

## 綠色/永續化學資訊共享

資料蒐集 ■ 國立中正大學化學暨生物化學系魏國佐教授

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## 2007 Presidential Green Chemistry Challenge Awards recognize

Cleaner, cheaper, and smarter chemistry. That's the popular description of the science and technology behind the Presidential Green Chemistry Challenge Awards. This year's class of five award winners, drawn from more than 100 nominees, was recognized for their superlative accomplishments during a ceremony held on June 26 at the National Academy of Sciences in Washington, D.C.

The Green Chemistry Challenge "strives to facilitate the discovery of new ways to protect human health and the environment through scientific creativity," commented Charles M. Auer, director of the Environmental Protection Agency's Office of Pollution Prevention & Toxics, which administers the awards program.

The awards highlight green chemistry's "core purpose of finding cleaner approaches to chemical and industrial processes so that we not only move forward as an innovative and productive society but also ensure that future generations will have a healthy environment in which to thrive," added American Chemical Society President Catherine T. Hunt. Since the awards program's inception in 1995, many observers have recognized that "the key to doing well by doing good is to be found in the best science and the best engineering," she said.

The 2007 award recipients and their technologies are as follows:

**Michael J. Krische** of the University of Texas, Austin, garnered the academic award for developing a broad class of efficient hydrogen-mediated carbon-carbon-bond-forming reactions that generate minimal waste. During these catalytic hydrogenations, two unsaturated organic molecules exposed to hydrogen gas couple via a new carbon-carbon bond to create a single, more complex product.

**NovaSterilis**, Ithaca, N.Y., was presented with the small-business award for creating an environmentally friendly medical sterilization technique. The system employs supercritical carbon dioxide and a peroxide, rather than the traditional toxic ethylene oxide or gamma radiation, for sterilizing bone and tissue transplants, implantable drug delivery devices, and medical instruments.

**Kaichang Li** of Oregon State University; **Columbia Forest Products**, Greensboro, N.C.; and **Hercules Inc.** joined forces to win the award for greener synthetic pathways for creating soy protein-based adhesives as low-toxicity replacements for conventional formaldehyde-based adhesives used to make plywood and other wood composites.

**Headwaters Technology Innovation**, Lawrenceville, N.J., was recognized with the greener reaction conditions award for devising a direct synthesis of hydrogen peroxide from H<sub>2</sub> and O<sub>2</sub> using a selective palladium-platinum nanocatalyst. The process, being commercially developed in collaboration with Degussa, is an advance over the commercial anthracene-anthraquinone process, which is more complex, energy-intensive, and expensive.

**Cargill** was selected in the designing greener chemicals category for coming up with a way to prepare polyols from soybean oil instead of petroleum. Polyols are monomers containing multiple alcohol groups that are coupled with an isocyanate monomer to make flexible and rigid polyurethane foams used in furniture, bedding, and automobiles.

James B. Gulliford, assistant administrator of EPA's Office of Prevention, Pesticides & Toxic Substances, described this year's award-winning technologies as "nothing short of incredible." He added that each recipient demonstrates "not only the value of scientific innovation but also how innovation partnered with good environmental practices translates into good business practices."

- **Stephen K. Ritter.** (<http://pubs.acs.org/subscribe/journals/cen/85/i27/html/8527news7.html> )

*More detail information about Presidential Green Chemistry Challenge Awards*

## 2007 Award Recipients

- **Greener Synthetic Pathways Award**

Professor Kaichang Li, Oregon State University ;Columbia Forest Products;Hercules Incorporated  
**Development and Commercial Application of Environmentally Friendly Adhesives for Wood Composites:**

**Innovation and Benefits:** Adhesives used in manufacturing plywood and other wood composites often contain formaldehyde, which is toxic. Professor Kaichang Li of Oregon State University, Columbia Forest Products, and Hercules Incorporated developed an alternate adhesive made from soy flour. Their environmentally friendly adhesive is stronger than and cost-competitive with conventional adhesives. During 2006, Columbia used the new, soy-based adhesive to replace more than 47 million pounds of conventional formaldehyde-based adhesives.

Since the 1940s, the wood composites industry has been using synthetic adhesive resins to bind wood pieces into composites, such as plywood, particleboard, and fiberboard. The industry has been the predominate user of formaldehyde-based adhesives such as phenol–formaldehyde and urea–formaldehyde (UF) resins. Formaldehyde is a probable human carcinogen. The manufacture and use of wood composite panels bonded with formaldehyde-based resins release formaldehyde into the air, creating hazards for both workers and consumers.

Inspired by the superior properties of the protein that mussels use to adhere to rocks, Professor Li and his group at Oregon State University invented environmentally friendly wood adhesives based on abundant, renewable soy flour. Professor Li modified some of the amino acids in soy protein to resemble those of mussels' adhesive protein. Hercules Incorporated provided a critical curing agent and the expertise to apply it to commercial production of plywood.

