

# ***Presidential Green Chemistry Challenge***

## **2003 Award Recipients**



Recycled/Recyclable — Printing with Vegetable Oil Based Inks  
on 100% Postconsumer, Process Chlorine Free Recycled Paper



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## Academic Category

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**Professor Richard A. Gross**  
**Polytechnic University**

### New Options for Mild and Selective Polymerizations Using Lipases

Isolated lipases, harvested from living organisms, have been used as catalysts for polymer synthesis *in vitro*. Professor Richard Gross's developments on lipase-catalyzed polymer synthesis have relied on the ability of enzymes to reduce the activation energy of polymerizations and, thus, to decrease process energy consumption. Further, the regioselectivity of lipases has been used to polymerize polyols directly. Alternative synthetic pathways for such polymerizations require protection-deprotection chemical steps. The mild reaction conditions allow polymerization of chemically and thermally sensitive molecules. Current alternative chemical routes require coupling agents (e.g., carbodiimides) that would be consumed in stoichiometric quantities relative to the reactants. Fundamental studies of these polymerizations have uncovered remarkable capabilities of lipases for polymerization chemistry. Selected examples include: (i) lipases catalyze transesterification reactions between high-molecular-weight chains in melt conditions; (ii) lipases will use non-natural nucleophiles such as carbohydrates and monohydroxyl polybutadiene ( $M_n$  19,000) in place of water; (iii) the catalysis of ring-opening polymerization occurs in a controlled manner without termination reactions and with predictable molecular weights; and (iv) the selectivity of lipase-catalyzed step-condensation polymerizations leads to nonstatistical molecular weight distributions (well below 2.0). These accomplishments are elaborated below.

A series of polyol-containing polyesters was synthesized via a one-pot lipase-catalyzed condensation polymerization. By using various mixtures of polyols (e.g., glycerol, sorbitol) with other diacid and diol building blocks, the polyols are partially or completely solubilized, resulting in highly reactive condensation polymerizations. By this method, organic solvents and activated acids (e.g., divinyl esters) are not needed. The polymerization reactions give high-molecular-weight products ( $M_w$  up to 200,000) with narrow polydispersities (as low as 1.3). Further, the condensation reactions with glycerol and sorbitol building blocks proceed with high regioselectivity. Although the polyols used have three or more hydroxyl groups, only two of these hydroxyl groups are highly reactive in

the polymerization. Thus, instead of obtaining highly crosslinked products, the regioselectivity provided by the lipase leads to lightly branched polymers where the degree of branching varies with the reaction time and monomer stoichiometry. By using lipase as the catalyst, highly versatile polymerizations result that can simultaneously polymerize lactones, hydroxyacids, cyclic carbonates, cyclic anhydrides, amino alcohols, and hydroxythiols. The method developed offers simplicity, mild reaction conditions, and the ability to incorporate carbohydrates, such as sugars, into polyesters without protection-deprotection steps.

Professor Gross's laboratory discovered that certain lipases catalyze transesterification reactions between high-molecular-weight chains that contain intrachain esters or have functional end groups. Thus, lipases, such as Lipase B from *Candida antarctica*, catalyze intrachain exchange reactions between polymer chains as well as transesterification reactions between a monomer and a polymer. For polymers that have melting points below 100 °C, the reactions can be conducted in bulk. Transacylation reactions occur because the lipase has the ability to accommodate large-molecular-weight substrates and to catalyze the breaking of ester bonds within chains. Immobilized *Candida antarctica* Lipase B (Novozyme-435) catalyzed transesterification reactions between aliphatic polyesters that had  $M_n$  values in excess of 40,000 g/mol. In addition to catalyzing metal-free transesterifications at remarkably low temperatures, lipases endow transesterification reactions with remarkable selectivity. This feature allows the preparation of block copolymers that have selected block lengths.

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## Small Business Category

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### *AgraQuest, Inc.*

#### Serenade®: An Effective, Environmentally Friendly Biofungicide

Serenade® Biofungicide is based on a naturally occurring strain of *Bacillus subtilis* QST-713, discovered in a California orchard by AgraQuest scientists. Serenade® has been registered for sale as a microbial pesticide in the United States since July 2000. It is also registered for use in Chile, Mexico, Costa Rica, and New Zealand. Registration is pending in the Phillipines, Europe, Japan, and several other countries. The product is formulated as a wettable powder, wettable granule, and liquid aqueous suspension. Serenade® has been tested on 30 crops in 20 countries and is registered for use in the United States on blueberries, cherries, cucurbits, grape vines, greenhouse vegetables, green beans, hops, leafy vegetables, mint, peanuts, peppers, pome fruit, potatoes, tomatoes, and walnuts. It is also registered for home and garden use. AgraQuest has been issued four U.S. patents and several international patents are pending on the QST-713 strain, associated antifungal lipopeptides, formulations, and combinations with other pesticides.

