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OSTC VISIONS

THE UNIVERSITY OF IOWA

Inside this issue:

Chemical Insights into Photopolymerization Processes

Professor Alec Scranton of the Department of Chemical and Biochemical Engineering is involved in a range of activities at The University of Iowa and beyond. In addition to serving as the College of Engineering's Associate Dean, he is an advisor to honors students, a mentor for undergraduate, graduate, and post-graduate researchers, the co-founder of a National Science Foundation-sponsored research center (see the description on page 3), and an active researcher in the Optical Science and Technology Center (OSTC). And it all started here. Scranton was an undergraduate student at The University of Iowa before leaving to attend graduate school at Purdue University. After 10 years on the faculty at Michigan State University, Scranton returned to join the faculty at The University of Iowa in 2000.

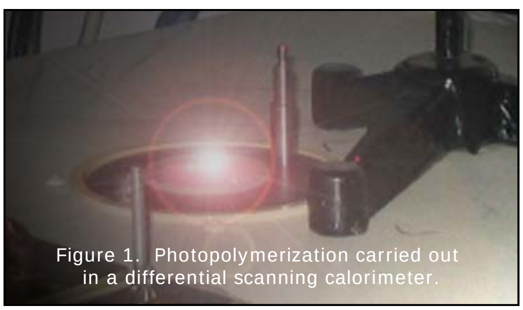

Figure 1. Photopolymerization carried out in a differential scanning calorimeter.

Scranton's research focuses on photopolymerization, which uses light to induce a chain reaction that converts liquid monomers into a solid polymer. Traditionally, polymerization reactions are initiated by using heat or solvents instead of light. Scranton points out that light is a much better initiator of such reactions because, compared to heat and solvent methods, light is faster, cheaper, more specific, and more environmentally friendly. Heat initiated reactions are slower because time is required for heat transfer processes throughout the solution. Light is also cheaper because it requires less energy to produce, and light is more specific because it can be focused to a selected location, thereby pinpointing exactly where the reaction occurs. Finally, optical methods eliminate the need for volatile organic solvents, which reduces the amount of waste generated during the process.

Today, photopolymerization techniques are used in the manufacturing of many common products, such as the creation of clear, scratch-resistant coatings for floors and furniture. Another application is in the production of optical fibers, which are created when molten glass is pulled in "drawing towers." In the past, the production of such fibers was limited by the rate at which a polymeric coating could be added and dried, or 'cured', because until the coating was applied, the fibers were extremely fragile. Scranton's research group is exploring potential future applications through extensive collaborations with research teams in the Departments of Chemistry and Dentistry, as well as with other members of the OSTC.

In his laboratories located within the Iowa Advanced Technology Laboratories (IATL), Scranton works with 10 graduate and undergraduate students to address fundamental issues of photopolymerization which could have an important industrial impact. Some current projects are briefly described below.

Photopolymerization of thick systems. Photopolymerization processes are ideally suited for rapid and efficient production of thin films and coatings, but are somewhat limited for the production of thick polymeric films. Thick polymerization systems would greatly benefit, however, from the spatial and temporal control provided by a light-induced reaction. Unfortunately, photo-

(Continued on page 3)

From the Director

Mark Arnold, Director

The Optical Science and Technology Center (OSTC) is all about interdisciplinary research for the advancement of science and technology. I'm pleased to acknowledge that the number of multi-investigator and multi-disciplinary projects is growing rapidly in our center. In a large way, my objective as Director of the OSTC is to establish an environment that promotes interdisciplinary activities and stimulates projects between research groups. My goal is to catalyze such activities across the spectrum of participants, including the faculty in all disciplines, of course, and also research scientists, research engineers, as well as undergraduate, graduate, and post-graduate students.

The most important way to promote interdisciplinary research is to showcase the research interests and accomplishments of our membership. By this, I mean we need to be constantly talking to each other about our most recent research findings in order to establish opportunities for collaborations. It is difficult to contribute to the problems and impediments in other research groups if you're not aware of

(Continued on page 2)

PUBLICATIONS

For a full listing visit: www.ostc.uiowa.edu/publications.htm

Song, W, **Grassian, VH, Larsen, SC**, "Fiber and film formation by self-assembly of colloidal silicalite-1 and copper coated silicite-1 nanocrystals," *Microporous and Mesoporous Materials* **88** 77-83 (2006).

Dakanali, M, Roussakis, E, **Kay, AR**, Katerinopoulos, HE, "Synthesis and photophysical properties of a fluorescent TREN-type ligand incorporating the coumarin chromophore and its zinc complex," *Tetrahedron Letters*, **46** 4193-4196, (2005).

Roper, TM, Lee, TY, **Guymon, CA**, Hoyle, CE, "*In-situ* characterization of photopolymerizable sytems using a thin-film calorimeter," *Macromolecules* **38** 10109-1011, (2005).

