Poly(limonene carbonate): An advanced bioplastic soon on the marketplace

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Called by Greiner's team "the perfect green platform polymer, from which many functional materials can be derived", (1) poly(limonene carbonate) (PlimC) is a thermoplastic polymer exhibiting excellent thermal, mechanical and optical properties whose catalytic synthesis by copolymerization of 1,2 limonene oxide (the *trans* isomer) and CO_2 mediated by a β-diiminate zinc catalyst was first reported by Coates and co-workers in the US in 2004 (2).

The original synthesis was optimized in Germany in 2016 to afford high-molecular-weight (>100 kDa) PlimC in kilogram amounts with further improved mechanical, thermal (glass transition temperature of 130 °C) and optical (higher transparency than bisphenol-A polycarbonate) properties; (3) followed by the discovery that PlimC has excellent CO_2 gas permeability which, along with good heat insulation, render it a "breathing glass" suitable for new generation windows in energy-efficient buildings (4).

Shortly afterwards, Kleij and co-workers in Spain reported a straightforward sequential route to poly(limonene) dicarbonate (PlimDC), a polymer with an unprecedented high glass transition temperature of up to 180 °C, starting from the commercially available mixture of *cis/trans* 1,2 limonene oxide and CO_2 as renewable reagents and aminotriphenolate Al(III) complex as catalyst. PlimC is now a synthetic intermediate whose subsequent copolymerization with CO_2 affords different PlimDC polymers of tunable molecular weight up to 15.1 kDa (5).

Remarkably, indeed, the PlimC polycarbonate can be further functionalized via derivatisation of the pendant double bond in the limonene molecule of each repeating unit, allowing its use as a platform system from which several new properties (mechanical, thermal, self-healing) may arise. Various groups quickly demonstrated the wide scope of this approach reporting functionalized PlimC polymers with different functionalities. Suffice it to mention here the antibacterial, (1) or protective coatings with good scratch and solvent resistance (6).

Much of this work has been highlighted by the press, due to the fact that limonene carbonates derived from *d*-limonene extracted from the citrus peel, (7) could in principle replace petroleum-derived bisphenol-A (BPA) polycarbonates, as BPA is a suspect endocrine-disruptor, neurotoxic, and carcinogenic agent whose employment in making baby bottles is banned for example in countries such as France, Turkey and Denmark.

Asked to comment on the forthcoming commercialization of limonene-based polycarbonates, Professor Kleij added:

"Clear opportunities exist to use the poly(limonene) carbonate and poly(limonene)dicarbonate technologies as drop-in solutions, i.e. the rigidity and functionality of the limonene (oxide) monomer makes it an attractive monomer for existing polycarbonates while replacing (partially) fossil fuel based monomers such as propylene oxide and BPA, and to design new and improved materials.

"Thus, in my view the introduction of new polymer formulations that incorporate this biobased monomer (limonene oxide specifically) will be gradual, and if successful may spark further development.

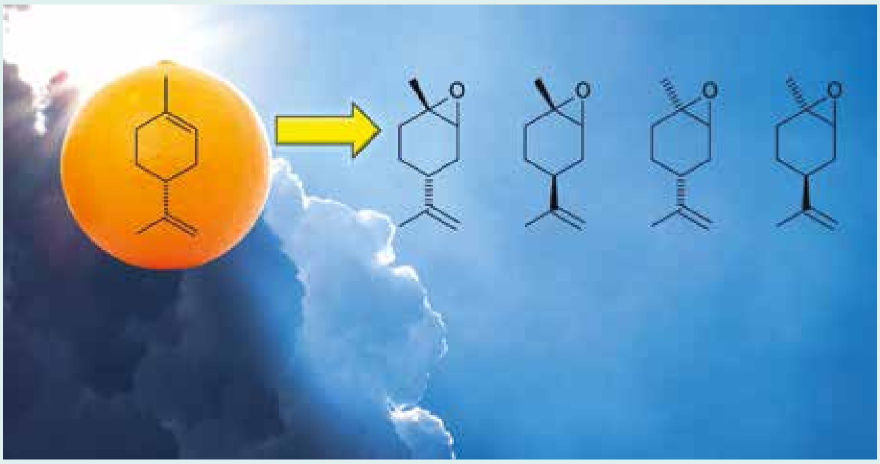
"I would like to add that there exist companies that operate biocatalytic processes that give rise to similar type of terpene monomers which may be equally interesting for polymer development. If such processes would deliver these functional monomers on a reasonable scale and cost then this can further spur industry to use and implement in wider sense biobased monomers".

Indeed, discovered in 1969 by Inoue and co-workers, (8) the ring opening copolymerization of epoxides with insertion of CO_2 was readily adopted by the chemical

SOLAR SYNTHESIS OF 1,2 LIMONENE OXIDE

Currently obtained on relatively small scale in industry by reacting limonene with perchloric acid (Prileschajew reaction), 1,2-limonene oxide is the bio-based building block whose *trans* isomer copolymerizes with CO_2 in the Coates synthesis of PlimC, whereas in Kleij synthesis, the cis isomer in the commercially available mixture of cis/ trans 1,2 limonene oxide is copolymerized.

In general, in light of forthcoming applications of limonene polycarbonates, a green and selective new route towards *cis*- and *trans*-limonene epoxides would be highly desirable.



Scheme 1. The solar route to limonene epoxide.

Lately discovered in Italy, one such process makes use of organically modified crystalline TiO_2 whose photocatalytic P25 commercial form commonly used for photocatalytic degradation of pollutants undergoes silylation (13). The resulting catalytic material is an highly selective catalyst for the aerobic limonene epoxidation to 1,2-limonene oxide under solar light irradiation (Scheme 1).

The mechanism proposed to explain the remarkable selectivity involves the singlet oxygen generated through energy transfer from the excited TiO_2 to adsorbed O_2 molecules.

industry to make polycarbonates mainly from propylene and cyclohexene oxides. This means that replacement of one oil-derived oxirane with a terpene-based epoxide such as 1,2 limonene oxide would configurate as a drop-in solution similar to those highly desirable in the chemical industry when dealing with new catalytic productions (9).

However, given the superior mechanical, thermal, optical and chemical properties of limonene-based polycarbonates and the limited amount of limonene available (around 50,000 tonnes extracted yearly, mainly from oranges) (10), the first applications of PlimC and PlimDC will likely start to materialize in high-revenue advanced uses where conventional polycarbonates derived from oil-based platform chemicals cannot compete in terms of properties.

Eventually, when the bottleneck of *d*-limonene limited availability will be solved by biotechnology companies (11), as done for example by Amyris with triteperpene squalene from sugarcane (12), limonene-based polycarbonates will become ubiquitous.

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