Oregon State University, Columbia Forest Products (CFP), and Hercules have jointly commercialized soy-based adhesives to produce cost-competitive plywood and particleboard for interior uses. The soy-based adhesives do not contain formaldehyde or use formaldehyde as a raw material. They are environmentally friendly, cost-competitive with the UF resin in plywood, and superior to the UF resin in strength and water resistance. All CFP plywood plants now use soy-based adhesives, replacing more than 47 million pounds of the toxic UF resin in 2006 and reducing the emission of hazardous air pollutants (HAPs) from each CFP plant by 50 to 90 percent. This new CFP plywood is sold under the PureBond™ name. During 2007, CFP will replace UF at its particleboard plant; the company is also seeking arrangements with other manufacturers to further the adoption of this technology.

With this technology, those who make and use furniture, kitchen cabinetry, and other wood composite materials have a high-performing formaldehyde-free alternative. As a result, indoor air quality in homes and offices could improve significantly. This technology represents the first cost-competitive, environmentally friendly adhesive that can replace the toxic UF resin. The technology can greatly enhance the global competitiveness of U.S. wood composite companies. In addition, by creating a new market for soy flour, currently in over-supply, this technology provides economic benefits for soybean farmers.

- **Greener Reaction Conditions Award**

Headwaters Technology Innovation

Direct Synthesis of Hydrogen Peroxide by Selective Nanocatalyst Technology

**Innovation and Benefits:** Hydrogen peroxide is an environmentally friendly alternative to chlorine and chlorine-containing bleaches and oxidants. It is expensive, however, and its current manufacturing process involves the use of hazardous chemicals. Headwaters Technology Innovation (HTI) developed an advanced metal catalyst that makes hydrogen peroxide directly from hydrogen and oxygen, eliminates the use of hazardous chemicals, and produces water as the only byproduct. HTI has demonstrated their new technology and is partnering with Degussa AG to build plants to produce hydrogen peroxide.

Hydrogen peroxide ( $H_2O_2$ ) is a clean, versatile, environmentally friendly oxidant that can substitute for environmentally harmful chlorinated oxidants in many manufacturing operations. However, the existing manufacturing process for  $H_2O_2$  is complex, expensive, and energy-intensive. This process requires an anthraquinone working solution containing several toxic chemicals. The solution is reduced by hydrogen in the presence of a catalyst, forming anthrahydroquinone, which then reacts with oxygen to release  $H_2O_2$ . The  $H_2O_2$  is removed from the solution with an energy-intensive stripping column and then concentrated by vacuum distillation. The bulk of the working solution is recycled, but the process generates a waste stream of undesirable quinone-derived byproducts that requires environmentally acceptable disposal.

Headwaters Technology Innovation (HTI) has produced a robust catalyst technology that enables the synthesis of  $H_2O_2$  directly from hydrogen and oxygen. This breakthrough technology, called NxCat™, is a palladium-platinum catalyst that eliminates all the hazardous reaction conditions and chemicals of the

existing process, along with its undesirable byproducts. It produces H<sub>2</sub>O<sub>2</sub> more efficiently, cutting both energy use and costs. It uses innocuous, renewable feedstocks and generates no toxic waste.

NxCat™ catalysts work because of their precisely controlled surface morphology. HTI has engineered a set of molecular templates and substrates that maintain control of the catalyst's crystal structure, particle size, composition, dispersion, and stability. This catalyst has a uniform 4-nanometer feature size that safely enables a high rate of production with a hydrogen gas concentration below 4 percent in air (i.e., below the flammability limit of hydrogen). It also maximizes the selectivity for H<sub>2</sub>O<sub>2</sub> up to 100 percent.

The NxCat™ technology enables a simple, commercially viable H<sub>2</sub>O<sub>2</sub> manufacturing process. In partnership with Degussa AG (a major H<sub>2</sub>O<sub>2</sub> manufacturer), HTI successfully demonstrated the NxCat™ technology and, in 2006, completed construction of a demonstration plant. This demonstration plant will allow the partners to collect the data necessary to design a full-scale plant and begin commercial production in 2009. The NxCat™ process has the potential to cut the cost of H<sub>2</sub>O<sub>2</sub> significantly, generating a more competitively priced supply of H<sub>2</sub>O<sub>2</sub> and increasing its market acceptance as an industrial oxidant. Except for its historically higher price, H<sub>2</sub>O<sub>2</sub> is an excellent substitute for the more frequently used—and far more deleterious—chlorinated oxidants. The NxCat™ technology has the benefit of producing an effective, environmentally preferable oxidant (H<sub>2</sub>O<sub>2</sub>) without the waste or high cost associated with the traditional process.

