

Polymers of Limonene Oxide and Carbon Dioxide: Polycarbonates of the Solar Economy

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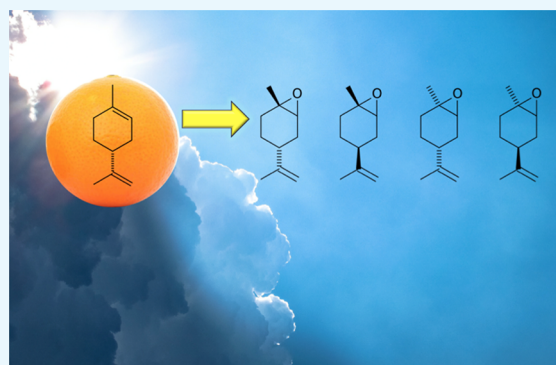
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ABSTRACT: Limonene epoxide (1,2-limonene oxide) readily reacts with carbon dioxide inserted in a ring-opening copolymerization reaction and forms polycarbonates of exceptional chemical and physical properties. Both poly(limonene carbonate) and poly(limonene 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 derived 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 byproduct 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, with delivered prices (adding shipping costs, duties, and intermediary traders' margins) exceeding \$12/kg.³

Limonene, whose commercial availability has been assessed lately,⁴ replaces toxic volatile organic compounds, used as industrial solvents, including those employed in 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 the

main ingredient to formulate broad scope and highly effective biopesticides.⁵

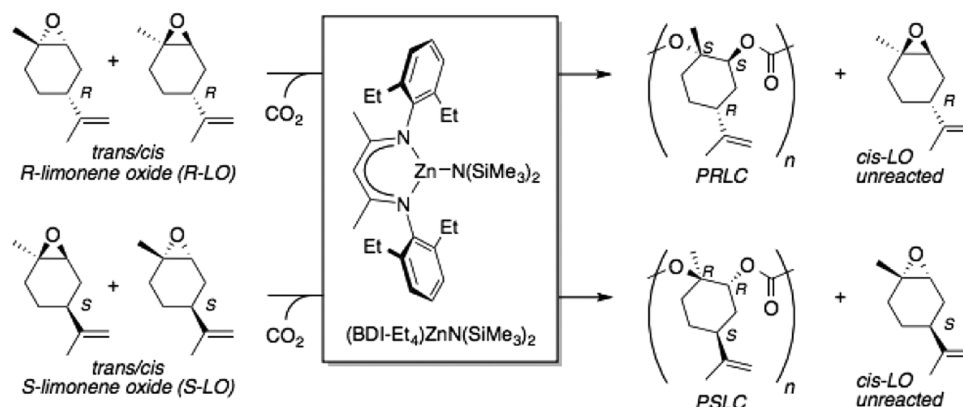
In this dramatically changing market context, a number of new uses of *d*-limonene as platform chemical were increasingly reported starting in the early 2000s,¹ including one that, as noted lately by Poland and Darensbourg, “stalled for over a decade”,⁶ namely, the synthesis of poly(limonene carbonate) (PLC or PlimC) via the alternating copolymerization of 1,2-limonene oxide, the trans isomer of the epoxide, and CO₂ mediated by a β -diiminato (BDI) Zn(II) catalyst.⁷

Since 2015, to quote Poland and Darensbourg 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 a high glass-transition temperature (T_g) of 180 °C (for comparison, the main commercial polycarbonate, polycarbonate from bisphenol-A (BPA), has a glass-transition temperature of 145 °C).⁸

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Scheme 1. Synthesis of Chiral PRLC and PSLC^a

^aReproduced from ref 16, with kind permission.

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 BPA-based polycarbonates. BPA indeed is a suspect endocrine disruptor as well as a neurotoxic and carcinogenic agent (a class 2B 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.

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 application?

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 CO₂ catalyzed by diethylzinc (ZnEt₂) at room temperature under 50 atm CO₂ provides an alternative route to the phosgene process, by which, to date, 80–90% of the ever-increasing amount of polycarbonates is produced yearly,¹⁴ even though highly successful productions of polycarbonate from CO₂ have been established and then rapidly expanded in the 2000s.¹⁵

Plentiful research efforts devoted to sustainable polycarbonates from epoxide/CO₂ 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

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 afterward, the team led by Greiner discovered that PLC has excellent gas permeability to molecules such as CO₂ and O₂, making the biobased polycarbonate suitable to manufacture new-generation windows for energy-efficient buildings (the polymer is also a good heat insulator).¹⁰

The same team showed how chemical derivatization 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,¹¹ whereas the high molecular rigidity and high hydrophobicity of PLC (contact angle to water of 94°) inhibit both enzymatic and hydrolytic degradation of the polymer via depolymerization.

