Polymers of limonene oxide and carbon dioxide: Polycarbonates of the solar economy

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This article is dedicated to the memory of Hermann Scheer (1944-2010)

Abstract: Limonene epoxide (1,2 limonene oxide) readily reacts with carbon dioxide in a ring opening copolymerization reaction with insertion of CO_2 and formation of polycarbonates of exceptional chemical and physical properties. Both poly(limonene carbonate) and poly(limonene dicarbonate) can be synthesized using low cost Zn or Al homogeneous catalysts. This study addresses selected relevant questions concerning the technical and economic feasibility of limonene and carbon dioxide polymers *en route* to the bioeconomy.

1. Introduction

Mostly extracted from the orange peel prior to squeezing the fruit, *d*-limonene is a cyclic monoterpene used in many different industrial sectors.[1] The terpene is the main component of orange oil obtained by centrifugation of the oil-water emulsion (0.5–2% in oil) obtained from the mechanical rupture of the fruit oil glands followed by oil capture with a stream of water vapor.[2]

The recent and current global demand of the resulting cold pressed oil is so high that orange oil, once a by-product of orange juice industry, now generates financial revenues equal or even higher than selling orange juice, at least for relatively small orange juice makers such as those existing in Sicily.

Remarkably, a spike in demand was accompanied by decreasing supply due to a disease (citrus greening) affecting orange plantations mostly in Florida. As a result, the price of orange oil reached its highest level in the summer of 2017 at $9.45/kg for bulk samples and delivered prices (adding shipping costs, duties and intermediary traders' margins exceeding $12/kg).[3]

Limonene, whose commercial availability of has been lately assessed,[4] replaces toxic volatile organic compounds (VOCs), used as industrial solvents including those employed by the oil industry to clean up the hull of ships engaged in remediation of oil spills at sea. Yet, orange oil from organically grown orange crops finds usages of much higher value including employment as main ingredient to formulate broad scope and highly effective biopesticides.[5]

In this dramatically changing market context, a number of new uses of *d*-limonene as platform chemical were increasingly reported starting in the early 2000s,[1] including one that, as noted lately by Poland and Darensbourg "stalled for over a decade",[6] namely the synthesis of poly(limonene carbonate) (PLC) via the alternating copolymerization of 1,2 limonene oxide, the *trans* isomer of the epoxide, and CO_2 mediated by a *β*-diiminate (BDI) Zn(II) catalyst.[7]

Since 2015, to quote Darensbourg and Poland again, "a torrent of new works has been published on the synthesis and uses of poly(limonene carbonate) from research groups across the globe",[6] culminating in 2017 with the discovery of a new copolymerization catalyst, an aminotriphenolate Al(III) complex, enabling access to thermoplastic biobased polycarbonates of unprecedented thermal resistance including poly(limonene)dicarbonate (PLDC), with high glass transition temperature (T_g) of 180 °C (for comparison the main commercial polycarbonate, polycarbonate from bisphenol A, has a glass transition temperature of 145 °C).[8]

In 2016, the Coates' catalytic synthesis was optimized in Germany to afford high-molecular-weight (>100 kDa) PLC in kilogram amounts with further improved mechanical (hardness), thermal (T_g = 130 °C) and optical (higher transparency than bisphenol-A polycarbonate) properties.[9]

Shortly afterwards, the team led by Greiner discovered that PLC has excellent gas permeability to molecules such as CO_2 and O_2 making the biobased polycarbonate suitable to manufacture gas separation membranes and new generation windows for energy-efficient buildings (the polymer is also a good heat insulator).[10]

Finally, in an intriguing work in which new antibacterial, mechanical, thermal, self-healing and protective coating properties were demonstrated,[11] the same team showed how simple chemical derivatisation of the pendant isoprene double bond of limonene moieties in each repeating unit of the polymer, allows the use of PLC as true polymeric platform system ("synthetic toolbox") from which several new properties may arise.