- **Designing Greener Chemicals Award**

Cargill, Incorporated

BiOH™ Polyols

**Innovation and Benefits:** Foam cushioning used in furniture or bedding is made from polyurethane, a man-made material. One of the two chemical building blocks used to make polyurethane is a "polyol." Polyols are conventionally manufactured from petroleum products. Cargill's BiOH™ polyols are manufactured from renewable, biological sources such as vegetable oils. Foams made with BiOH™ polyols are comparable to foams made from conventional polyols. As a result, each million pounds of BiOH™ polyols saves nearly 700,000 pounds of crude oil. In addition, Cargill's process reduces total energy use by 23 percent and carbon dioxide emissions by 36 percent.

Polyols are key ingredients in flexible polyurethane foams, which are used in furniture and bedding. Historically, polyurethane has been made from petrochemical polyols. The idea of replacing these polyols with biobased polyols is not new, but the poor performance, color, quality, consistency, and odor of previous biobased polyols restricted them to limited markets. Previous biobased polyols also suffer from poor chemical reactivity, resulting in foam with inferior properties.

Cargill has successfully developed biobased polyols for several polyurethane applications, including flexible foams, which are the most technically challenging. Cargill makes BiOH™ polyols by converting the carbon-carbon double bonds in unsaturated vegetable oils to epoxide derivatives and then further

converting these derivatives to polyols using mild temperature and ambient pressure. BiOH™ polyols provide excellent reactivity and high levels of incorporation leading to high-performing polyurethane foams. These foams set a new standard for consistent quality with low odor and color. Foams containing BiOH™ polyols retain their white color longer without ultraviolet stabilizers. They also are superior to foams containing only petroleum-based polyols in standard tests. In large slabstock foams, such as those used in furniture and bedding, BiOH 5000 polyol provides a wide processing window, improved comfort factor, and reduced variations in density and load-bearing capacity. In molded foams such as automotive seating and headrests, BiOH 2100 polyol can enhance load-bearing or hardness properties relative to conventional polyols.

Use of BiOH™ polyols reduces the environmental footprint relative to today's conventional polyols for polyurethane production. BiOH™ polyols "harvest" carbon that plants remove from the air during photosynthesis. All of the carbon in BiOH™ polyols is recently fixed. In conventional polyols, the carbon is petroleum-based. Replacing petroleum-based polyols with BiOH™ polyols cuts total energy use by 23 percent including a 61 percent reduction in nonrenewable energy use, leading to a 36 percent reduction in carbon dioxide emissions. For each million pounds of BiOH™ polyol used in place of petroleum-based polyols, about 700,000 pounds (2,200 barrels) of crude oil are saved, thereby reducing the dependence on petroleum. BiOH™ polyols diversify the industry's supply options and help mitigate the effects of uncertainty and volatility of petroleum supply and pricing. Cargill is the first company to commercialize biobased polyols on a large scale in the flexible foam market. Formulators can now use biobased polyols in flexible foam without compromising product performance. That the top North American polyol users choose BiOH™ polyols is validation of Cargill's accomplishment.

- **Small Business Award**

NovaSterilis Inc.

**Environmentally Benign Medical Sterilization Using Supercritical Carbon Dioxide**

**Innovation and Benefits:** Sterilizing biological tissue for transplant is critical to safety and success in medical treatment. Common existing sterilization techniques use ethylene oxide or gamma radiation, which are toxic or have safety problems. NovaSterilis invented a technology that uses carbon dioxide and a form of peroxide to sterilize a wide variety of delicate biological materials such as graft tissue, vaccines, and biopolymers. Their Nova 2200™ sterilizer requires neither hazardous ethylene oxide nor gamma radiation.

None of the common methods for medical sterilization is well-suited to sterilizing delicate biological materials. The sterility of these materials is critical. Distribution of contaminated donor tissues by tissue banks has resulted in serious infections and illnesses in transplant patients. The two most widely used sterilants (ethylene oxide and gamma radiation) also raise toxicity and safety concerns. Ethylene oxide is a mutagenic, carcinogenic, volatile, flammable, reactive gas. Residues of ethylene oxide remain in the sterilized material, increasing the risk of toxic side effects. Gamma radiation is highly penetrating and is

lethal to all cells. Neither ethylene oxide nor gamma radiation can sterilize packaged biological products without eroding their physical integrity.

NovaSterilis, a privately held biotechnology company in Ithaca, NY, has successfully developed and commercialized a highly effective and environmentally benign technique for sterilizing delicate biological materials using supercritical carbon dioxide (CO<sub>2</sub>). NovaSterilis licensed a patent for bacterial inactivation in biodegradable polymers that was issued to Professor Robert S. Langer and his team at the Massachusetts Institute of Technology. NovaSterilis then enhanced, expanded, and optimized the technology to kill bacterial endospores. Their supercritical CO<sub>2</sub> technology uses low temperature and cycles of moderate pressure along with a peroxide (peracetic acid) and small amounts of water. Their Nova 2200™ sterilizer consistently achieves rapid (less than one hour) and total inactivation of a wide range of microbes, including bacterial endospores. The mechanism of bacterial inactivation is not well-understood, but does not appear to involve bacterial cell lysis or wholesale degradation of bacterial proteins.

