Nomination for the Presidential Green Chemistry Challenge Awards Program

Utilization of Carbon Dioxide and Carbon Monoxide for the Synthesis of Biodegradable Polymers

December 31, 2011

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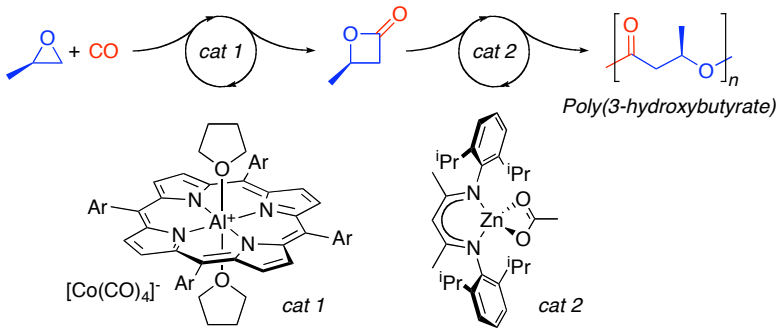
Utilization of Carbon Dioxide and Carbon Monoxide for the Synthesis of Biodegradable Polymers

Most recent milestone

WO 2011163309, "Carbonylative polymerization methods" Coates, Geoffrey W.; Dunn, Erin (Cornell University). Issued December 29, 2011.



This patent focuses on a highly efficient catalytic method for the synthesis of poly(3-hydroxy-butyrate) (P3HB) by the carbonylative polymerization of propylene oxide. The polymer P3HB is a naturally-occurring biodegradable polyester, however its current synthesis using fermentation of sugar is energy intensive and produces a significant amount of waste. The use of compatible epoxide carbonylation and lactone polymerization catalysts allows for a one-pot reaction and eliminates the need to isolate and purify the toxic beta-butyrolactone intermediate. This method is significantly more energy and cost effective than fermentation.

The nominated technology is eligible for an academic award.

EPA award focus area: This work is relevant to all foci areas, but especially addresses area 1: the use of greener synthetic pathways (*vide infra*).

Components of the nominated technology that occurred within the United States

All components (research and development) of the nominated technologies originated at Cornell University in Ithaca, New York.

Abstract of the Nominated Technology

It is difficult to imagine a world without plastics, which improve our daily lives in countless ways. At the same time, plastics pose a serious threat to our environment. Virtually all plastics are derived from fossil fuels – scarce resources that pose their own danger to the natural world, with leaking oil wells and CO_2 induced global warming. Of the 150 million tons of plastics that are made worldwide each year, only a small fraction are recycled – the rest end up in landfills, or worse, as pollution in the environment.

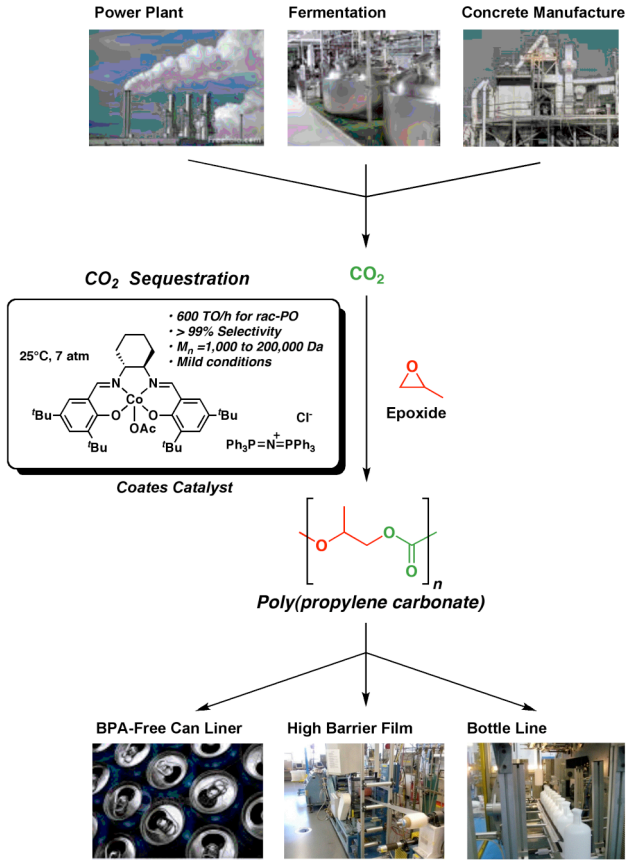
This nomination concerns the academic research of Professor Geoffrey Coates of Cornell University. Professor Coates has developed innovative processes for the synthesis of plastics from inexpensive biorenewable substances, such as carbon dioxide, carbon monoxide, plant oils, and lactic acid. The plastics formed are biodegradable, rendering them safe for the environment. This nomination will focus on Professor Coates' new catalysts for the utilization of carbon dioxide and carbon monoxide for polymer synthesis. Carbon monoxide and dioxide are ideal feedstocks for polymer synthesis. They can be derived from multiple sources, including biorenewable agricultural waste, abundant coal, even from industrial waste gas that is currently vented into the atmosphere. The challenge with utilizing carbon monoxide and dioxide lies in developing reactions that can efficiently convert them into useful products. Prof. Coates has developed a family of catalysts over the last decade that can effectively turn these waste products into valuable polymers. Importantly, use of carbon dioxide and carbon monoxide result in polymers that contain ester and carbonate linkages, producing materials that are ultimately biodegradable, leaving no long-term impact on the environment.