Much of this work has been highlighted by the general press, also due to the fact that limonene carbonates derived from *d*-limonene extracted from the citrus peel could, in principle, replace petroleum-derived bisphenol-A (BPA) polycarbonates. BPA indeed is a suspect endocrine-disruptor, neurotoxic, and carcinogenic agent (a class 2 B reproductive toxin for several food safety and health organizations), whose polycarbonate to make baby bottles is banned in countries as large as France and Turkey, and whose carcinogenicity status is currently being reconsidered.[12]

This study addresses several practical relevant questions concerning the technical and economic feasibility of limonene and carbon dioxide polymers *en route* to the bioeconomy.

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Is it realistic to expect near term commercialization of these biobased polycarbonates? What are the main hurdles to overcome prior to industrial manufacturing? Will limonene polymer production be inevitably limited by the citrus oil supply? Which, if any, will be the first practical applications?

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2. Limonene carbonates

Discovered in the late 1960s by Inoue and co-workers in Japan,[13] the ring opening copolymerization of epoxides with insertion of CO_2 catalyzed by diethylzinc ($ZnEt_2$) at room temperature under 50 atm CO_2 provides an alternative route to the phosgene process by which, still today, 80-90% of the ever increasing amount of polycarbonates are produced yearly,[14] even though highly successful productions of polycarbonate from CO_2 have been established and then rapidly expanded in the first decade of year 2000s.[15]

For comparison, Figure 1 shows that the 14-year average (red line) supply of orange oil has been around 57,000 tons, with a 9,000 tons shortage in 2016/2017 due to constant decline of Florida's production hit by citrus greening disease.

Plentiful research efforts devoted to sustainable polycarbonates from epoxide/CO_2 copolymerization processes have been lately reviewed by Poland and Darensbourg including a thorough and comprehensive discussion of advances concerning PLC and PLDC updated to August 2017.[6]

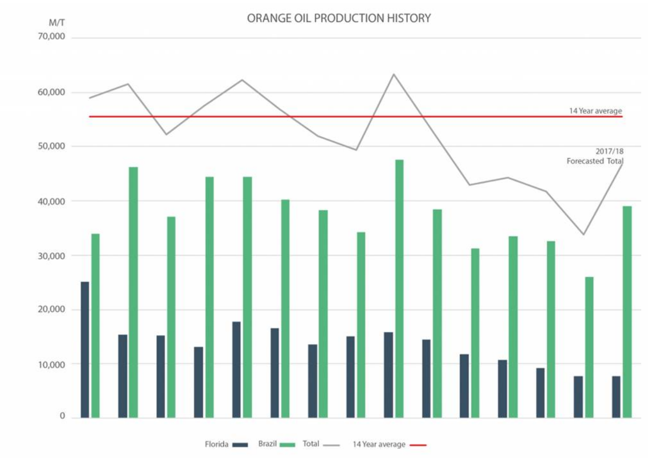
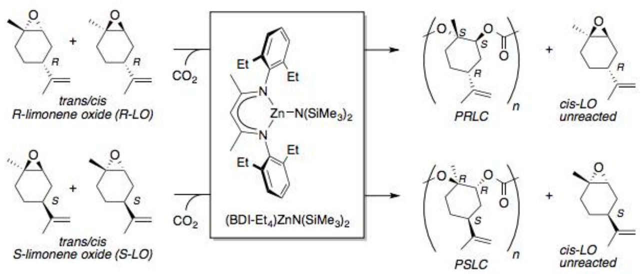


Figure 1. Global supply of orange oil between 2003/2004 and 2017/2018 (expected). Total output is the grey line. The red line is the 14-year average. The bars are production in Florida and in Brazil. [Reproduced from Ref. 3, with kind permission].

As mentioned above, Coates' team in the US discovered in 2004 that enantiomerically pure PLC can be synthesized starting from a mixture of (*R*)- and (*S*)-limonene epoxide at room temperature under 6.8 atm CO_2, and in the presence of a *β*-diiminate zinc acetate complex (0.4 mol%) as the catalyst.[7] The catalyst polymerizes the *trans* diastereomer of limonene oxide leaving the *cis* diastereomer unreacted, in an exquisite selectivity that excludes also the formation of ether linkages.