The new technology is compatible with sensitive biological materials and is effective for a wide range of important biomedical materials including: (a) musculoskeletal allograft tissue (e.g., human bone, tendons, dermis, and heart valves) for transplantation; (b) biodegradable polymers and related materials used in medical devices, instruments, and drugs; (c) drug delivery systems; and (d) whole-cell vaccines that retain high antigenicity. Besides being a green chemical technology, supercritical CO<sub>2</sub> sterilization achieves “terminal” sterilization, that is, sterilization of the final packaged product. Terminal sterilization provides greater assurance of sterility than traditional methods of aseptic processing. Sterilization of double-bagged tissue allows tissue banks to ship terminally sterilized musculoskeletal tissues in packages that can be opened in operating rooms by surgical teams immediately prior to use. NovaSterilis’s patented technology addresses the market need in tissue banks as well as other needs in the biomedical, biologics, medical device, pharmaceutical, and vaccine industries. By the end of 2006, NovaSterilis had sold several units to tissue banks.

- **Academic Award**

Professor Michael J. Krische , University of Texas at Austin

Hydrogen-Mediated Carbon–Carbon Bond Formation

**Innovation and Benefits:** A fundamental aspect of chemistry involves creating chemical bonds between carbon atoms. Chemical processes commonly used to make such bonds usually also generate significant amounts of waste. Professor Krische developed a broad new class of chemical reactions that make bonds between carbon atoms using hydrogen and metal catalysts. This new class of reactions can be used to convert simple chemicals into complex substances, such as pharmaceuticals, pesticides, and other important chemicals, with minimal waste.

Reductions mediated by hydrogen, termed “hydrogenations”, rank among the most widely used catalytic methods employed industrially. They are generally used to form carbon–hydrogen (C–H) bonds.

Professor Michael J. Krische and his coworkers at the University of Texas at Austin have developed a new class of hydrogenation reactions that form carbon–carbon (C–C) bonds. In these metal-catalyzed reactions, two or more organic molecules combine with hydrogen gas to create a single, more complex product. Because all atoms present in the starting building-block molecules appear in the final product, Professor Krische’s reactions do not generate any byproducts or wastes. Hence, Professor Krische’s C–C bond-forming hydrogenations eliminate pollution at its source.

Prior to Professor Krische’s work, hydrogen-mediated C–C bond formations were limited almost exclusively to the use of carbon monoxide in reactions such as alkene hydroformylation (1938) and the Fischer-Tropsch reaction (1923). These prototypical hydrogen-mediated C–C bond formations are practiced industrially on an enormous scale. Yet, despite the importance of these reactions, no one had engaged in systematic research to develop related C–C bond-forming hydrogenations. Only a small fraction of hydrogenation’s potential as a method of C–C coupling had been realized, and the field lay fallow for nearly 70 years.

Professor Krische’s hydrogen-mediated couplings circumvent the use of preformed organometallic reagents, such as Grignard and Gilman reagents, in carbonyl and imine addition reactions. Such organometallic reagents are highly reactive, typically moisture-sensitive, and sometimes pyrophoric, meaning that they combust when exposed to air. Professor Krische’s coupling reactions take advantage of catalysts that avoid the hazards of traditional organometallic reagents. Further, using chiral hydrogenation catalysts, Professor Krische’s couplings generate C–C bonds in a highly enantioselective fashion.

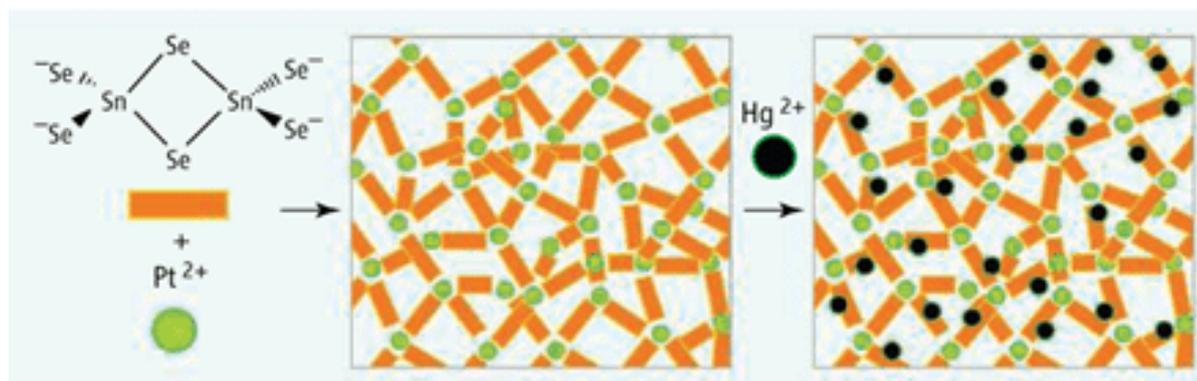
Catalytic hydrogenation has been known for over a century and has stood the test of time due its efficiency, atom economy, and cost-effectiveness. By exploiting hydrogenation as a method of C–C bond formation, Professor Krische has added a broad, new dimension to one of chemistry’s most fundamental catalytic processes. The C–C bond-forming hydrogenations developed by Professor Krische allow chemists to create complex organic molecules in a highly selective fashion, eliminating both hazardous starting materials and hazardous waste. Commercial application of this technology may eliminate vast quantities of hazardous chemicals. The resulting increases in plant and worker safety may enable industry to perform chemical transformations that were too dangerous using traditional reagents.

