. Peebles Professor and IAMM Chair of Excellence. “A dedicated facility that brings Eastman employees to UT’s campus with a constant presence will substantially increase future collaborations. It is a win-win for both organizations.”

UT and Eastman extended a master research agreement that continues the research partnership through 2026. In doing so, Eastman has committed to at least $1 million for funded research. Killian said that because UT has acumen in areas strategic to Eastman, it is likely that Eastman will exceed the $1 million in research funding by that time.

“We’re excited for the possibilities of the innovation center because UT’s well-known expertise in fields like neutron science and additive manufacturing,” Killian said. “Through our early funded research proposals, we’re already seeing potential innovation in our window films, Eastman Tritan™ copolyester, cellulose esters, and Eastman Tetrashield™ for can coatings. We expect significant mutual benefit. We’re committed to solving some of the world’s greatest problems through innovation, and collaboration between institutions like Eastman and UT will accelerate that work. In turn, UT students get the opportunity to work on projects with real-world impact.”

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Sustainability Synergies

In the process of discussing that research partnership, senior leaders in Knoxville and Kingsport, Tennessee, expanded discussions of overlapping sustainability initiatives and goals.

"We see abundant opportunities—especially on climate and material circularity—where we can work together to make a meaningful impact not only for the university and Eastman, but also for the state and especially for the East Tennessee region," UT's Crawford said.

UT and Eastman collaborated on a recycling project in 2021 to show how plastic collected at UT football games can be processed by Eastman's molecular recycling technologies and reborn in the form of reusable water bottles. Initiatives like this will continue at Neyland Stadium in 2022. This year marks the 30th anniversary of "Good Sports Always Give Back," a UT recycling program of which Eastman is a founding partner.

Ongoing research collaborations between UT and Eastman focus on the development of next-generation structural and functional materials that are sustainable for use in a variety of applications including automotive manufacturing.

"Cars, trucks, and buses currently contribute approximately 16 percent of the world's carbon dioxide emissions, leading to an increase in global temperatures and affecting climate," said Penumadu. "A key strategy of reduced carbon footprint is to consider light-weight materials, such as fiber reinforced polymer composites, where both fiber and resin are made from natural materials or recycled materials from Eastman's molecular recycling technologies, which process hard-to-recycle plastics an infinite number of times. These use-inspired research projects are rapidly developing innovative manufacturing and materials with university and industry collaborations right here in East Tennessee."

Eastman's Crawford summarized the wider impact of the UT–Eastman research collaboration, saying,

"This is about mutual benefit, but it's also about a greater purpose—serving the public good. Those 'big ideas' for renewables and circularity that we're able to develop in the next few years can be applied across the region and the world."

UNDERGRADUATE STUDENT SPOTLIGHT

Earlier this year **Macy Hudson**, undergraduate student in the Department of Chemistry, co-authored a publication with a team of UT faculty, researchers, and students. The paper "Reactive Oxygen Species (ROS) Activated Liposomal Cell Delivery Using a Boronate-Caged Guanidine Lipid" was published in *Chemistry: A European Journal* in late May.

Hudson, a senior, began her time at the university with a plan; she wanted to study organic chemistry, get some experience in a lab, then continue to graduate school. Despite challenges presented by the onset of COVID-19 in early 2020, which sent students home for virtual learning and paused work in labs across campus, she continued to pursue these goals.

"During my sophomore year I really started looking at how to get involved in undergraduate research," said Hudson. "I asked around the department and was advised to look at what our individual faculty members are researching, reach out to them directly and see if they had any projects that suited my area of study."

This active pursuit of her research interests eventually led Hudson to the research group of **Michael Best**, professor of chemistry. Best's group works with the design and creation of organic molecules for uses relevant to biological systems. The publication Hudson co-authored describes the results of one such project with applications in the pharmaceutical industry.

"The goal of this project was to create a lipid and then use a disease-associated trigger to cleave off the head group of the lipid. When that happens, it creates a positive charge, and if we can create enough positive charge, nanocarriers called liposomes composed of this lipid can be absorbed into cells. This method can be used for drug delivery by putting drug molecules inside the liposome which the cell then absorbs," said Hudson. Her work on the project was very hands-on, synthesizing and testing the lipid repeatedly, the results of which were included in the publication.

Hudson plans to continue working in organic chemistry, and specifically in drug design and delivery, by pursuing a PhD after graduation. She hopes to eventually work in development in the pharmaceutical industry. Hudson credits her time in the Department of Chemistry with preparing her to pursue these goals.

"I've had a really great experience. Getting involved beyond research and classes has really helped. I joined our undergraduate chemistry club and worked as an undergraduate teaching assistant, which allowed me to build relationships with faculty members and teach the material that I love," said Hudson.

RESEARCH UPDATES

Zhao Group published a communication in *J. Am. Chem. Soc.* titled "Adaptable Multivalent Hairy Inorganic Nanoparticles." Caleb A. Bohannon and Andrew J. Chancellor are the co-first authors.

Sheng Dai is among an elite group recognized for exceptional research influence, demonstrated by the production of multiple highly-cited papers that rank in the top 1% by citations for field and year in the Web of Science™. Each year, Clarivate™ identifies the world's most influential researchers—the select few who have been most frequently cited by their peers over the last decade. In 2021, fewer than 6,700, or about 0.1%, of the world's researchers, in 21 research fields and across multiple fields, have earned this exclusive distinction.

Kostas Vogiatzis received this year's National Science Foundation's Faculty Early Career Development Program (CAREER) Award, the organization's most prestigious grant in support of early-career faculty. Vogiatzis research centers on the development of new computational methods that interface quantum chemistry with machine learning. The title of his award is "CAREER: CAS-Climate: Data-driven Coupled-Cluster for Biomimetic CO^2 Capture.

The Dai Group published their latest research "Intra-crystalline mesoporous zeolite encapsulation-derived thermally robust metal nanocatalyst in deep oxidation of light alkanes" in *Nature Communications*.

The research group of **Michael Best**, led by graduate student Jinchao Lou, recently published an article describing the development of ATP-responsive liposomes in the *Journal of the American Chemical Society*. The nanocarriers reported in this work show strong prospects for enhancing clinical drug delivery applications. A provisional patent has been filed for this ATP-responsive liposome technology. Additionally, the Best Group is currently working on advancing this platform for clinical delivery applications and developing liposomes that respond to other disease-associated small molecule metabolites.

The **Brantley group** recently published a paper in *JACS* titled "Electroediting of Soft Polymer Backbones" Alan Fried, Breana Wilson, and Nick Galan contributed to the research, under the supervision of Johnathan Brantley. The paper discusses new methodology for degradation and functionalization of olefin-containing polymers through electrochemistry. This method can be carried out in both homogeneous and heterogeneous systems, in addition to using mild conditions and being experimentally simple. The work was completed in memory of Alan Fried.

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Eastman Innovation Center Dedicated on UT Campus

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