Across the Board: Arjan Kleij

Arjan W. Kleij*[a][b]

In this series of articles, the board members of *ChemSusChem* discuss recent research articles that they consider of exceptional quality and importance for sustainability. This entry features Prof. Arjan W. Kleij, who discusses the use of terpenes as raw materials for the synthesis of biobased polyesters and polycarbonates, and the opportunities and challenges that lie ahead for these renewable polymers in the area of material science trying to meet the requirements of a circular economy.

Terpenes: turning Waste into Value

One of the biggest problems that society faces today is to find a solution for the notorious "plastic soup" we have created over the years by uncontrolled disposal of plastic waste in our environment.[1] More sustainable solutions are therefore warranted to reduce the negative environmental footprint associated with the production, use and disposal of wide-ranging consumer products that are (partially) based on plastics. The requisite polymers to produce these plastics are typically derived from fossil fuels with low biodegradability potential, but recently there has been an upsurge of new polymers assembled from biobased monomers, including those derived from carbohydrates, (unsaturated) fatty acids and terpene scaffolds.[2] It is important to emphasize that for most of these biobased polymer alternatives the potential biodegradable character remains to be validated.

Terpene monomers (Figure 1) represent a category of renewable and structurally diverse scaffolds with built-in olefinic bonds useful for the creation of functional monomers for various polymerization processes, and more specifically have been the subject of intense studies in the context of ring-opening copolymerization (ROCOP)[3] towards the formation of two important classes of polymers, *viz*. polycarbonates[4] and polyesters.[5] These polymers find application in many consumer products ranging from (functional) coatings to plastic bottles and textile products. Therefore, contemporary research has been focusing on the use of alternative, bioderived monomers to prepare polymers that can provide similar and/or improved properties compared with conventionally prepared poly-carbonates and –esters. In this perspective, new legislation that restricts the use of certain monomers such as bis-phenol A (a monomer that is commercially applied to prepare polycarbonate with attractive mechanical and thermal features) has also provided new incentives to use more sustainable biomonomers. The opportunities and limitations of the use of terpene scaffolds for polymer applications are discussed below together with a valorisation of the current potential and requirements for a successful implementation on an industrial level. A critical assessment of the state of the art in catalyst technology is presented, helping to define the gap that exists between the current academic achievements and future industrial needs.

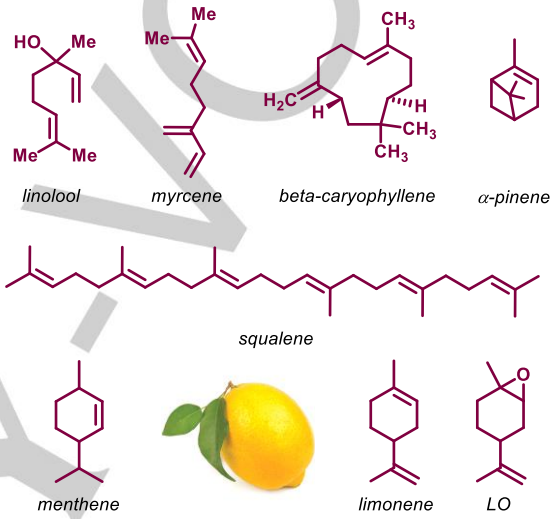

Figure 1. Molecular diversity within a selected family of terpene (oxide) monomers.

Polycarbonates based on Limonene

The first report on the use of limonene (as its mono-epoxide LO, see Figure 1) in polycarbonate synthesis unveiled a Zn-diiminate (Zn-BDI) complex as an active catalyst for the ROCOP of LO with carbon dioxide to provide poly(limonene-*alt*-carbonate), PLC (Scheme 1, path (a)).[6a] More recently, several research groups have further advanced this class of Zn-BDI catalyst for PLC synthesis, providing processes that can address important features including scalability (producing PLC with an M_n > 100 kDa, T_g = 130 ºC),[6b] versatility,[6c] using PLC as a platform molecule towards functional diversity,[6d-f] and markedly improved thermal resistance with T_g´s reaching a record-high 180 ºC.[6f] The BDI based catalysts typically convert only the *trans* isomer of commercial LO (which comes as a mixture of *cis* and *trans* isomers), but leave the *cis* isomer unreacted. In terms of process cost and optimization of raw material usage, catalysts that can convert both diastereoisomers could offer additional potential.

Catalysts showing activity towards the ROCOP of LO and CO_2 are scarce, and apart from the Zn-BDI complexes developed/used by Coates, Greiner, Rieger and Koning/Sablong,[6a-e] the only other known catalyst effective for the copolymerization of LO and CO_2 is based on an Al(III) aminotriphenolate complex.[7] This Al(III) complex is capable of converting both diastereoisomers of commercial LO, but shows inferior activity and produces much lower molecular weight (up to 16 kDa) compared against the BDI systems mentioned above. From a practical point of view, however, the Al(III)