- from “ <http://www.epa.gov/greenchemistry/pubs/pgcc/past.html> ”

## **Random gel networks formed from chalcogenide clusters and metal ions can selectively remove heavy metal ions from water.**

A new type of porous inorganic gel with semiconducting properties and large surface areas also has the ability to bind heavy metals (*Science* **2007**, 317, 490). Unlike most porous inorganic gels in use, the new materials are not based on silica or other oxides. **Mercouri G. Kanatzidis** at Northwestern University and colleagues built on a known strategy for organizing inorganic clusters with metal ions around surfactant

supports. They linked sulfides or selenides of germanium or tin to platinum ions, but without using a surfactant. For example, clusters such as  $[\text{Sn}_2\text{Se}_6]^{4-}$  react with  $\text{Pt}^{2+}$  in water to form a random, polymeric cross-linked network (shown). Drying the material with supercritical carbon dioxide replaces the water in the pores with air and yields a type of aerogel. The researchers call the materials "chalcogels" because they include chalcogenides (sulfur and selenium.) They tested one chalcogel containing  $[\text{Ge}_4\text{S}_{10}]^{4-}$  and found it removed 645 mg/g of  $\text{Hg}^{2+}$  from aqueous solution because the heavy-metal ions bind to sulfur. Tests on materials involving less expensive metals than platinum are under way. (C&EN July 30, 2007 Volume 85, Number 31 p. 50)



Chalcogel formation and mercury absorption. Bag *et al.* show that chalcogenido molecular ions or clusters such as  $\text{Sn}_2\text{Se}_6^{4-}$  (orange bar) can react with  $\text{Pt}^{2+}$  (green sphere) in water to form a polymeric cross-linked network. This network can absorb up to ~650 mg of mercury per gram of chalcogel from contaminated solutions.

- published at ( <http://www.sciencemag.org/cgi/reprint/317/5837/490.pdf> )

## Chemical Society Presidents Pledge Support for Sustainable Development

Six leaders forge global pact at meeting in Paris by Linda R. Raber

The presidents of six leading chemical societies, representing nearly 300,000 members, pledged last week at a meeting in Paris to, in the words of a joint statement, "work together to promote global sustainable development, demand responsible use of resources, and ensure that the next generation of scientists protects and maintains the well-being of Earth and its



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inhabitants."

The presidents of the American Chemical Society, the Royal Society of Chemistry (RSC), the Chemical Society of Japan, the German Chemical Society (GDCh), the French Chemical Society, and the Dutch Chemical Society developed and signed the statement because "the need to address these intertwined issues is urgent, and chemistry is absolutely essential to the development of solutions," they wrote. They agreed that sustainable development presents scientific, political, social, and economic challenges that are far more complex and urgent than generally conveyed. Unless these challenges are more widely recognized, "we risk being lulled into a false sense of security," they said.

The so-called C6 chemical societies, which are among the largest chemical societies in the world, have been meeting about every two years for the past eight years. They share experiences and challenges and generally develop a few collaborative programs.

This year, the French Chemical Society hosted the meeting in Paris, on July 13–15, prior to a major international scientific meeting commemorating its 150th anniversary.

"Sustainability clearly is the topic that we all felt exceptionally strongly about," said Catherine T. Hunt, ACS president. "Earth's systems, upon which we all depend, are facing complex and imminent threats. Pressures are intensifying on worldwide food, water, and energy supplies. Crucial agricultural and valuable natural ecosystems are under severe strain. If we do not change course toward a more sustainable future, it will have dire consequences for Earth and all its inhabitants."

To address the sustainability challenges, the societies agreed to collaborate with stakeholders in government, academia, industry, and other sectors of the international community to promote education, innovation, and communication, in collaboration with others, as the basis for solving the most important challenge now facing humankind.

Specifically, the society presidents said their societies will "support chemists in developing their skills to ensure the sustainability of our planet; develop a roadmap and priorities for chemistry's contributions to sustainability and advocate for the resources needed to develop and deploy technologies globally; and convene academia, industry, and government to better understand chemistry's contributions to sustainability and the need for action."

According to Dieter Jahn, president of GDCh and BASF's senior vice president, science relations, and innovation management, "Chemistry delivers important solutions to the most challenging problems of our planet—supplies of energy and water, improving energy efficiency, climate change, and sustainable development. Because these problems are of a global nature, we need global solutions."

