The Center for Applied Polymer Science Research:

15 Years of Undergraduate Research in UV-Polymerization

By Byron K. Christmas, Ph.D.

In 1994, the Center for Applied Polymer Science Research (CAPSR) was established at the University of Houston-Downtown (UH-Downtown) in Houston, Texas. The central focus of the program was to provide undergraduate students of the natural sciences the opportunity to learn about UV-polymerization chemistry and technology, and to participate directly in basic and applied research in that field. At that time, the Department of Natural Sciences' only chemistry degree was a bachelor of science degree with a major in industrial chemistry. This degree was designed to prepare students specifically to work in industrial laboratories while giving them the course work required for graduate work in chemistry. The major component missing from the undergraduate curriculum was a viable research program in which students could learn about chemistry and the chemical industry in a non-structured environment beyond the classroom.

University of Houston-Downtown in Houston, Texas.

Collecting a few pieces of equipment with potential research utility, the outlines of a research laboratory began to take shape in 1993. However, no instrumentation was available for making UV polymers or for testing the films thus produced. Clearly, outside support would be needed to acquire the necessary equipment.

Several companies were contacted concerning support. Fortunately, several manufacturers of oligomers, monomers and photoinitiators were more than happy to provide their products for the new research program and that support has continued to the present day. Without this support, CAPSR could not have been sustained for the past 15 years.

In addition to this initial and essential corporate support, a proposal was presented in 1994 to the Robert A. Welch Foundation of Texas to garner their support for the research program. This private philanthropic organization's mission is to support chemical education within the state of Texas. The Welch Foundation graciously accepted the proposal for a "Chemistry Departmental Grant" in 1994 and has provided significant financial support to CAPSR and other chemistry-related research within the Department of Natural Sciences every year since then. The latest funding was received in June 2009 and will give support to CAPSR and

Dr. Byron Christmas in his lab.

other department chemistry research programs for the next three years.

No UV-curing station was yet available in the CAPSR laboratory in 1993-94, so a project was developed to look at simple physical properties of binary monomer blends as a function of blend composition. Densities, viscosities and refractive indices of these blends were determined as a function of their composition and attempts were made to correlate monomer structure with the observed properties. This work was a stopgap measure while efforts were underway to find UV-curing equipment. Wajid Mirza, Scott Ferree and Semir Yusef were the students who worked on this initial project. The results of their work were reported at the RadTech '96 UV/EB Conference in Nashville, Tenn., in a presentation entitled, "UV-Polymerizable Monomer Comparisons 2: Physical Properties of Acrylate Functional Monomer Blends."[1] This work was a follow-up to work done at Celanese Specialty Resins 10 years earlier and presented at the last "Radcure" conference, Radcure '86 in Baltimore, Md.[2]

While monomer blend work was ongoing, Fusion UV Systems, Inc., agreed to provide CAPSR with a UV-curing station that included a 600-Watt/in lamp. With this new resource, a project was immediately initiated to investigate the effects total UV energy density (often called "UV dose") and peak irradiance on the mechanical properties of UV-polymerized films. This investigation required the development of one or more "model" formulations that would respond significantly to changes in the UV parameters. An acrylate-functional aliphatic urethane oligomer (ALU-350 provided by Echo Resins and Laboratory) was selected and was formulated with a monomer mixture containing a trifunctional, difunctional and monofunctional monomer in equal mass ratios.

These monomers were provided by the company now known as Cytec Surface Specialties. Ciba Specialty Chemicals provided the photoinitiator. These companies are representative of the type of support that CAPSR has received from the beginning. Many other companies have also supported the work in various ways, ranging from gratis calibration services (EIT), to significant discounts on the purchase of equipment (TA Instruments, FlackTec), to direct grants of equipment (Brookfield Engineering) or raw materials (Sartomer, Carbon Nanotechnology, SouthWest Nano Technology). Thus, undergraduate research at UH-Downtown has involved strong academic/industrial collaborations from the beginning.