Professor Coates' technical innovations form the scientific foundation of Novomer Inc., a venture capital backed start-up company. Of particular relevance to the nomination criteria is Novomer's January 2010 announcement of the development of a new material using Coates' catalysts to replace the bisphenol-A (BPA) coatings that lines the majority of food and drink cans worldwide. This is of rapidly growing importance, as BPA can migrate out of coatings over time and is a suspected endocrine disrupter.

1. The Chemistry of the Award Nomination

A. Polycarbonates from Epoxide/CO_2 Copolymerization

Carbon dioxide is an ideal synthetic feedstock since it is abundant, inexpensive, nontoxic, and nonflammable. Nature uses CO_2 to make over 200 billion tons of glucose by photosynthesis each year, however synthetic chemists have had limited success in developing efficient catalytic processes that exploit CO_2 as a raw material. Epoxides can be copolymerized with CO_2 to yield aliphatic polycarbonates that are biodegradable. The renewable nature of CO_2 as a building block and the benign properties of the resulting polycarbonates make the development of new catalysts for epoxide/ CO_2 copolymerization a significant goal.

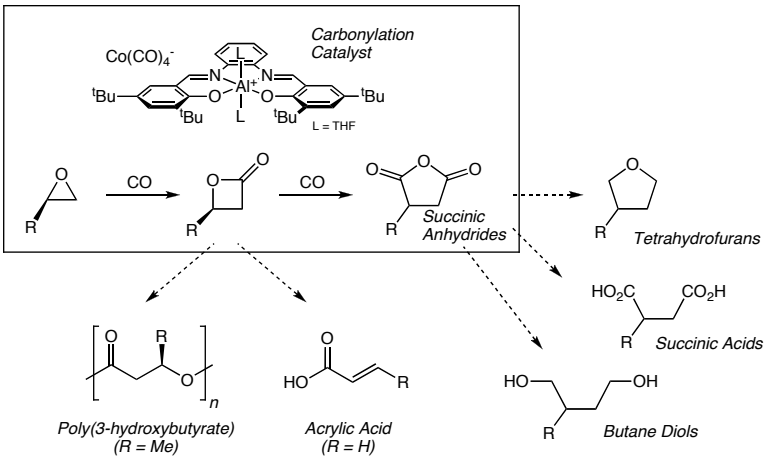


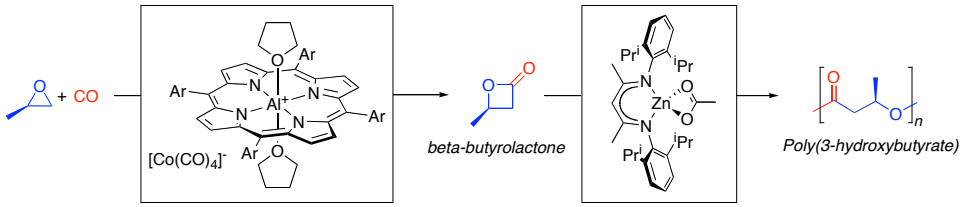
Prof. Coates has invented the first catalyst for the copolymerization of epoxides and CO_2 that exhibits high activity (600 turnovers per hour), high turnover number (over 10,000 turnovers demonstrated), operates at room temperature and low pressure, exhibits near perfect selectivity (no linkage defects or unwanted by-products), and can make a wide range of molecular weights.[1,2,3,4,5] This catalyst is now being used on the industrial scale by Novomer Inc. for the synthesis of epoxide/ CO_2 copolymers that will be used to replace the potentially gene disrupting bisphenol-A (BPA) materials that coat most food and beverage cans.[6] The polymer is currently being sold to companies engaged in the manufacture of electronics, as the thermally degradable nature of the polymer allows for more efficient production of electronic components. Applications under development are biodegradable plastic films and bottles that have unprecedented barrier properties, allowing new food packaging that reduces food spoilage due to oxidation.

