IUCRC Promotes World-Class Research

By Jon P. Scholte and C. Allan Guymon

The Industrial/University Cooperative Research Center (IUCRC) for Fundamentals and Applications of Photopolymerization was founded in 2000 at the University of Colorado and the University of Iowa to create an environment for world-class academic research in the photopolymerization field with industrial input, perspective and oversight. This advice and direction serves to strengthen the academic research in advancing both the fundamental and applied aspects of photocured systems.

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In conjunction with 17 partner companies over the years, the IUCRC has pursued 30 advanced research projects, resulting in 90 journal publications and 12 patent disclosures. The IUCRC has also received several awards and recognitions, including the 2007 Cooperative Research Award from the American Chemical Society. This award is given each year in recognition of sustained productive partnerships between nationally funded or academic researchers and researchers working in industry.

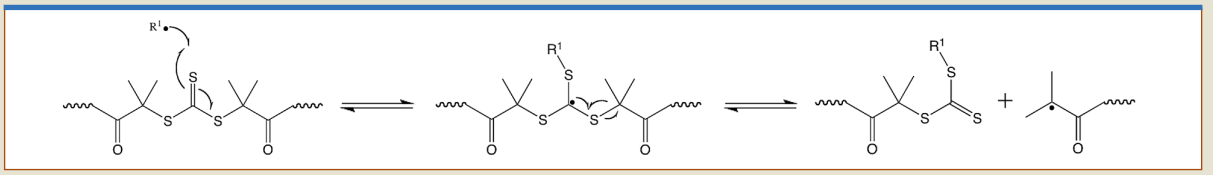
The academic aspect of the IUCRC is led by two directors—Professor Christopher Bowman (University of Colorado) and Professor Allan Guymon (University of Iowa). Faculty from both universities participate in IUCRC-supported research, including Julie Jessop, Chris Coretsopoulos and Alec Scranton (a former director of the IUCRC) from the University of Iowa; and Jeff Stansbury, Charles Musgrave and Kristi Anseth from the University of Colorado. Overall, the IUCRC has supported more than 30 graduate students and post-doctoral researchers with many continuing to contribute to the field of photopolymerization after graduation, and approximately 25 percent of these students currently employed by member companies.

The principal goal of the IUCRC is to further fundamental understanding of photopolymerization mechanisms and kinetics to increase, enhance and improve the use of photopolymerization in applications. The IUCRC accomplishes this goal through unique cooperative opportunities between current member companies (3M, Henkel, DSM Functional Materials, Avery Dennison and Boeing) and faculty and students at both universities. The ability to focus academic research with the aid of industrial advising and assistance has led to numerous cutting-edge projects, including:

- Property Evolution in Photopolymer Systems
- Methods to Reduce Oxygen Inhibition
- Fundamental Studies of Thiol-ene Photopolymerizations
- Photoinitation Profiles in Thick Polymerization Systems

FIGURE 1

The RAFT Mechanism



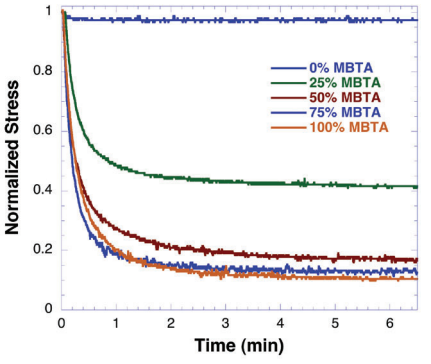
- Novel (Meth)acrylate Monomers for Ultra-rapid Photopolymerization
- Structural Evolution in Photocrosslinked Films
- Characterization of Crosslinked Degradable Networks
- Kinetic Studies of Hybrid Cationic/ Radical Photopolymerizations
- Structured Illumination for Control of Polymerization Shrinkage Stresses
- Development of Parallel Evaluation Scheme for UV Monomer Formulations
- Photopolymerizable Clay Nanocomposites Using Reactive Dispersants
- Molecular Fillers for Enhanced Polymer Mechanical Properties: Photopolymerized Molecularly Filled Composites
- Measurement and Modeling of Oxygen Inhibition Layer in Radical Photopolymerization
- Photoenforced Stratification in Coating and Adhesive Materials
- Photopolymerization Utilizing LEDs
- Dark Cure and Shadow Cure in Photopolymerization Systems

A noteworthy recent center project combining both advances in fundamentals and application incorporated functionalized clay nanoparticles in photopolymer formulations. This effort was led by graduate students Kwame Owusu-Adom and Soon Ki Kim, and was supervised by Professor Allan Guymon. (For details, see article in the next issue of the *RadTech Report*.) This work has led to eight peer-reviewed publications, one of which was co-authored by Joel Schall, a senior scientist at Henkel who helped examine shrinkage properties of the clay nanocomposite systems. This project also resulted in doctoral degrees and jobs in the field for both Owusu-Adom (3M) and Kim (SK Chemical).