The societies will be following up with a specific agenda in the coming weeks and also inviting other chemical societies to sign the declaration. In addition to Hunt and Jahn, society presidents who signed the

statement are Jim Feast, RSC; Peter Folstar, Royal Netherlands Chemical Society; Akira Fujishima, Chemical Society of Japan; and Armand Lattes, French Chemical Society.

In addition to discussing sustainable development, the C6 society presidents, governance representatives, and staff members discussed activities at the boundaries of chemistry with other disciplines, collaboration with other scientific societies, public appreciation of chemistry, interaction with industry, and education. Others attending from ACS were ACS Board Chair Judith L. Benham; ACS Executive Director and CEO Madeleine Jacobs; Director of Membership & Scientific Advancement Denise L. Creech; and Acting Director of the ACS Green Chemistry Institute Tamara Nameroff.

( <http://pubs.acs.org/isubscribe/journals/cen/85/i30/html/8530news1.html> )

## Plastics Recycling: Depolymerizing Plastics

### Ionic liquids can be used to convert polymers into monomers

**THE MOST THOROUGH WAY** to recycle plastics is to depolymerize them into their monomeric building blocks, which then can be used to make new polymers. Most depolymerization methods developed so far require high temperatures, careful solvent selection, or specialized high-pressure equipment. Now, using ionic liquids as solvents and standard, ambient-pressure laboratory equipment, Akio Kamimura and Shigehiro Yamamoto of Yamaguchi University, in Japan, have demonstrated a unique way of converting plastics back to the stuff they were originally made of (*Org. Lett.* **2007**, *9*, 2533).



Back to basics Nylon 6 breaks down into its monomeric building block when heated with a catalyst in an ionic liquid.

Their depolymerization process still relies on high temperatures, but that's not a problem for the ionic liquids they use, Kamimura says. Compared with other solvents used for depolymerizations, he notes, "ionic liquids are less volatile under such high temperatures."

With an eye on recycling nylon and other polyamide plastics, the researchers experimented with a number of solvents and different reaction conditions. In a procedure they describe as "quite simple," they combined a sample of nylon 6, an ionic liquid, and a catalyst in a vessel and stirred the mixture under nitrogen at 300 °C and ambient pressure for about 1 hour. The ensuing depolymerization yielded the nylon's caprolactam monomer, which the researchers collected by distillation. The best yield of

caprolactam—86%—was obtained with N-methyl-N-propylpiperidinium bis(trifluoro-methylsulfonyl)imide as the solvent and N,N-dimethyl-aminopyridine as the catalyst.

"This looks like very interesting and potentially useful work," comments Ted Aulich of the Energy & Environmental Research Center at the University of North Dakota, Grand Forks, where he has worked on waste plastics recycling.

Besides recovering reusable monomers, the researchers found they could recycle their reaction solvent five times without substantial loss of monomer yield. This is an advantage with regard to green chemistry, Kamimura says. The researchers continue to examine solvent recycling limits and application of this depolymerization method to other plastics. –by Raychelle Burks.

( <http://pubs.acs.org/isubscribe/journals/cen/85/i27/html/8527notw7.html> )

## Advocating Green Chemistry in the Lab

It's an age-old ritual for college science majors around the country: every year, a new wave of students takes a series of chemistry laboratory courses which, while interesting, often inspire much dread and stress. Students are expected to work with hazardous chemicals under cramped conditions to complete a set of preordained, stepwise experiments with speed and precision. Ken Doxsee and James E. Hutchison, both professors of chemistry at the University of Oregon, thought there ought to be a better way.



“We were meeting every evening and on Saturday mornings. It was just inappropriate for everyone involved,” said Doxsee, referring to the rigorous lab schedule he and his students were subjected to just a few years ago. Hutchison and Doxsee started tinkering around with several new ideas, such as altering the class curriculum to emphasize less toxic, instrument-heavy experiments, to cut down on lab time and

open up more space for students. Many of these schemes eventually bore fruit and have now provided the model for a new movement in chemistry: "green chemistry."

Contrary to what its name may suggest, green chemistry doesn't necessarily involve environmental science experiments; instead, it simply refers to the process of doing science with an environmental ethic.

*“We look at a chemical reaction or a chemical process. We look at everything that goes into it, whether it's a starting material or a reagent or a solvent or materials to run the reaction in, and we look at everything that comes out, which is what you want, and any byproduct, and consider each of those things as something where you ought to think about health and safety and the environment. If you're making a byproduct, do you have to? If you're using a solvent, do you have to?...If you start with two reactants, do you incorporate both of them in your product or does 50 percent of one of them get thrown away as waste? If you have to start with a material, does it require you to isolate it from petroleum, or can you get it from a renewable source?” says Doxsee.*

“Practical needs can bring about changes,” says Doxsee. “I would like to believe that the whole world is being thoughtful about the future. I think a lot of interest may come from the practical realization of what green chemistry can offer.” Though still a nascent field (it's only briefly mentioned in most chemistry textbooks as an aside), green chemistry has already found several applications in the realms of industry and education.