With one or two model formulations selected, work was initiated to determine the effects of changes in UV parameters on the tensile strength, elongation and modulus of the resulting urethane acrylate polymer films. The literature review failed to uncover any previous research wherein total UV-energy density and peak irradiance were both rigorously controlled. "Conventional wisdom" at the time was that, if the peak irradiance was too high, there would be problems with film degradation during cure. However, a systematic study (extending over several years) of the effects of changing peak irradiance failed to show any degradation of polymer mechanical or other properties. In contrast, systematic changes in total UV-energy density at constant peak irradiance produced results fully consistent with existing theoretical understanding of how the free radical polymerization process works.

The initial results obtained from this project were reported at RadTech '96 in Nashville, Tenn., by Christopher Matranga, an undergraduate student in CAPSR at the time. His paper, entitled, "The Effects of UV Dose and Peak Irradiance on the Tensile Properties of UV-polymerized Films,"[3] received the "Founder's Award for Best Technical Paper" for that conference and was one of several subsequent papers on this subject co-authored by undergraduates. This significant accomplishment by Christopher—now Dr. Matranga—demonstrated that undergraduate students could excel in research in UV-polymerization chemistry and technology and that they could successfully present their work in a large international forum.

In subsequent years, CAPSR students were involved in a variety of other research activities and presented many papers and/or posters at RadTech conferences and at other meetings, both at UH-Downtown and in other venues. CAPSR students investigated the effects of UV parameters on the solvent-extractables obtainable from UV-polymerized films. They also investigated thiolene technology for several years and they explored briefly, without success, the use of CO_2 (g) as an inerting agent for UV-polymerization.

More recently, CAPSR students have been investigating the use of carbon

nanotubes (CNTs), both single-walled (SW) and multi-walled (MW), in UV-polymerizable formulations. This work was initially reported at the RadTech 2006 UV/EB Conference in Chicago by Vien Lam in a paper entitled, "UV-Polymerizable Systems Containing Single-Walled Carbon Nanotubes (SWNTs)."[4] Ms. Lam received the "Best Student Paper Award" for her paper during that conference. In that paper, she reported on a novel technique for preparing polymer/CNT composites wherein the nanotubes were encapsulated in a crosslinked polymer. This was different from much of the polymer/CNT work reported in the literature in which linear or perhaps branched polymers were used due to the necessity of either melting or dissolving the polymer prior to introduction of the CNTs. By dispersing the CNTs in low-viscosity, acrylate-functional formulations and, subsequently, polymerizing them with UV, the dispersion process was greatly simplified and the resulting composite was crosslinked.

CAPSR students over the last two years have been involved in investigations of the polymer property differences observed when acrylate-functional formulations are polymerized with a traditional electrodeless lamp with fluctuating photon output versus a newer continuous photon output lamp. This work is ongoing and CAPSR students are now investigating these effects on CNT composite materials. Additionally, since summer 2008, students have been developing new "model" formulations with different oligomers and photoinitiators. These formulations are being polymerized with both types of UV lamps and differences in thermomechanical properties are being determined.

Timothy Morales and Elda Rueda making the first UV-polymer film using the new continuous photon output electrodeless lamp from Fusion UV Systems, Inc.

UH-Downtown students Shakti Sharma, Vien Lam, Jannie Dilber and Brian Rodriguez at the 2006 RadTech Conference and Exposition in Chicago, Ill. Ms. Lam's paper won the "Best Student Paper Award" for the conference.

Since 1993, 83 different students have been involved in undergraduate research in UV-polymerization chemistry and technology in the CAPSR laboratory at UH-Downtown. Many of these students have participated as authors, co-authors or presenters for three papers in RadTech Report, 14 papers or posters presented at RadTech International North America conferences, one paper presented at RadTech Japan in Yokohama in 1997, and one paper presented during the May 2008 Fusion UV Systems Japan Conferences in Tokyo and Osaka, Japan, as well as Seoul, Korea. In addition, many other posters or papers have been presented at UH-Downtown in Student Research Conferences held in the spring each year or at the Graduate School and Internship Fair held every fall. Finally, several posters have been presented by students at Sigma Xi conferences and have won awards at those conferences.