As mentioned above, Coates' team in the United States 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 CO₂ and in the presence of a β-diiminato 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.

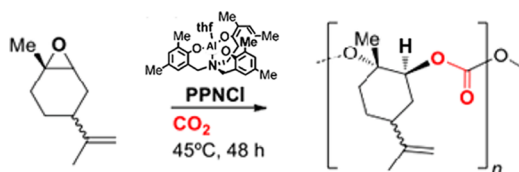
In 2015, along with Auriemma and co-workers in Italy, Coates reported also the first example of co-crystallization of two amorphous enantiomeric polymers in two specular polymeric chains (Scheme 1) by precipitating a 1:1 mixture of regio- and stereoregular amorphous PLC copolymers, namely, poly(1*S*,2*S*,4*R*-limonene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

The replacement of oil-derived oxirane with a terpene-based epoxide, such as 1,2-limonene oxide, configures as a drop-in solution similar to the highly desirable solutions 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 CO₂ with a binary catalyst system composed 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

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 CO₂ 3 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 CH₂Cl₂ (50 mL) and oxidized to poly(limonene-8,9-oxide

Scheme 2. Synthesis of PLC Using the Process Developed by Kleij^a

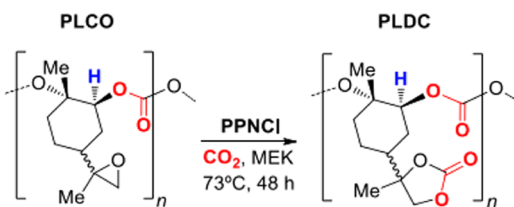


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carbonate) (PLCO) with 3-chloroperbenzoic acid at 0 °C for 12 h.

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

Scheme 3. Synthesis of PLDC from PLCO in Methyl Ethyl Ketone in a Teflon Vessel within a Stainless Steel Reactor under 20 bar CO₂, According to the Process Developed by Kleij^a



^aReproduced from ref 8, with kind permission.

The white polymer composed of poly(limonene)dicarbonate (PLDC) thereby obtained has a T_g of 180 °C, which is the highest among all CO₂-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.

In the context of their research on nonisocyanate polyurethanes (NIPUs), Mülhaupt and co-workers showed in 2012 how PLDC can also be produced from limonene dioxide/CO₂ copolymerization using tetrabutylammonium bromide as homogeneous catalyst at 140 °C under 30 bar CO₂ pressure. The alkoxide ion formed following the epoxy ring opening by the halide (Cl⁻) attacks the CO₂ molecule to afford the five-membered cyclic carbonate ring. In contrast to NIPU based on seed oils, the absence of ester groups in PLCO preventing unwanted reactions during amine curing and the unprecedented high carbonate content in a rigid structure, eventually affords NIPUs of high Young's modulus, high glass-transition temperature, and low elongation at break.¹⁸

These biobased polymers hold great potential for practical utilization, given both their excellent sustainability profile (with complete back-to-monomer recyclability)¹⁹ and a vast scope of potential applications, which include protecting coatings,²⁰ 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, the limited supply of limonene, needs to be overcome.

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),²¹ limonene along with geraniol, linalool, menthol, and camphor belongs to monoterpenoids (C₁₀, Figure 1), volatile biological compounds present in numerous plants.

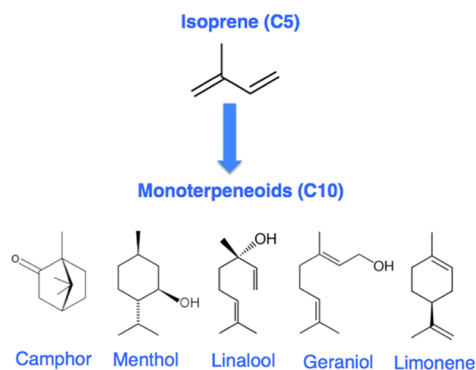
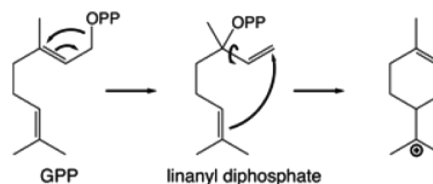


Figure 1. Monoterpenoids (C₁₀) derived from two isoprene units. (Adapted from ref 27, with kind permission).