B. New Catalysts for the Carbonylation of Epoxides

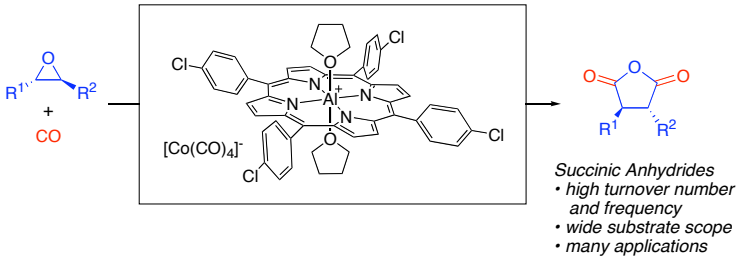
Prof. Coates has invented a unique class of catalysts that will controllably insert one or two molecules of CO into an epoxide ring, resulting in beta-lactones and succinic anhydrides.[7,8,9] Both of these small molecules have countless uses in the synthesis of pharmaceutical compounds, fine chemicals, and plastics. Given that CO is a waste product of industrial processes such as steel and aluminum production, any efficient process that can be used to convert it to useful products would have obvious beneficial environmental implications.

There are three specific chemical processes that are being pursued that are based on the carbonylation technology (see figure at right). First, this catalyst allows the synthesis of beta-butyrolactone, which is a monomer for the synthesis of naturally-occurring poly(3-hydroxybutyrate). In contrast to the current biochemical fermentation process which is energy and capital intensive, the chemical synthesis is greatly favored and allows control over molecular architecture and composition in a way that is not possible using fermentation. The catalysts also allow the direct formation of poly(3-hydroxybutyrate) via a tandem carbonylation and polymerization approach (see figure at right).[10,11]





Second, the catalyst is being used for the double carbonylation of epoxides to give succinic anhydrides. Cyclic anhydrides are valuable feedstocks for the chemical and polymer industry. Many commercial cyclic anhydrides are derived from maleic anhydride, which is currently formed from the poorly controlled oxidation of butane. Subsequent reduction to succinic anhydride or functionalization (i.e. using the 'ene' reaction) gives useful derivatives. The carbonylation of ethylene oxide directly to succinic anhydride represents a significantly improved route. The carbonylation of functional epoxides results in a direct approach to succinic anhydrides.

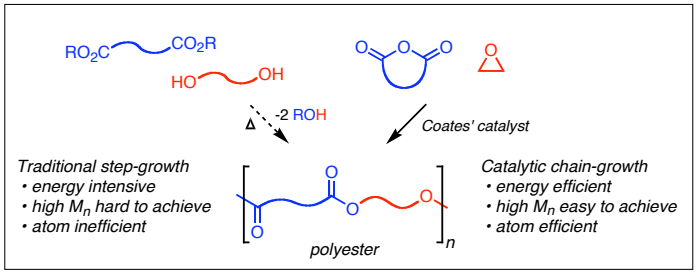


Third, the monocarbonylation of ethylene oxide to beta-propiolactone and subsequent isomerization to acrylic acid represents a route to this essential chemical that is significantly more efficient than the current propylene oxidation route.[12,13] Furthermore, with the introduction of bio-derived ethylene by Braskem/Dow,[14] it is now possible to produce fully bio-derived acrylic acid when bio-based CO is used. This process is being commercially developed.[15]

C. Synthesis of Biodegradable Polyesters from Epoxides and Anhydrides

Although not employing either CO_2 or CO, a process that is mechanistically related to epoxide/CO_2 copolymers involves the substitution of CO_2 with a cyclic anhydride. As aliphatic polyesters constitute an important class of polymers due to their biodegradability and

biocompatibility, which enables their use in drug delivery systems, artificial tissues, and commodity materials. These polymers are commonly produced through condensation polymerization; however, this method is energy intensive, requiring high temperature and removal of the alcohol or water by-product to achieve high molecular weight (M_n) polymers. Professor Coates has reported the first catalysts for the alternating copolymerization of epoxides and cyclic anhydrides under mild reaction conditions.[16,17] This invention opens the door to a wide range of biodegradable polyesters under mild synthesis conditions.