As the Director of CAPSR, it has been a great privilege for me to work with these students since 1993—to see how quickly and enthusiastically they learn the basics of UV polymerization technology, how adept they are at presenting their work, and how enthusiastic they are for the science. Many of these students were not chemistry or industrial chemistry majors. Yet they demonstrated the ability to conduct meaningful research in this field and to present their work in a very professional manner.

I now make it a practice to try to identify bright students with real research potential in their first year of taking chemistry courses. The earlier the students are engaged in research, the more time there is for them to be involved and the more quickly they assimilate laboratory skills and gain insights into "real-world chemistry." Virtually none of the CAPSR students had ever heard of UV polymerization before coming to the lab. In fact, few have any meaningful conceptual understanding of polymers. But, by

the end of their time in the CAPSR lab, most have a much better appreciation for this fascinating technology and a few have selected chemistry as their major because of their experience in undergraduate research.

This and other similar programs create value for those involved with UV-polymerization processes. The students do a significant amount of work to develop a clearer understanding of the basic science of UV polymerization, work which could be done by professional chemists but which often is not done for a variety of reasons.

Their experience in undergraduate research also introduces students to this valuable "green" technology at the very time when society is finally "getting the message" about its importance.

Additionally, these students represent an invaluable future resource as potential research and development chemists in the UV/EB industry. Those who participate directly in RadTech conferences are even able to begin developing strong professional networks before they graduate. For those who enter other technical fields, they not only take technical experience with them from CAPSR and similar labs, but they provide the potential for promoting UV/EB in their respective companies.

Finally, students who have been involved in undergraduate research in this field represent a strong candidate pool for the many fine graduate programs that conduct research in UV polymerization in the U.S. and other countries.

Undergraduate research in UV-polymerization chemistry and technology is continuing in the CAPSR laboratory and in other fine universities. Such research provides significant value to all interested in UV polymerization and represents a clear step toward the future as many excellent young people are embracing the technology with skill, intellect and enthusiasm.

The health and vitality of such programs, of course, depends heavily on the strong support of the UV/EB industry. Economic realities are leading to reductions in the technical workforce. Yet these reductions will be reversed eventually. When that happens, the industry needs to be positioned to bring on board the next generation of scientists and technicians who can continue the excellent growth this industry has seen throughout its relatively short history. Support of undergraduate, as well as graduate research, can help insure that growth and prosperity will continue into the future.

References

1. "UV-Polymerizable Monomer Comparisons 2: Physical Properties of Acrylate Functional Monomer Blends," co-authored with Scott Ferree and Semir Yusuf (UH-Downtown students), presented at the RadTech '96 Conference in Nashville, Tennessee, May 1, 1996.
2. "UV-Curable Monomer Comparisons I: Cured Film Properties of Oligomer/Monomer Blends," co-authored with Dr. Ed Zey, *Speciality Chemicals*, 1988. Also presented at the Radcure '86 Conference in Baltimore, Maryland, 1986.
3. "The Effects of UV Dose and Peak Irradiance on the Tensile Properties of UV-Polymerized Films," co-authored with Chris Matranga (UH-Downtown student), presented by Chris Matranga at RadTech '96 Conference in Nashville, Tennessee, May 1, 1996. *This paper won the "Founders' Award for Best Technical Paper" at the conference.*
4. "UV-Polymerizable Systems Containing Single-Walled Carbon Nanotubes (SWNTs)," co-authored with Vien Lam, Giovanna Patino, and Colin Carandang, *2006 e/5 UV&EB Technical Conference Proceedings* (CD Format), RadTech International North America. Presented by Ms. Vien Lam, Chicago, IL, April 2006. *This paper won the "Best Student Paper" award for the Conference.*

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