Scientists see it as an inevitability that as the public's attention continues to fixate on the threats posed by global warming, an increasing focus will be placed on ways to minimize greenhouse gas emissions, even at the level of chemistry laboratories in colleges and research facilities. In addition, cost- and safety-conscious companies will see an opportunity in shifting production towards less hazardous, less tightly regulated materials that require less expensive disposal procedures.

The need to conserve materials and shift to more sustainable, low energy technologies has already sparked a lot of innovation in college laboratories. In one instance, Thomas Goodwin, a professor of chemistry at Hendrix College, and a student circumvent the use of toluene, a petrochemical solvent, for an experiment by running it without it. Surprisingly, it still worked. Such experimentation is really at the base of what it means to do chemistry: a clear understanding of the underlying concepts and grasp of different chemicals' properties should be all a student needs to complete a reaction, not a series of minute detailed steps.

Goodwin now commonly encourages his students to think about the environmental consequences of their experiments with questions that ask, "what was green about the procedure, what was not green about the procedure and how could I improve it?" The ramifications of inspiring this type of engaging, environmentally responsible debate on a national level would be huge: it would help produce a new breed of eco-conscious scientists (and not only chemists) more willing to experiment with new ideas and more likely to question the status quo.

So what's the ultimate goal of green chemistry: its "hope," if you will? As Hendrix's Liz Gron, an associate professor of chemistry, put it, it "is that someday we'll stop talking about it. That everyone will

do it, that part of being an ethical chemist is that you consider the environmental consequences of your work.”

-by J. E. Jacquot from “ [http://www.treehugger.com/files/2007/06/advocating\\_green\\_chemistry.php](http://www.treehugger.com/files/2007/06/advocating_green_chemistry.php) ”

### **Greening the Lab (Related story of above article)**

Laboratory space was at a premium at the University of Oregon back in 1996. The organic chemistry course alone had 265 students clamoring for spots in a lab built for 17.

So there were 17 lab sections. “51 hours of lab a week,” says Ken Doxsee, a professor of chemistry. “We were meeting every evening and on Saturday mornings. It was just inappropriate for everyone involved.” Frustrated, Doxsee and his colleague, Professor James E. Hutchison, decided to look for less toxic experiments students could conduct in labs lacking fume hoods, opening up whole new spaces to handle the overflow. “It started,” Doxsee says, “with very pragmatic considerations like that.”

The tale may read as an amusing anecdote, but the beginnings of green chemistry at Oregon – a pioneer and leader in the still fledgling field – may be emblematic of the rise of green chemistry in industry and education more generally. “Practical needs can bring about changes,” says Doxsee. “I would like to believe that the whole world is being thoughtful about the future. I think a lot of interest may come from the practical realization of what green chemistry can offer.”

As colleges and companies increasingly “go green” – or say they are, anyway – many chemists believe the attention to what materials come into and out of the lab is poised to grow. Beakers bubbling with toxic waste and greenhouse gas byproducts no longer fly as standard costs of doing science in an increasing number of college laboratories across the country.

Parallel, and perpendicular, to all this, the external pressures to teach green chemistry in the university classroom and laboratory are likewise mounting, says John Warner, director of the Center for Green Chemistry at the University of Massachusetts at Lowell. Companies, he says, see the dollar value in producing less waste – and lowering hefty disposal expenses – and the cheaper cost of doing business that comes along with producing less hazardous, less tightly regulated products. “Industry’s not stupid. They want to make the safe materials. The reality is that we don’t teach people how,” Warner says.

“Nationally, there is a big push for sustainability. Campuses have to be sustainable. So what does that mean, that we run around and change light bulbs? That’s all we know how to do,” Warner says.

“When [the] curriculum starts to get into sustainability, that’s the tipping point.”

### **‘Smart’ Chemistry**

Liz Gron, an associate professor of chemistry at Hendrix College, which has embraced a green chemistry curriculum on a departmental level, describes green chemistry as an “ethic you apply to the science you do.”

Contrary to what some might suppose, green chemistry does not necessarily refer to the study of environmental topics, but instead the infusion of an environmental ethic regardless of what topic, be it thermodynamics or plastics, is being taught or studied. One of the earliest green chemistry experiments undertaken at Oregon, for example, featured a more benign approach for synthesizing adipic acid, a major component of nylon that, when produced commercially, has typically resulted in the production of nitrous oxide, a pollutant.

“We look at a chemical reaction or a chemical process. We look at everything that goes into it, whether it’s a starting material or a reagent or a solvent or materials to run the reaction in, and we look at everything that comes out, which is what you want, and any byproduct, and consider each of those things as something where you ought to think about health and safety and the environment,” says Doxsee, who, with Hutchison, leads National Science Foundation-funded summer workshops in green chemistry education at Oregon.

“If you’re making a byproduct, do you have to? If you’re using a solvent, do you have to?...If you start with two reactants, do you incorporate both of them in your product or does 50 percent of one of them get thrown away as waste? If you have to start with a material, does it require you to isolate it from petroleum, or can you get it from a renewable source?” asks Doxsee.