Friscic, T, Hamilton, TD, Papaefstathious, GS, **MacGillivray, LR**, "A template-controlled solid-state reaction for the organic chemistry laboratory," *Journal of Chemical Education*, **82** 1679-1681, (2005).

Arnold, MA, Small, GW, "Noninvasive glucose sensing," *Analytical Chemistry*, **77** 5429-5439, (2005).

Johnston, WJ, Yildirim, M, **Prineas, JP**, Smirl, AL, "All-optical, spin-dependent polarization switching in Bragg-spaced quantum well structures," *Applied Physics Letters* **87** 10113, (2005).

Choi, JL, **Gillan, EG**, "Solvothermal synthesis of nanocrystalline copper nitride from an energetically unstable copper azide precursor," *Inorganic Chemistry*, **44** 7385-7393, (2005).

Lau, WH, **Flatté, ME**, "Electric field dependence of spin coherence in (001) GaAs/AlxGa1-xAs quantum wells," *Physical Review B*, **72** 161311, (2005).

Mermer, O, Veeraraghavean, G, Francis, TL, Sheng, Y, Nguyen, DT, **Wohlgenannt, M**, Kohler, A, Al-Suti, MK, Khan, MS, "Large magnetoresistance in nonmagnetic pi-conjucated semiconductor thin film devices," *Physical Review B*, **72** 205202, (2005).

Jain, K, Klier, J, **Scranton, AB**, "Photopolymerization of butyl acrylate-in-water microemulsions: Polymer molecular weight and end-groups," *Polymer*, **46** 11273-11278, (2005).

FROM THE DIRECTOR...CONTINUED

(Continued from page 1)

what these problems are! Effective synergism demands persistent communication between researchers in both formal and informal fora.

Future collaborations require that all OSTC members be aware of new developments and innovative research opportunities. For example, do you know the number of new startup companies that have been established recently as off-shoots of OSTC research programs? The answer is two! I have partnered with Gary Small and Jonathon Olesberg to form ASL Analytical, Inc., which is a small startup company with the objective of developing noninvasive near infrared sensing technology for commercial and clinical applications. In addition, Markus Wohlgenannt has partnered with several of his recent students to form OMR Sensors, Inc., for the purpose of developing and commercializing interactive organic light-emitting diode displays based on the patented discovery that organic semiconductor light-emitting diodes are unusually sensitive to magnetic fields. Both companies are exploring various opportunities for Small Business Innovative Research (SBIR) funding. Now that you know, potential collaborations with these young startup companies are possible.

The OSTC membership has established a number of effective mechanisms to broadcast the latest research developments in our groups. One example is *Visions*, which provides basic descriptions of the OSTC research programs. I plan to improve this coverage by providing more in-depth descriptions. This issue of *Visions*, for example, focuses on Alec Scranton's research in Chemical and Biochemical Engineering. In this article, Alec and I have tried to increase the depth of coverage by providing a description of the chemistry associated with several of his projects. A bit of data is even provided for your enjoyment. Of course, our newsletter is ultimately intended for a general audience, so other mechanisms are needed for genuine scientific exchanges.

Our annual OSTC Symposium is an excellent avenue for exchanging scientific ideas. Our next OSTC Symposium is entitled "Optics and Materials" and is scheduled for Monday, April 10th in the IATL Conference Room. Speakers this year include OSTC professors Sarah Larsen, John Wiencek, Allan Guymon, and Markus Wohlgenannt. I am pleased to welcome Professor Richard Van Duyne from Northwestern University as our outside speaker this year. As in previous years, a poster session is scheduled for the afternoon and I strongly encourage posters from all OSTC research groups. Registration for the symposium is free, so please signup today at our website (www.ostc.uiowa.edu).

A new OSTC seminar series was announced in the last newsletter. Professor Mark Young will give the first OSTC seminar on Tuesday, February 21st starting at 12:30 in the IATL Conference Room. I encourage everyone to attend this seminar to hear about Mark's research to explore atmospheric chemistry on aerosol particles. The title of his presentation is "Atmospheric Chemistry at the Nexus: Links to Global Cycles, Climate and Health." Please feel free to bring your lunch and ask lots of probing questions.

I would like to propose yet another mechanism to broadcast significant research findings from OSTC researchers. Shortly, a new area of the OSTC website will be dedicated to the announcement of "OSTC Breakthroughs." I hope to receive announcements of significant breakthroughs and major research accomplishments from all OSTC groups so we can put a brief summary and link for more information on our website. This way, other OSTC researchers can become aware of these major advances in a timely manner. In addition, this will be a place for prospective graduate students, administrators, and funding agencies to discover the latest and greatest accomplishments from our research enterprise.