Formed by head-to-tail condensation of isopentenyl diphosphate and dimethylallyl diphosphate, the activated form of isoprene units, geranyl diphosphate (GPP), is the precursor of *d*-limonene as well as of linalool and geraniol.²²

Limonene synthase (the water-soluble enzyme present in the orange flavedo)²² is the terpenoid synthase catalyzing cyclization and formation of limonene via a carbocationic driven mechanism common to all terpenoid synthases²³ in which, specifically, GPP is isomerized to linalyl diphosphate, followed by C1 repositioning prior to addition to the C6–C7 double bond to eventually form the cyclized α -terpinyl cation (Schemes 3 and 4), which, following methyl group deprotonation, yields limonene.²⁴

Scheme 4. GPP Cyclization Affording the α -Terpinyl Cation^a



^aAdapted from ref 23, with kind permission.

Figure 2 shows that the 14 year average (red line) supply of orange oil has been around 57 000 tons, with a 9000 tons shortage in 2016/2017 due to constant decline of Florida's production hit by citrus greening disease.

As it happened with triterpenoid squalene, which is currently mostly obtained from sugarcane fermentation rather than from shark liver oil or from olive oil distillates,²⁵ the bottleneck of limited supply of limonene 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.²⁶ However, although engineering yeast metabolism has been successful to produce

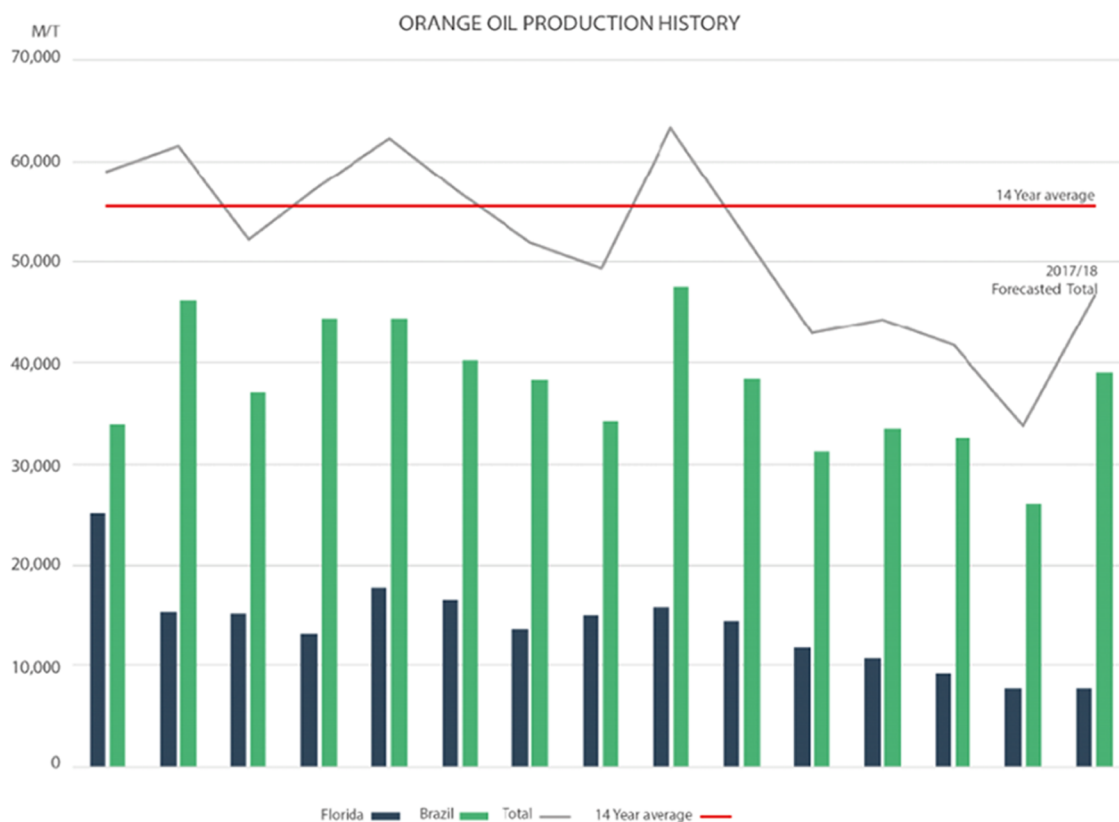


Figure 2. Global supply of orange oil between 2003/2004 and 2017/2018 (expected). The total output is the gray line. The red line is the 14 year average. The bars are production in Florida and in Brazil. (Reproduced from ref 3, with kind permission).