Serenade® works through a complex mode of action that is manifested both by the physiology of the bacteria and through the action of secondary metabolites produced by the bacteria. Serenade® prevents plant diseases first by covering the leaf surface and physically preventing attachment and penetration of the pathogens. In addition, Serenade® produces three groups of lipopeptides (Iturins, agrastatins/plipastatins, and surfactins) that act in concert to destroy germ tubes and mycelium. The iturins and plipastatins have been reported to have antifungal properties. Strain QST-713 is the first strain reported to produce iturins, plipastatins, and surfactins and two new compounds with a novel cyclic peptide moiety, the agrastatins. The surfactins have no activity on their own, but low levels (25 ppm or less) in combination with the iturins or the agrastatin/plipastatin group cause significant inhibition of spores and germ tubes. In addition, the agrastatins and iturins have synergistic activities towards inhibition of plant pathogen spores.

The Serenade® formulation is available as a wettable powder, wettable granule, and aqueous suspension that is applied just like any other foliar fungicide. It can be applied alone or tank mixed; it can also be alternated with traditional chemical pesticides. Serenade® is not toxic to beneficial and nontarget organisms, such as trout, quail, lady beetles, lacewings, parasitic wasps, earthworms, and honey bees. Serenade® is exempt from tolerance because there are no synthetic chemical residues and it is safe to workers and ground water. Serenade®'s wettable granule formulation is listed with the Organic Materials Review Institute (OMRI) for use in organic agriculture and will continue to be listed under the National Organic Standards, which were enacted in the United States in October 2002.

Serenade®'s novel, complex mode of action, environmental friendliness, and broad spectrum control make it well-suited for use in integrated pest management (IPM) programs that utilize many tools, such as cultural practices, classical biological control, and other fungicides. Serenade® can be applied right up until harvest, providing needed pre- and post-harvest protection when there is weather conducive to disease development around harvest time.

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## Alternative Synthetic Pathways Category

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### *Süd-Chemie Inc.*

#### A Wastewater-Free Process for Synthesis of Solid Oxide Catalysts

Some major achievements in pollution reduction have been made recently through advancement of catalytic technologies. One such effort is in the area of hydrogen and clean fuel production. However, the synthesis of catalysts for such reactions is often accompanied by the discharge of large amounts of wastewater and other pollutants, such as  $\text{NO}_x$ ,  $\text{SO}_x$ , and halogens.

As a result of their commitment to continuously develop and invest in new and improved catalyst synthesis technologies, Süd-Chemie successfully developed and demonstrated a new synthetic pathway that is able to achieve virtually zero wastewater discharge, zero nitrate discharge, and no or little  $\text{NO}_x$  emission. Meantime, it substantially reduces the consumption of water and energy. For example, it is estimated that about 378,900 tons of wastewater discharges, about 14,300 tons of nitrate discharges, and about 3,800 tons of  $\text{NO}_x$  emissions can be eliminated for every 5,000 tons of oxide catalyst produced.

The new synthetic pathway is based on very simple chemistry. Instead of acid-base precipitation typically using metal nitrate as raw material, the new process starts with a clean metal that is readily and economically available in commercial quantities. The synthesis proceeds by reaction of the metal with a mild organic acid in the presence of an oxidation agent. The function of the acid is to activate the metal and extract electrons to form the oxide precursor. With assistance of the oxidation agent (typically air), a porous solid oxide is synthesized in one step at ambient temperature without any wastewater discharge. The other active ingredients of the catalyst can be incorporated using the concept of wet-agglomeration. In contrast, the precipitation process requires intensive washing and filtration to remove nitrate and the other salts. Further, the new process substantially reduces the consumption of water and energy for production of solid oxide catalysts over conventional methods. The emission in the entire process is only pure water vapor and a small amount of  $\text{CO}_2$  that is generated during spray drying and after-burning of hydrogen.



This wastewater-free process for making solid oxide catalysts has been demonstrated and more than 300 kg of the metal oxide catalysts has been produced. Patent protection is being sought for the development. The catalysts made by the green process give superior performance in the synthesis of clean fuels and chemicals. The market for such solid oxide catalysts is estimated to be approximately \$100 million. Süd-Chemie is the first in the industry to use the green process for making a catalyst for the synthesis of "green" fuels and chemicals.

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## Alternative Solvents/ Reaction Conditions Category

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### *DuPont*

#### Microbial Production of 1,3-Propanediol

DuPont is integrating biology in the manufacture of its newest polymer platform, DuPont Sorona® polymer. Combining metabolic engineering with polymer science, researchers are introducing a microbial process in a business that, historically, has relied solely on traditional chemistry and petrochemical feedstock. This achievement, comprising biocatalytic production of 1,3-propanediol from renewable resources, offers economic as well as environmental advantages. The key to the novel biological process is an engineered microorganism that incorporates several enzyme reactions, obtained from naturally occurring bacteria and yeast, into an industrial host cell line. For the first time, a highly engineered microorganism will be used to convert a renewable resource into a chemical at high volume.