“Basically, that’s what the green principles say, is to look at everything and make sure you’re being smart.”

It sounds simple, but while chemists who jumped on the bandwagon as it started moving back in the 1990s say they see real signs of growth, it’s still slow-going. “I still have the impression that there are pockets of activity at the undergraduate level, rather than the wholesale adoption of green chemistry,” says Mary Kirchhoff, who came to her position as the director of the American Chemical Society’s education division in December with a green chemistry background. “Like any new idea, it just takes time...to build up the resources that people need and to provide the opportunities to train faculty members and teachers in how to teach green chemistry in the classroom,” says Kirchhoff, the former assistant director of the Green Chemistry Institute.

The relative lack of teaching resources seems to be among the primary obstacles. As anyone in the movement will tell you, without resources available so that professors can easily substitute in greener labs to demonstrate the core chemical principles they teach, the compounding forces of inertia and insufficient time will slow any large-scale change. What’s essential, advocates for green chemistry say, is that a large number of green labs and lecture guides be available, enabling professors to plop them in and teach some green chemistry as they continue teaching the topics they’ve always taught.

Yet, green chemistry is still relegated to “special topics boxes” at the end of the chapter in most chemistry textbooks. In an informal survey of textbook publishers at last fall’s ACS national meeting in San Francisco, Michael C. Cann, a professor of chemistry at the University of Scranton, evaluated the market’s offerings in terms of green chemistry coverage. Out of 141 books he examined, 33 included some form of green chemistry. “But most of them are simply supplemental materials,” Cann says. “Very few of them have any substantial amounts of green chemistry infused into them.”

It’s worth noting though that while the resources might still be limited, they’re growing like all things green. The University of Oregon’s Julie Haack maintains an online database, Greener Educational Materials for Chemists, some collections of green undergraduate experiments are available and the *Journal of Chemical Education* includes a “Topics in Green Chemistry” feature on a regular basis that usually consists of lab experiments, says Kirchhoff, the editor for the feature.

Strong attendances at green chemistry symposia during national ACS meetings are also a promising sign, Kirchhoff says: “A number of presenters are people I’ve never met before – which is excellent because it means there are people out there doing work that we don’t know about.”

“For awhile, we were all talking to ourselves.”

### **‘The Hope of Green Chemistry’**

In those pockets where green chemistry is happening in the university laboratory, innovation and energy levels are high. Thomas Goodwin, a professor of chemistry at Hendrix, describes for instance adapting a reaction described in the *Journal of Chemical Education*. Unhappy with the use of toluene, a petrochemical solvent, as the literature called for, Goodwin and a student tried running the experiment without the solvent, just to see if it worked. It did.

Then, they decided to lower the temperature called for in the literature: Rather than running the reaction at 90 degrees Celsius, “We said, ‘Let’s just mix these two things together at room temperature — and it also worked.’” That was a particularly unusual reaction to have worked in that combination of circumstances, Goodwin conceded – “But we never would have tried these things” without a green ethos.

In Goodwin’s courses, students have to write up the environmental implications of laboratory experiments in their notebooks, answering in their conclusion sections not only what they learned about the topic at hand, but also “what was green about the procedure, what was not green about the procedure and how,” Goodwin says, “could I improve it?”

Back at the University of Massachusetts Lowell, Amy Cannon, an assistant professor, requires the students in her chemistry for non-majors course to design green experiments for eighth-graders as a service learning project. One group of students for instance designed a method of making ice cream, using human energy as opposed to electricity, to be included in a middle school unit on energy. Basically,

Cannon says, students would put the ingredients along with some ice in a coffee can, and then roll and shake it to create their desired output – ice cream.

At Gordon College, organic chemistry students design a final green chemistry literacy project in which they either do outreach to local high schools or undertake a green research initiative. For example, Irv Levy, a professor of chemistry and chair of the department, is working with students to develop a green laboratory module that would test the eco-toxicity of common chemicals — building upon the outgrowth of one of those SMEAGOL (Student Motivated Endeavors Advancing Green Organic Literacy) projects. The acronym is borrowed from Tolkien.

“The ultimate point of green chemistry is human health and the environment,” Levy says of the lab they’re developing. Yet, “chemists are normally not trained in that field, which is toxicology.”

“We need to get it into the psyche of our future chemists, so that they view all chemistry as green. [So] they look at any chemistry and think, ‘How can we make this chemistry greener?’ It has to be a part of the thought process. If somebody doesn’t think about something, they’re never going to change their habits, they’re never going to change their ways,” says Cann of the University of Scranton.

“The hope of green chemistry,” says Hendrix’s Gron, “is that someday we’ll stop talking about it. That everyone will do it, that part of being an ethical chemist is that you consider the environmental consequences of your work.”

by Elizabeth Redden ( <http://insidehighered.com/news/2007/06/25/chemistry> )