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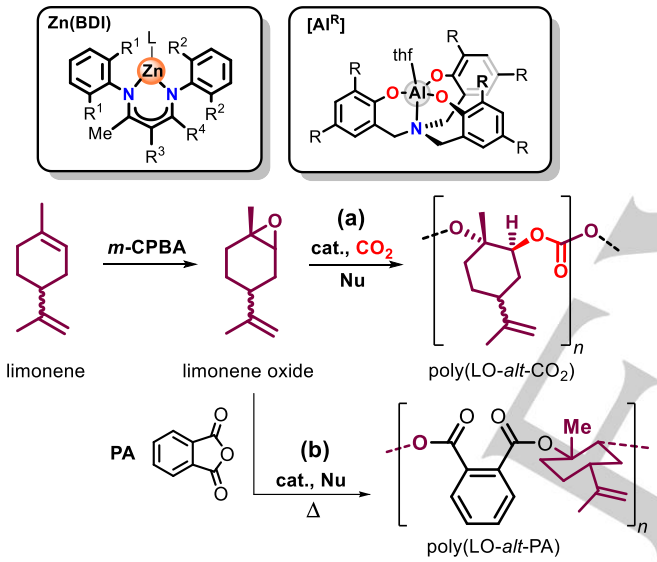
aminotriphenolates are more stable and can handle low amounts of moisture and can be handled in air, which may be useful for the large-scale production of oligomers serving as macro-initiators that can be chain-extended to produce di-, tri- and multi-block copolymers.[8]

Key to future success of terpene-based, and more specifically limonene-based polycarbonates, will be a large-scale availability of these monomers. Limonene, extracted from the peel of citrus fruits, is currently obtained in amounts close to 57 kton/year,[9] but its price has been fluctuating and above 10 USD/kg. In addition, new applications of limonene-based polymers would have to compete with already existing limonene uses such as in cleaning and personal care products. It seems, therefore, that terpenes as building blocks for consumer plastics for the time being will only create sufficient economic value as co-monomers for existing polycarbonates, thereby expanding their mechanical/thermal properties or being used as components of specialty polymers.



Scheme 1. A polycarbonate and polyester based on limonene. Also shown are the general Zn(BDI) and Al aminotriphenolate catalyst components.

Arjan W. Kleij is ICREA professor and Group Leader at the Institute of Chemical Research of Catalonia (ICIQ) in Tarragona (Spain). He received his MSc and PhD (*cum laude*) from the University of Utrecht working on organometallic chemistry and dendrimer-enlarged catalysts. He was a postdoc at the Autonomous University of Madrid and the University of Amsterdam, and spent three years in industry at Avantium and Hexion focusing on industrially related catalysis topics. At ICIQ, he currently develops sustainable catalysis processes using waste materials such as carbon dioxide and terpenes, and their valorization into fine chemicals and biobased polymers. Apart from other editorial appointments, for *ChemPubSoc Europe* he is a board member of the journal *ChemSusChem.*

Polyesters derived from Terpenes

In addition to polycarbonates, (functional) polyesters derived from terpenes (for an example see Scheme 1, path (b)) have recently materialised as potentially interesting alternatives to conventional polyesters. The use of terpenes may offer access to more functional polyesters (*cf.*, poly(lactide)s), whose properties can be tuned by variation of the terpene and/or co-monomer (typically a cyclic anhydride) structure and post-synthetic curing protocols. Recent work from the Coates group demonstrated that tricyclic anhydrides (partially) based on terpene precursors offer a way to expand on the thermal resistance of aliphatic polyesters, and relatively high glass transitions of up to 109 ºC were reported.[10a] Not much later, a wider series of aliphatic polyesters was prepared under Al(III) or Fe(III) catalysis giving access to polyesters of high molecular weight, and importantly, glass transition temperatures of up to 184 ºC were attained.[10b] By combining terpene oxides and aromatic monomers such as phthalic anhydride, semi-aromatic polyesters with T_g´s beyond 200 ºC have also been prepared.[11]

Despite this notable progress, there is still a need for suitable catalysts that show tolerance to a wide(r) family of sterically demanding terpene oxide monomers while producing high(er) molecular weight polyesters. As for polycarbonates, polyesters based on biomonomers such as terpene oxides would be useful alternatives but important issues remain to be examined, including their biodegradation potential, an assessment of their mechanical properties under industrial conditions and scaling up of their synthesis while meeting economic requisites. This also raises the question how to produce large amounts of terpene precursors, and biocatalysis could offer the necessary technology to advance the development of sustainable platform molecules for the polymer industry.[9a] The typical functional character of the terpene-based poly-carbonates and -esters allows for the creation of new and improved properties through cross-linking, chemical derivatization or blending. The future era of bioplastics will hopefully unleash the full potential of these new polymer formulations exploiting the modular and functional character of renewable terpene scaffolds.

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Keywords: material science • polycarbonates • polyesters • renewables • terpenes

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Entry for the Table of Contents:

VIEWPOINTS

What´s in a waste: Our board member Prof. Arjan W. Kleij highlights the recent use of terpene monomers in the preparation of partially and fully biobased polycarbonates and –esters as alternatives for fossil fuel based congeners. The current potential is assessed together with the future needs in these subareas of biobased polymer space, with a crucial importance for specific features related to scalability and biodegradation potential.

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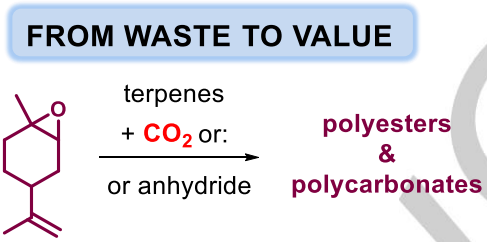

Page No. – Page No.

Across the Board: Arjan Kleij