Unsaturated polyester resins for windmill blades, boat hulls, synthetic stone etc. have been made using maleic anhydride

2. Human Health and Environmental Benefits

The nominated technologies offer significant human health and/ or environmental benefits. The synthetic processes outlined above have many beneficial advantages, including:

- The utilization of CO and CO_2 is perhaps the most important advantage of this technology. These small molecules are produced in countless industrial processes – in many cases they are simply vented into the atmosphere. The sequestration of these molecules into useful products represents a long-standing scientific problem. The catalytic systems outlined above represent rare approaches to the utilization of these abundant waste streams.
- The polymers produced in these processes are as stable in ordinary use as current commodity plastics, yet in the water or in soil, the linkages in the polymers allow hydrolysis, and eventual biodegradation to CO_2 and water. In the case of polypropylene carbonate, the hydrolysis product propylene glycol is non-toxic and easily degraded. In the case of poly(3-hydroxyalkanoate)s, these are natural products with a well-documented mode of degradation.
- Significant advantages of these catalyst systems include their high selectivities, turnover frequencies, and turnover numbers. As a result, a small amount of catalyst can convert monomer to polymer in a time and chemically efficient manner. This allows *the economically viable synthesis of existing and new polymeric materials*, which is a vital prerequisite for commercial production. The catalysts can also be supported to allow continuous flow processes, which are highly efficient.

3. Applicability and Impact

The nominated technologies meet many important points of all three 'focus areas' of Green Chemistry. Regarding "*the use of greener synthetic pathways*", the use of CO and CO_2 feedstocks are of clear relevance. It is our opinion that the catalysts are truly unique; in the case of epoxide carbonylation, there are simply no other catalysts, and in the case of CO_2 chemistry, our cobalt catalysts are uniquely active and stable during the catalysis. All of the processes are highly atom economical as all atoms of the starting materials end up in the products. Regarding

"*the use of greener reaction conditions*", epoxide/CO_2 copolymerizations are performed in continuous flow processes where the epoxide serves as a *substrate and solvent*. As a result there are no solvents to dispose of or to recycle. In the case of epoxide carbonylation, again the epoxide can be used as solvent and are easily removed from the low-volatility lactone or anhydride products. All of the reactions proceed at ambient temperature, and low pressures of CO or CO_2. Regarding '*the design of greener chemicals*", importantly, all of the polymers will biodegrade under composting conditions and in either soil or water. Although as polymers they do not have an impact on the atmosphere, the use of CO or CO_2 that was destined to be vented into the atmosphere would have obvious beneficial implications. Preliminary studies have shown that our catalyst system is stable to the common impurities present in CO_2 derived from concrete manufacture.

It is very difficult to accurately assess the practicality and cost effectiveness of an early-stage academic technology. Without being able to predict future chemical prices, economic development and legislative changes, it is simply impossible to know what the future holds for any new technology. The only quantitative data that can be provided regarding the practicality of the aforementioned technologies come from our 'real-world' experiences at Novomer. Novomer has raised $50+ million in grants and venture capital to date, including a highly competitive $18.4 million Phase II grant in 2010 from the US Department of Energy under their "Carbon Capture & Sequestration from Industrial Sources and Innovative Concepts for Beneficial CO_2 Use" announcement.[18] Novomer's CO_2 based polycarbonates met the US DOE's requirement that a significant amount of CO_2 be sequestered by the proposed processes. Life-cycle analyses performed by Novomer scientists and hired consultants were able to document that at full market penetration, Novomer's materials will permanently convert 97 billion pounds of CO_2 per year, and the low energy synthetic process will avoid the combustion of fossil fuel that would emit 270 billion pounds of CO_2 per year. Although this is just a fraction of the CO_2 that the world adds annually to the atmosphere, it is clear that a decrease in atmospheric CO_2 levels will involve many integral solutions.

DSM and Novomer's press release of January 2010 announcing the world's first new coating in more than a decade quantifies some of the measurable impacts of this technology.[19] The Novomer polycarbonate will require 50% less petroleum to produce, and will sequester up to 50 wt% CO_2. Perhaps most importantly, it will replace bisphenol-A based coatings that are currently used to coat the vast majority of the world's food and drink cans. In recognition of its progress to date, in October 2011 Novomer was named as a 2011 ICIS Innovation Award winner in the category of "Innovation with Best Environmental Benefit category".[20] Since Novomer's materials are based on the catalysts discovered in Professor Coates' laboratory, perhaps these awards provide a reliable assessment of the promise of the technologies highlighted above.

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