several terpenoids in such high yield to become commercial,²⁷ 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).²⁸

In agreement with what Beekwilder and co-workers wrote in 2016,²⁶ such limonene titer values would need to increase 2 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.²⁹

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 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 titer of 12.5 g/L, which is more than 2 times higher than the toxicity limit of limonene for *E. coli* or *Saccharomyces cerevisiae* varying between 0.02 and 0.5% (5 g/L).

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 CO₂, respectively, in the Coates' and Kleij's syntheses of PLC.

In light of forthcoming applications of limonene polycarbonates, a green and selective new route toward 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 to convert limonene into LO in an epoxidation reaction catalyzed by Ti(O^{*i*}Pr)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".³⁰ The team concluded that more research is needed to develop a clean alternative limonene oxidation route.

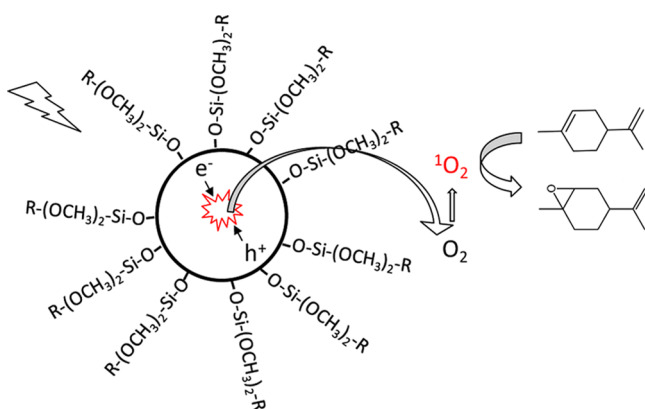
One such new process makes use of organically modified crystalline TiO₂ obtained by silylation of photocatalytic P25 commercial titania used for photocatalytic degradation of pollutants. The resulting catalytic material selectively mediates the aerobic epoxidation to 1,2-limonene oxide under solar light irradiation.³¹

A mechanism explaining the remarkable selectivity observed involves singlet oxygen ¹O₂ generated through energy transfer from the surface of the organically modified semiconductor to the O₂ molecules adsorbed at the catalyst's outer surface (Scheme 5).

5. FORTHCOMING APPLICATIONS

Writing about the solar economy in the early 2000s,³² 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 useful products we obtain today starting from petroleum-based

Scheme 5. Oxidation of Limonene in the Presence of Silylated TiO₂ (R = C₁₆H₃₃)^a



^aAlthough 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 31, with kind permission).

feedstock. Energy, in its turn, will originate from renewable energy sources (RES).

Almost 2 decades later, Germany obtained 36.5% of its huge electricity demand in 2017 from RES,³³ showing that the transition to 100% renewable energy even in large industrial economies is no longer an unrealistic dream of environmental activists, although still requiring significant advances in energy-storage technologies.³⁴

Achievements in the transition from the oil-based to the biobased 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 United States. Eventually, the glycerol surplus created as byproduct of biodiesel led in 2007 to the first large-scale chemical production of a key plastic (epoxy resin) precursor, epoxide epichlorohydrin, from a biological resource.³⁵

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.³⁶ The industry, furthermore, has grown at a striking 8.6% compound annual growth rate from 1950 to 2015, with polycarbonate being one of the most lucrative segments forecasted to grow at a 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.³⁷

This is a 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), however, 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 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 rigid, heat-resistant, and transparent resins, we forecast that three-dimensional printing of poly(limonene carbonate) bioplastics, similar to that lately pioneered by Ananikov's team,³⁸ will advantageously be used to manufacture functional goods for advanced applications.