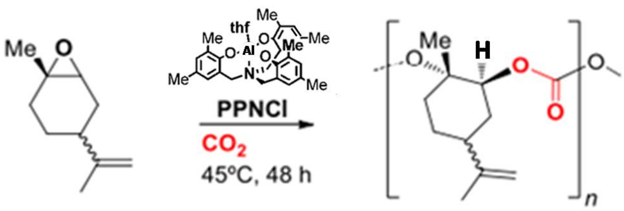
In 2015, along with Auriemma and co-workers in Italy, Coates reported also the first example of co-crystallization of two amorphous enantiomeric polymers in two specular polymeric chains (Scheme 1) by precipitating a 1:1 mixture of regio- and stereoregular amorphous PLC copolymers, namely poly(1*S*,2*S*,4*R*-limonene carbonate) (PSLC) and poly(1*R*,2*R*,4*S*-limonene carbonate (PRLC), dissolved in *n*-hexane.[16]



Scheme 1. Synthesis of chiral PRLC and PSLC. [Reproduced from Ref. 15, with kind permission].

The replacement of an oil-derived oxirane with a terpene-based epoxide such as 1,2 limonene oxide, configurates as a drop-in solution similar to those highly desirable in the chemical industry when dealing with new catalytic productions proposed by researchers to renew synthetic processes in use.[17]

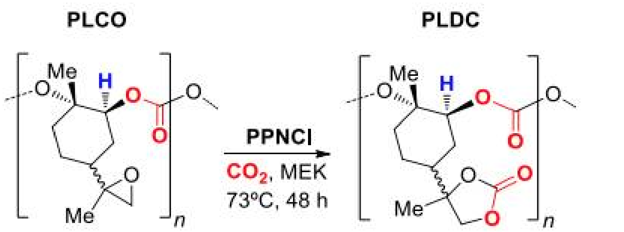
The same holds true for the oxidation protocol proposed by Kleij, in which limonene oxide is copolymerized with CO_2 with a binary catalyst system comprised of an aminotriphenolate Al(III) complex combined with *bis*-triphenylphosphine iminium chloride (PPNCl) to access different grades of PLC with molecular weights ranging from 1.3 to 15.1 kg/mol.[8]



Scheme 2. Synthesis of PLC using the process developed by Kleij. [Reproduced from Ref. 8, with kind permission].

To show the simplicity of the process, limonene oxide (4 mL, *cis*/*trans* mixture or solely the *cis* isomer), the Al catalyst (74 mg, 0.14 mmol) and PPNCl (40 mg, 70 µmol) are mixed in a Teflon vessel placed in a stainless steel reactor. The mixture is purged with CO_2 three times eventually bringing the pressure at 15 bar after which the reactor heated to an inside temperature of 45 °C is left to react for 48 h (Scheme 2).[8] The PLC thereby obtained (1.74 g, 8.88 mmol of alkene units) is dissolved in CH_2Cl_2 (50 mL) and oxidised to poly(limonene-8,9-oxide carbonate) (PLCO) with 3-chloroperbenzoic acid at 0 °C for 12 h.

In the optimized reaction procedure, the latter epoxide is copolymerized with carbon dioxide by simply using PPNCl as nucleophile for chloride-assisted carboxylation (Scheme 3).



Scheme 3. Synthesis of PLDC from PLCO in methyl ethyl ketone (MEK) in a Teflon vessel within a stainless steel reactor under 20 bar CO_2, according to the process developed by Kleij. [Reproduced from Ref. 8, with kind permission].

The white polymer comprised of poly(limonene)dicarbonate (PLDC) thereby obtained has a T_g of 180 °C which is the highest amongst all CO_2-derived polycarbonates known so far, due to the highly rigid molecular structure.[8]

In general, the presence of epoxy- and cyclic carbonate groups in PLCO/PLDC, the team concluded, enables the design of functional polymers via straightforward conversion of the oxirane/carbonate units.

These biobased polymers hold great potential for practical utilization, given both their excellent sustainability profile (with complete back-to-monomer recyclability)[18] and a vast scope of potential applications which include protecting coatings,[19] breathing-glass windows,[10] and the addition of permanent antibacterial activity and hydrophilization.[11]

Prior to that, however, the main hurdle to their large-scale commercialization needs to be overcome: the limited supply of limonene.