RECENT FUNDING

Sarah Larsen/Vicki H. Grassian—$50,000 from DOE/National Energy Technology Laboratory, "Enhanced activity of nanocrystalling zeolites for Selective Catalytic Reduction of NOx."

William Eichinger—$405,753 from the U.S. Department of Agriculture, "A new approach to emissions from animal husbandry facilities."

CHEMICAL INSIGHTS...CONTINUED

(Continued from page 1)

initiation of thick systems is inherently non-uniform and much more complex than photopolymerizations of thin films. A fundamental understanding of the underlying chemical and physical processes is required in order to identify critical reaction variables to ensure proper selection of reaction components and the design of effective reaction systems. The Scranton group is exploring these fundamental processes for photopolymerization systems that may be several centimeters thick.

Results demonstrate that a photo-initiation reaction front moves from the illuminated surface through the depth of the sample. A number of important factors influence the maximum photo-initiation rate by affecting the height of the propagating front and the rate at which the front moves through the sample. A mathematical model accurately describes this photo-initiation process and this model provides an invaluable tool for selection of reaction components and design of thick photopolymerization systems. The model describes the spatial and temporal evolution of the light intensity gradient, the initiator concentration gradient, and the photoinitiation rate profile in thick systems. The utility of this model is illustrated in Figure 2, where key properties of the wave front are established as a function of time.

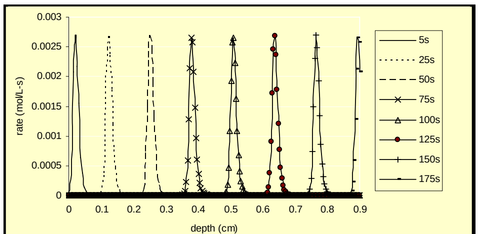

Figure 2. Simulated data showing the position (depth) and magnitude (reaction rate) of the photopolymerization wave front at selected reaction times.

Photochemical method to eliminate oxygen inhibition. A major commercial problem in the production of photo-cured acrylate coatings is oxygen inhibition at the coating surface. The Scranton research group is exploring unique and practical solutions to this problem. Their primary strategy is to develop light-modulated chemistry to eliminate oxygen from the reaction region. This is accomplished by including a singlet-oxygen generator and a singlet-oxygen trapper in the reactive formulation. A schematic of the basic process is presented in Figure 3, where the porphyrin Zn-tpp is the singlet-oxygen generator and dimethylanthracene is the singlet-oxygen trapper. In this process, Zn-tpp in the ground state absorbs a photon to generate an excited singlet state (^{1}Zn-tpp*) that is rapidly converted to a triplet state (^{3}Zn-tpp*) by inter-system crossing (ISC). This triplet-state excited zinc porphyrin then generates singlet-oxygen ($^1O_2$*) upon relaxation to its original ground state. The singlet-oxygen species is than trapped by dimethylanthracene and the resulting endoperoxide complex subsequently dissociates to produce free radical centers. This reaction process is catalytic in the sense that the original singlet-oxygen generator is recovered and is available for repeated excitation and reaction with oxygen.

Results from the Scranton research group indicate that a variety of photo-induced singlet oxygen generators are possible with different light absorption spectra. Porphyrins, however, are especially attractive because they allowed singlet oxygen to be produced using light in the red or the near IR regions of the spectrum. Therefore, the oxygen-consumption chemistry can be initiated with wavelengths of light that are different than those used to initiate the photopolymerization reactions. This is important because it allows individual control of these processes so oxygen can be consumed before the polymerization reactions begin. Overall, this research provides a method to reduce or eliminate the impact of ambient oxygen, thereby enhancing photopolymerization processes carried out in air.

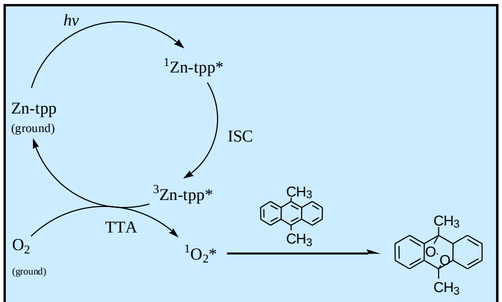

Figure 3. Schematic of the light-modulated reactions designed to eliminate the adverse effects of ambient oxygen on the rate of photopolymerization of acrylate materials.