The catalytic efficiency of the engineered microorganism allows replacement of a petroleum feedstock, reducing the amount of energy needed in manufacturing steps and improving process safety. The microbial process is environmentally green, less expensive, and more productive than the chemical operations it replaces. 1,3-Propanediol, a key ingredient in the Sorona® polymers, provides advantageous attributes for apparel, upholstery, resins, and nonwoven applications.

Scientists and engineers from DuPont and Genencor International, Inc. redesigned a living microbe to produce 1,3-propanediol. Inserting biosynthetic pathways from several microorganisms into an industrial host cell line allows the direct conversion of glucose to 1,3-propanediol, a route not previously available in a single microorganism. Genes from a yeast strain with the ability to convert glucose, derived from cornstarch, to glycerol were inserted into the host. Genes from a bacterium with the ability to transform glycerol to 1,3-propanediol were also incorporated. Additionally, the reactions present naturally in the host were altered to optimize product formation. The modifications maximize the ability of

the organism to convert glucose to 1,3-propanediol while minimizing its ability to produce biomass and unwanted byproducts. Coalescing enzyme reactions from multiple organisms expands the range of materials that can be economically produced by biological means.

For more than 50 years, scientists have recognized the performance benefits of polyesters produced with 1,3-propanediol; however, the high cost of manufacturing the ingredient using petroleum feedstock and traditional chemistry kept it from the marketplace. The biological process using glucose as starting material will enable cost-effective manufacture of Sorona® polymer, which will offer consumers fabrics with softness, stretch and recovery, easy care, stain resistance, and colorfastness. A unique kink in the structure of the polymer containing 1,3-propanediol allows recovery at a high rate when it is stretched. As a result, Sorona® improves fit and comfort because a fabric quickly recovers its original shape when stretched, for example, in knees or elbows. The resilience of Sorona® also adds beneficial features to automotive upholstery and home textiles. In resin applications, Sorona® barrier characteristics protect moisture, taste, and odor.

Biology offers chemical manufacturers attractive options for the production of chemicals while adhering to the principles of Green Chemistry. This microbial production of a key polymer ingredient from renewable sources is one example. By integrating biology with chemistry, physics, and engineering, DuPont develops new solutions that enhance the environment and improve upon existing materials.

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## Designing Safer Chemicals Category

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### *Shaw Industries, Inc.*

#### EcoWorx™ Carpet Tile: A Cradle-to-Cradle Product

Historically, carpet tile backings have been manufactured using bitumen, polyvinyl chloride (PVC), or polyurethane (PU). While these backing systems have performed satisfactorily, there are several inherently negative attributes due to their feedstocks or their ability to be recycled. Although PVC has, to-date, held the largest market share of carpet tile backing systems, it was our intent to design around PVC due to the health and environmental concerns around vinyl chloride monomer, chlorine-based products, plasticized PVC-containing phthalate esters, and toxic byproducts of combustion of PVC, such as dioxin and hydrochloric acid. While some claims are accepted by the Agency for Toxic Substances and Disease Registry and the U.S. Environmental Protection Agency, those resulting from publicly debated consumer perceptions provide ample justification for finding a PVC alternative.

Due to the thermoset cross-linking of polyurethanes, they are extremely difficult to recycle and are typically downcycled or landfilled at the end of their useful life. Bitumen provides some advantages in recycling, but the modified bitumen backings offered in Europe have failed to gain market acceptance in the United States and are unlikely to do so.

Shaw selected a combination of polyolefin resins from Dow Chemical as the base polymer of choice for EcoWorx™ due to the low toxicity of its feedstocks, superior adhesion properties, dimensional stability, and its ability to be recycled. The EcoWorx™ compound also had to be designed to be compatible with nylon carpet fiber. Although EcoWorx™ may be recovered from any fiber type, nylon-6 provides a significant advantage. Polyolefins are compatible with known nylon-6 depolymerization methods. PVC interferes with those processes. Nylon-6 chemistry is well known and not addressed in first generation production.

From its inception, EcoWorx™ met all of the design criteria necessary to satisfy the needs of the marketplace from a performance, health, and environmental

standpoint. Research indicated that separation of the fiber and backing through elutriation, grinding, and air separation proved to be the best way to recover the face and backing components, but an infrastructure for returning postconsumer EcoWorx™ to the elutriation process was necessary. Research also indicated that the postconsumer carpet tile had a positive economic value at the end of its useful life. The cost of collection, transportation, elutriation, and return to the respective nylon and EcoWorx™ manufacturing processes is less than the cost of using virgin raw materials.

With introduction in 1999 and an anticipated lifetime of ten to fifteen years on the floor, significant quantities of EcoWorx™ will not flow back to Shaw until 2006 to 2007. An expandable elutriation unit is now operating at Shaw, typically dealing with industrial EcoWorx™ waste. Recovered EcoWorx™ is flowing back to the backing extrusion unit. Caprolactam recovered from the elutriated nylon-6 is flowing back into nylon compounding. EcoWorx™ will soon displace all PVC at Shaw.