3. New routes to limonene

According to Ruzicka's 1953 classification of terpenoids based on the number of isoprene units from which they are biogenetically derived (isoprene rule),[20] limonene along with geraniol, linalool, menthol, and camphor belongs to monoterpenoids (C10, Figure 2), volatile biological compounds present in numerous plants.

Formed by head to tail condensation of isopentenyl diphosphate (IPP) and dimethylallyl diphosphate (DMAPP) activated forms of isoprene units, geranyl diphosphate (GPP) is the precursor of limonene as well as of linalool and geraniol.[21]

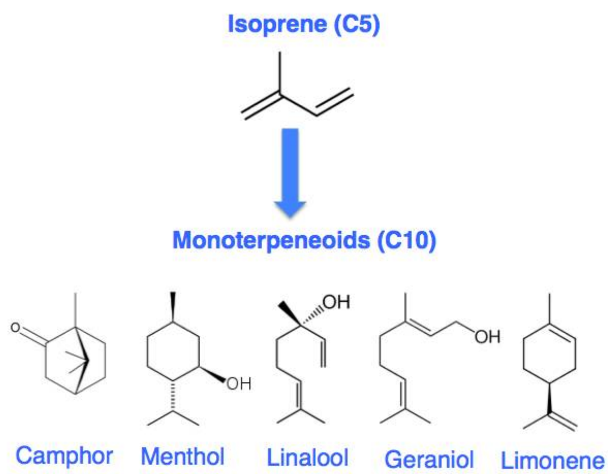
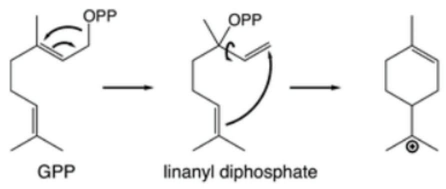


Figure 2. Monoterpenoids (C10) derived from two isoprene units. [Adapted from Ref. 26, with kind permission].

Limonene synthase (the water soluble enzyme present in the orange flavedo)[21] is the terpenoid synthase catalyzing cyclization and formation of limonene via a carbocationic driven mechanism common to all terpenoid synthases[22] in which, specifically, GPP is isomerized to linalyl diphosphate (LPP), followed by C1 repositioning prior to addition to the C6–C7 double-bond to eventually form the cyclized *α*-terpinyl cation

(Scheme 3) which, following methyl group deprotonation, yields limonene.[23]



Scheme 4. GPP cyclization affording the α-terpinyl cation. [Adapted from Ref. 22, with kind permission].

As happened with triterpenoid squalene, which is currently mostly now obtained from sugarcane fermentation rather than from shark liver oil or from olive oil distillates,[24] the bottleneck of limonene limited supply needs to be solved by innovation in biotechnology.

The first approach attempted was to use engineered microorganisms as a cell factory to produce terpenoids from cheap and readily available glucose.[25] However, whereas engineering yeast metabolism has been successful to produce several terpenoids in such high yield to become commercial,[26] limonene is highly toxic to microbes limiting its concentration in fermentation broths to very low levels (*i.e.* 2.7 g/L of *l*-limonene over recombinant *Escherichia coli* from glycerol as carbon source).[27]

In agreement with what Beekwilder and co-workers wrote in 2016,[25] such limonene titre values would need to increase two orders of magnitude to reach the current prices of citrus limonene.

That lately reported by Bowie and co-workers producing limonene from the free enzymes, rather than from whole cells in unprecedented high yield is therefore a breakthrough holding the potential to open the route to large-scale production of limonene from low cost and overly abundant sugars.[28]

In detail, the team designed a system comprising 27 enzymes for the conversion of glucose into monoterpenes. Different monoterpenes (limonene, pinene and sabinene) could be produced from GPP by changing the terpene synthase enzyme, which in the case of limonene is limonene synthase extracted from the orange peel.