Fundamental characterization of cationic photopolymerizations. Cationic light-induced polymerization is a versatile technique with numerous advantages over thermal and free radical polymerization reactions. Advantages include: 1) polymerization of important classes of monomers; 2) excellent physical and chemical properties of the cured films; and 3) no inhibition by ambient oxygen, which is a severe disadvantage of the more typical free-radical photopolymerization processes. A critical feature of cationic photopolymerization is the long lifetimes of the active centers. The Scranton research group is characterizing the reactivity and mobility of long-lived active centers. An interesting property of these systems is the continued activity of the active centers after illumination has ceased. The Scranton group is exploring this "dark cure" phenomenon by exploring the kinetics of the underlying chemical reactions and determining the termination mechanisms for these active centers. An improved understanding of this chemistry will enhance flash photopolymerization processes by reducing the need for long illumination times.

Overall, Scranton sees exciting times ahead for photopolymerization researchers. Photopolymerization provides researchers the opportunity to engage in creative chemistry as they seek creative solutions to create new materials, add flexibility to the development of polymers, and replace solvent and heat-initiated reactions. "It's only just beginning to have the effect it can have," Scranton notes. "There's a lot of work to be done."

NSF - Industry/University Cooperative Research Center

In addition to his research with the OSTC, Professor Scranton is a co-founder, with Christopher Bowman of the University of Colorado, of the NSF-sponsored Industry/University Photopolymerization Center. This center is an active collaboration between university researchers and companies and is intended to provide industry oversight of academic researchers in order to facilitate technology transfer. Some of the companies involved include 3M, DuPont, Cytek, Henkle, and DSM Desotech. Currently, nine Center projects are underway, all of which look at fundamental properties of photopolymerization. This kind of fundamental research can lead to a better understanding of the mechanisms of photopolymerization as a way to improve how polymers are used in a variety of applications in industry. More information about the Center can be found at http://css.engineering.uiowa.edu/~cfap/.

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Working together in research

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Founded in 1994, The Optical Science and Technology Center consists of faculty members from the University Departments of Chemistry, Chemical and Biochemical Engineering, Electrical and Computer Engineering, Physics and Astronomy, Biological Sciences, and Environmental and Civil Engineering. Among the faculty are distinguished scientists who have developed international reputations for innovative research on the frontiers of optical science and engineering. Current general research areas include: nanoscience, photopolymerization, environmental sciences, biomedical devices, and semiconductor materials.

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The next issue of *Visions* will focus on efforts related to economic development by several OSTC research groups.

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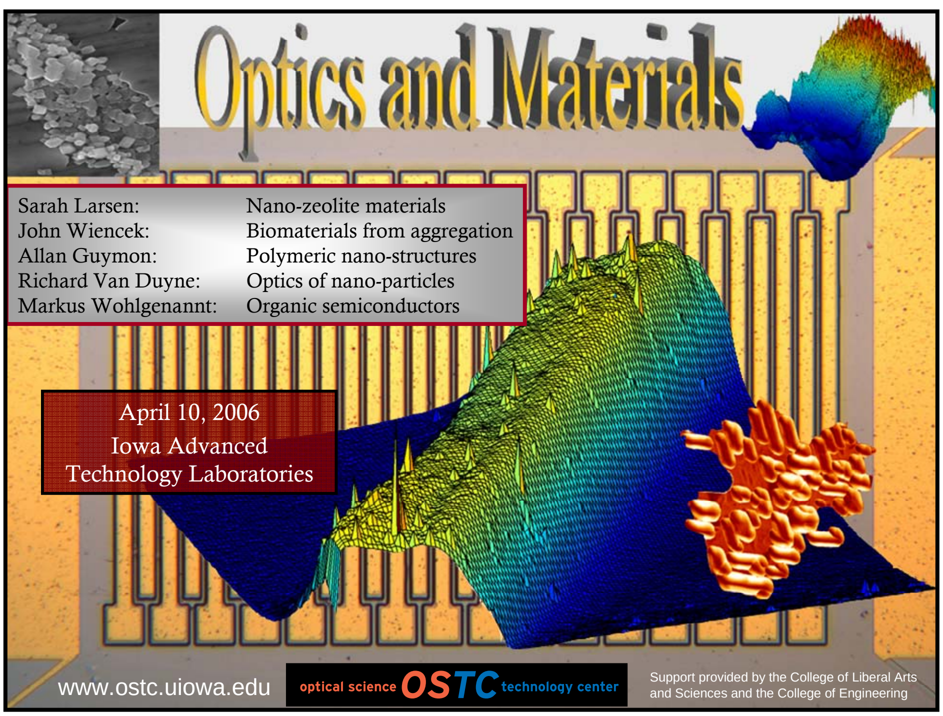
optical science OSTC technology center
2006 Seminar Series

12:30 IATL Conference Room

2/21/06
Mark Young, Chemistry
"Atmospheric Chemistry at the Nexus:
Links to Global Cycles, Climate and Health"

3/21/06
Julie Jessop, Chemical and Biochemical Eng.
"Peering into Polymer Time and
Space with Raman Spectroscopy"

Join us for the next OSTC Symposium
April 10, 2006



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