Another project that shows great promise in advancing photocured materials focuses on Covalent Adaptable Networks (CANs) that can offer benefits over conventional thermosets and other photopolymerized systems. This work, directed by Professor Chris Bowman at the University of Colorado, has demonstrated that CANs are covalently crosslinked polymer networks, but contain specific functionalities either in the network backbone or at linkage points that allow the bonded structure of the network to rearrange in response to light or heat. Thermal CANs utilize reversible Diels-Alder adducts that form covalent bonds at low temperature and reversibly de-bond at high temperatures. In these systems, polymer networks can be polymerized and set under

FIGURE 2

Stress relaxation behavior versus AFCT agent concentration



The networks were formulated with a 1:1 thiol:acrylate functional group ratio using pentaerythritol tetra (3-mercaptopropionate) (PETMP) and tetraethylene glycol diacrylate (TEGDA). The acrylate component was varied to contain from 0 to 100% MBTA. Network polymerization was catalyzed with 1 wt% of triethylamine. Stress relaxation was catalyzed by incorporating 2.5 wt% of photoinitiator (Irgacure 651) and were irradiated at 20 mW/cm^2 UV light.

one condition (e.g., ambient) and depolymerized at another condition (e.g., high temperature). Photochemical CANs, on the other hand, use light-triggered radical reactions to undergo rearrangement. The photochemically initiated mechanism that gives rise to the network rearrangement in photo-induced CANs is known as addition-fragmentation chain transfer (AFCT) or reversible addition-fragmentation chain transfer (RAFT) as illustrated in Figure 1. Incorporating RAFT agents into polymer networks enables rearrangement during and after polymerization, resulting in significant stress relaxation within the network. The degree of stress relaxation can be substantial as demonstrated for a thiol-acrylate network with varying concentrations of the RAFT moiety methylene propane bis(thioethyl acrylate) (MBTA) in Figure 2. By varying the concentration of RAFT moieties, the amount of network stress relaxation is varied without changing the overall network properties.

"This work on covalently adaptable networks is exactly the type of project that the center should work on, and is a great example of why 3M continues to be a strong supporter of the center," said Wayne Mahoney, a senior scientist at 3M. "These covalently adaptable networks are novel materials that have potential commercial applications in areas where the use environment is different from that of the application environment. Also, the ability to reduce polymerization stress is of fundamental importance to coating and adhesive applications."

To facilitate such advances, the IUCRC convenes each spring and fall for collaborative meetings that include discussions on current projects, proposals for future projects, poster sessions and student mentor discussions with industrial scientists. This past spring 3M hosted a very successful IUCRC meeting attended by more than 100 scientists and engineers from member companies. DSM Functional Materials has agreed to host the spring meeting for 2013.

"DSM is a strong supporter of the IUCRC for Photopolymerization because it provides a great avenue for collaboration between the corporate and academic worlds to advance the field of photopolymerization," said Beth Rundlett, a senior scientist at DSM. "The IUCRC also allows companies to come together in a noncompetitive environment to address common problems within the UV radiation industry. By hosting the next IUCRC meeting, DSM will continue to foster the spirited cooperation the center was built upon, and inspire students to become our next generation of corporate scientists."

At each spring meeting, students give oral progress report presentations detailing their ongoing research. Industrial mentors meet with students to give individual direction, including possible solutions to the students' research problems as well as suggest possible avenues of exploration. In addition to research guidance and support, industrial partners also aid students with career development and advice. At the IUCRC meeting at 3M in 2012, students were able to participate in mock interviews and an industrial poster session in which member companies presented their applications of photopolymerization to students.

During the fall meeting, hosted by one of the two participating universities, new projects are proposed to the industrial partners. The proposals are prioritized and funded based on relevance to both fundamentals and applications in the photopolymerization field. Additionally, poster sessions are held to allow direct communication about the progress of each project between students and industrial members.

Participating companies help not only in guiding fundamental research but also receive advanced access to patent information, intellectual property and scientific findings that originate from center research. The proceedings of both spring and fall meetings are compiled and disseminated via the members-only section of the IUCRC website. Research is also aided by member companies which provide access to expertise and instrumentation not available at the academic institutions. Conversely, several industrial members have spent time in the academic labs at both universities to investigate relevant industrial research. The center also provides significant interactions for a cadre of students supported by the center and others working on photopolymer-related projects with training for positions within the member companies.

For more information about the IUCRC for Fundamentals and Applications of Photopolymerization, visit our website at *http://css.engineering.uiowa.edu/~cfap/* or contact the center directors:

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