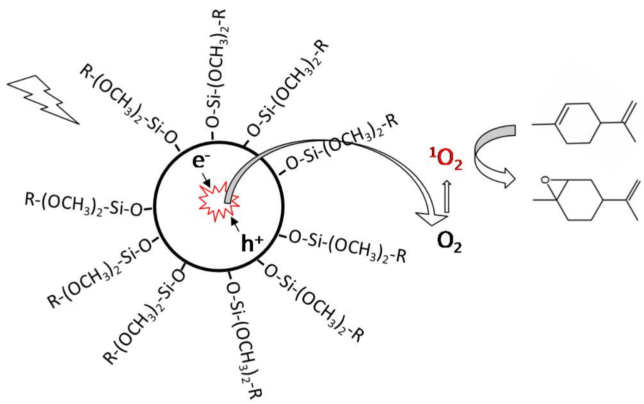
Operated continuously for 7 days, the reaction affords a stable production of limonene from a single addition of glucose with a total yield of ca. 90% pointing to moderate loss of carbon due to side reactions and a limonene titre of 12.5 $g\,L^{-1}$, which is more than 2 times higher the toxicity limit of limonene for *E. coli* or *S. cerevisiae* varying between 0.02 and 0.5% (5 $g\,L^{-1}$).

4. New routes to limonene oxide

Currently obtained by a reaction of limonene with an organic peroxide, 1,2-limonene oxide is the biobased building block whose *trans* and *cis* diastereoisomers copolymerize with CO_2, respectively, in the Coate's and Kleij's syntheses of PLC.

In light of forthcoming applications of limonene polycarbonates, a green and selective new route towards *cis*- and *trans*-limonene epoxides would be highly desirable. Indeed, a recent thorough life cycle analysis of the individual stages of the PLC production process found that the use of an equimolar amount of *tert*-butyl hydroperoxide (TBHP) to convert limonene into LO in a epoxidation reaction catalyzed by $Ti(O^iPr)_4$ bound to silica (75% conversion and 88% selectivity at room temperature) has "a significant negative impact on the overall process despite its low quantities".[29] The team conclude that more research is needed to develop a clean alternative limonene oxidation route.

One such new process makes use of organically modified crystalline TiO_2 obtained by silylation of photocatalytic P25 commercial titania used for photocatalytic degradation of pollutants. The resulting catalytic material selectively mediates the aerobic epoxidation to 1,2-limonene oxide under solar light irradiation.[30]



Scheme 5. Oxidation of limonene in the presence of silylated TiO_2 (R = $C_{16}H_{33}$). Although anchoring may occur through all of the three methoxy groups of the silane, only one oxygen bridge per silane molecule has been depicted for the sake of clarity. [Adapted from Ref. 30, with kind permission].

A mechanism explaining the remarkable selectivity observed involves singlet oxygen $^1O_2$ generated through energy transfer from the surface of the organically modified semiconductor to the O_2 molecules adsorbed at the catalyst's outer surface (Scheme 5).

4. Bioeconomy aspects

Writing about the solar economy in the early 2000s,[31] Scheer, a long time and successful advocate of solar energy, argued that in such forthcoming economy "real biotechnology" would be used to convert plant sources ("solar raw materials") into the

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useful products we obtain today starting from petroleum-based feedstocks. Energy, in its turn, will originate from renewable energy sources (RES).

Almost two decades later, Germany obtained 36.5% of its huge electricity demand in 2017 from RES,[32] showing that the transition to 100% renewable energy even in large industrial economies is no longer an unrealistic dream of environmental activists, though still requiring significant advances in energy storage technologies.[33]

Achievements in the transition from the oil-based to the bio-based chemical industry, however, lag much behind. For decades, the only large scale chemical bioproduction has been bioethanol fuel obtained via yeast fermentation of sugarcane sugars in Brazil, and maize starch in the US. Eventually, the glycerol surplus created as by-product of biodiesel led in 2007 to the first large scale chemical production of a key plastic (epoxy resin) precursor, the epoxide epichlorohydrin, from a biological resource.[34]