One of the first applications of PLC might be as glazing material. Greiner, Hauenstein, and co-workers suggested that this could occur in the construction industry to make new-generation windows and greenhouses,¹⁰ since, compared to the main commercial glazing materials (BPA-polycarbonate, poly(methyl methacrylate), and soda lime glass), PLC has similarly excellent optical clarity, but it is the lightest material (specific gravity) and is 1 (with respect to BPA-polycarbonate) or 2 (with respect to poly(methyl methacrylate)) orders of magnitude more permeable than O₂ and CO₂ gas molecules.³⁹

Another key application of limonene polycarbonates, especially of PLDC as lately shown again by Mülhaupt's team,⁴⁰ will be in the manufacturing of nonisocyanate polyurethanes, namely, a polyurethane prepared by the reaction of cyclocarbonates (which do not contain ester groups, which can interfere with the amine curing and amine advancement reactions) and amines without use of phosgene or of toxic isocyanates of improved mechanical, thermal, and chemical resistance compared to conventional polyurethanes.

Another advanced application will be in the field of functional coatings use, as pioneered by Hauenstein and Greiner, who first successfully demonstrated new antibacterial, mechanical, thermal, self-healing, and new protective coating

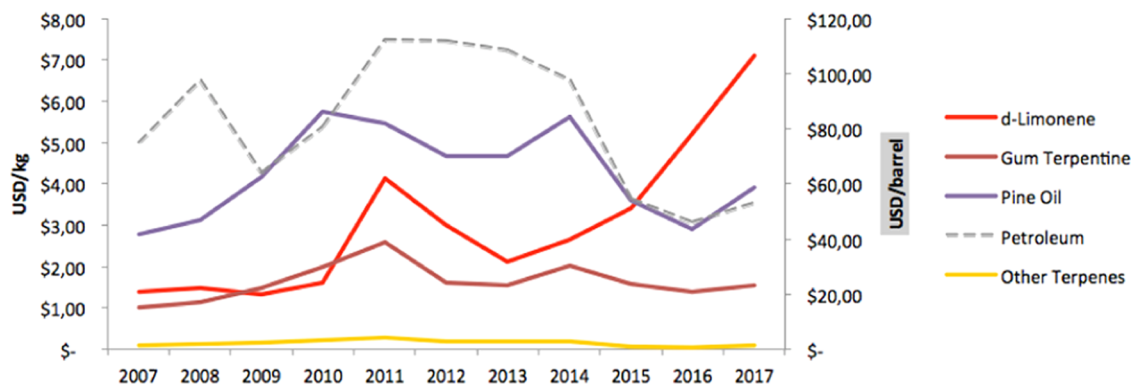


Figure 3. Price of *d*-limonene, gum turpentine, pine oil, and other terpenes in the 2007–2017 decade. For comparison, also the price of petroleum is displayed. (Image courtesy of Fabio Thomazelli, Citrosuco, 2018).

properties for different PLC-derived polymers obtained by thiol-ene chemistry derivatization of the double bond of the limonene moiety.¹¹

Pointing to emerging industrial interest, the use of PLC cross-linked by thiol-ene reaction with trimethylolpropane tris(3-mercaptopropionate) affording promising solvent-resistant and scratch-resistant coatings²⁰ has seen the involvement of a large coatings company (DSM).

Asked to comment on the forthcoming possible introduction of PLC and PLDC in industrial products, Professor Kleij responded: “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”.⁴¹

6. OUTLOOK AND PERSPECTIVE

Whether obtained from citrus peel, as it happens today, or from sugar fermentation as it will shortly happen, *d*-limonene is an eminent bioproduct deriving from plants, whose existence ultimately relies on photosynthesis. Hence, limonene polycarbonates obtained from polymerization of *d*-limonene oxide(s) and CO₂ ideally retrieved from the air are an eminent example of polymers of the emerging solar economy, namely, the economy in which both energy and functional materials currently mostly derived from oil will rather be derived from renewable energy sources and renewable feedstock abundant in nature. In this epochal shift, which is eventually taking place, the role of chemistry and chemical innovation, such as that briefly summarized in this account, will be of paramount importance.⁴²

From the manufacturing viewpoint, the 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/CO₂ copolymerization relying on abundant and low-cost Zn and Al metals and easily synthesized ligands, namely, β -diiminate zinc and aminotriphenolate aluminum/PPNCl complexes.

The relatively low CO₂ 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 insensitive to water and catalyzes the polymerization of the cis isomer.

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,²⁹ 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

The second need, lately emphasized by Li and Koning, calls for “a one-pot, two-step reaction”,⁴³ 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.⁴⁴

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

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Notes

The authors declare no competing financial interest.

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DEDICATION

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

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