The single largest product of the petrochemical industry is indeed plastics, with most of the 322 million tons produced in 2015 being obtained from oil-derived feedstocks.[35] The industry, furthermore, has grown at the striking 8.6% compound annual growth rate from 1950 to 2015, with polycarbonate being one of the most lucrative segments, forecasted to grow at similar fast pace (of almost 7% up to 2024), with nearly half of the overall consumption in transportation, electrical and electronics sectors and the remainder, thanks to optical clarity, to make headlamps, face shields, laminates, and windshields.[36]

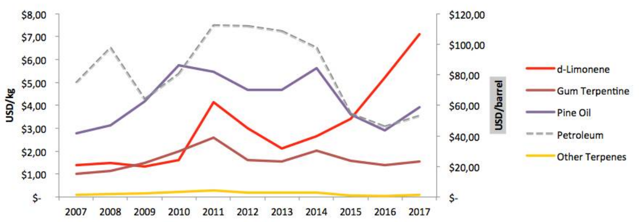

Figure 3. Price of *d*-limonene, gum turpentine, pine oil and other terpenes in the 2007-2107 decade. For comparison, also the price of petroleum is displayed. [Image courtesy of Fabio Thomazelli, Citrosuco, 2018].

This is the highly competitive (and huge) market in which poly(limonene carbonates) would enter once produced on commercial scale. The current supply of citrus limonene, coupled to high and increasing price (Figure 3), prevents large scale bioplastics productions based on limonene, leaving room for selected advanced applications in which the superior properties of PLC and PLDC may justify even today the use of an expensive and rare monomer such as limonene.

In other words, given the superior mechanical, thermal, optical and chemical properties of limonene-based polycarbonates, the first applications of PLC and PLDC 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.

Furthermore, given the high value of PLC and PLDC transparent resins, waste-free 3D-printing of bioplastics such as that lately pioneered by Ananikov's team,[37] will advantageously be used to manufacture functional goods for the above mentioned high-technology applications.

5. Outlook and perspective

From the manufacturing viewpoint, recent accelerated progress makes possible the production of enantiomerically pure poly(limonene carbonates) of high molecular weight using either one of the two catalysts active in limonene oxide/CO_2 copolymerization relying on abundant and low cost Zn and Al metals and easily synthesized ligands, namely beta diiminate zinc and amino triphenolate aluminum/PPNCl complexes.

The relatively low CO_2 reaction pressures (6-20 bar) and low temperatures employed (up to 73 °C) mean that no costly and hazardous high-pressure equipment is required for the manufacture of limonene carbonates.

Remarkably, furthermore, the catalysts are complementary. The zinc catalysts are sensitive to moisture and selectively mediate the copolymerization of the *trans* isomer of 1,2 limonene oxide; whereas the aminotriphenolate aluminum/PPNCl species is unsensitive to water and catalyzes the polymerization of the *cis* isomer.

According to Kleij, "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".[38]

The main hurdle to be overcome is the limited supply of citrus limonene. The cell-free, multienzyme synthetic biochemistry approach to limonene synthesis from sugars pioneered by Bowie and co-workers,[28] however, holds significant potential to open the route to the commercial production of monoterpenes from glucose, leaving the orange oil yearly supply available for high-value uses as key ingredient to formulate fragrance, cosmetic, personal care and biopesticide products.[1]

In forthcoming industrial applications, we argue in conclusion, it is also likely that some or all the enzymes enabling the one-pot biomanufacturing of monoterpenoids will be immobilized over a solid support thereby enhancing the enzyme stability for prolonged use with easy product separation from the biocatalyst mixture.[39]

The second need, lately emphasized by Li and Koning, calls for "a one-pot, two-step reaction"[40] in which the copolymerization catalyst is added to the reaction mixture containing the limonene epoxide directly after the limonene epoxidation reaction.

The latter requirement may be met by shifting the solar-driven photocatalytic aerobic epoxidation process from batch to flow, using new generation flow chemistry systems combining the advantages of heterogeneous catalysis in batch with the benefits of flow photochemistry.[41]

Once the main practical issues identified in this study will be addressed, limonene polycarbonates, true polymers of the solar bioeconomy, will become ubiquitous.

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Notes
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