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From terpenes to sustainable and functional polymers

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Our dependence on fossil-fuel based raw materials and alarming plastics accumulation in the environment has inspired many scientists to design and implement more sustainable approaches for polymer synthesis. The identification and assessment of new and renewable biobased monomers has become a major topic of interest *en route* to a circular economy. In this respect, terpenes and terpenoid scaffolds have attracted much attention due to their ubiquitous nature and high functionality. This minireview uncovers recent advancements in the synthesis of terpene-based polymers, and specifically discusses the formation of terpene-derived polycarbonates, polyesters, polyurethanes and polyamides. The potential of these polymers in post-synthetic curing and modifications is also highlighted to illustrate the opportunities that exist to develop new polymer formulations beyond bench scale.

1. Introduction

Modern society is facing severe environmental problems due to uncontrolled disposal of large quantities of single-use plastic waste.[1,2] A clear testament of the global nature of this issue is and continues to be plastic accumulation in the oceans also referred to as "*plastic soup*".[3] This consequently impacts marine life negatively,[4–7] while potentially causing health hazards due to the formation of micro-plastic particles. Nowadays the production of polymeric materials is still largely based on oil-dependent chemistry. In our era, with climate change gaining importance on the political and social agendas of many countries, there is a growing awareness that we should lower the dependence of both our energy consumption and chemical production on natural fossil resources.[7–9] Hence, it is clear that a transition toward the use of renewable

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Dr Francesco Della Monica obtained his Master degree in Chemistry (2013) and PhD in Chemistry (2018) at the University of Salerno (Italy) in the group of Prof. Carmine Capacchione. His work was mainly devoted to the development of new iron-based catalysts for the reaction of carbon dioxide with epoxides. He spent one year as postdoctoral researcher at the same institute, working on the green, catalytic production of value-added products from renewable resources. In July 2019, he joined the research group of Prof. Arjan W. Kleij as a MSCA-IF fellow to develop new terpenoid monomers for the synthesis of sustainable polymers.

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resources may help to meet the growing environmental concerns, and several regulations and restrictions with respect to the use of certain chemicals and polymeric materials have already been adopted.[10–12]

Since natural polymers such as cellulose,[13] and poly(hydroxyalkanoates)[14–20] are well-known and have been extensively used,[21] nature may further serve as a source of inspiration for the identification of other types of bio-based raw materials for the production of sustainable polymers.[22–26] Various research communities have directed their attention to the production and utilisation of new types of starting materials derived from renewable feedstock.[27–29] An illustrative example is presented by the production of L-lactide from starch, and its use in the industrial production of poly(lactic acid), **PLA**.[30] This role model example has spurred numerous studies focussing on the creation of renewable monomers starting from starch,[31] sugar,[32] vegetable oils,[33] cellulose[34] and lignin.[35] In parallel, extensive efforts have been made in the valorisation of other molecules (often considered as waste) such as carbon dioxide in sustainable polymer development.[36–38]

Within this framework, bio-derived terpene-based monomers are attracting growing attention.[39–44] Polyisoprene (a major constituent of natural rubber) has been known for more than a century,[45–47] and other terpenes (such as pinene,[48–50] limonene,[51–54] pirocarvone,[55] myrcene,[56–64] alloocimene,[65] ocimene[66,67] and farnesene[68,69]) have also been used in the preparation of polyolefins (for an example see Fig. 1, top).

Additional advances in the synthesis of different terpene-based polymers have been achieved in relatively recent times. Their structural diversity (*i.e.*, being linear, cyclic or polycyclic) and the presence of double bonds with different reactivity render terpenes as highly versatile and easy to functionalize building blocks.[70–72]

Limonene, a commercial monoterpene that can be isolated from citrus fruits (Fig. 1),[73] represents a terpene structure that comprises of two distinct double bonds that can be easily modified, for instance by epoxidation or thiol-ene click reactions. These features, together with the availability of this terpene feedstock, has allowed forging structurally diverse polymeric materials thus showcasing limonene as a potential platform molecule (Fig. 1).

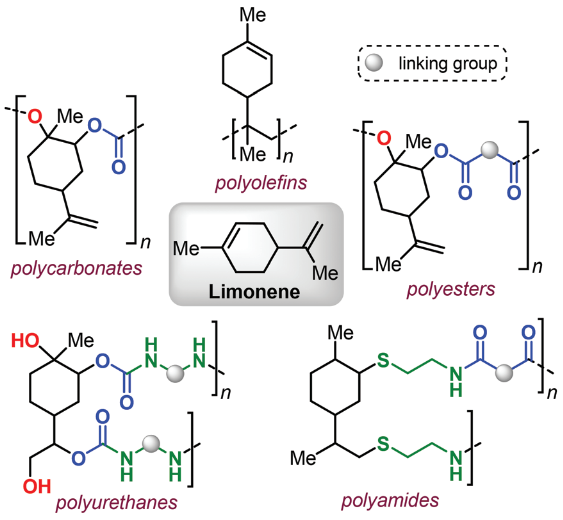

Fig. 1 Polymer diversity created from limonene.

In this minireview, we describe recent developments in the use of terpene-based monomers in the construction of more sustainable and functional polymers. Specifically, the most important types of polymers that have been targeted are addressed and their prospective post-modification is also highlighted to demonstrate the opportunities that exist to design polymer properties that can be advantageous in the realisation of future materials.

2. Polycarbonates

Polycarbonates (PCs) can be divided into aromatic and aliphatic PCs on the bases of the chemical structure of their repeating units. Commercial PC is based on bis-phenol-A (BPA), and displays high-performance optical, thermal and above all mechanical properties.[74] BPA-based PCs find application as engineering plastics in construction, in the automotive industry and in electronics. The preparation and use of BPA derived PCs has two significant problems: (1) the industrial production involves the use of highly toxic phosgene;[75] and (2) polymer hydrolysis/degradation may release BPA metabolites accumulating in the environment, with some of these metabolites believed to act as endocrine disruptors.[76,77] On the contrary, *aliphatic* PCs are generally bio-compatible and -degradable, and they have emerged as possible substitutes of BPA-based PC.[78,79]

Unfortunately, applications of aliphatic PCs, such as poly(propylene carbonate) (**PPC**) are currently limited as they display a narrow window of mechanical and thermal properties,[80] and hence are mainly employed as oligomeric polyols (*cf.*, chain extension) in polyurethane production.[81,82] Thus, the identification of new, structurally rigid monomers derived from renewable and non-toxic resources can help to increase the application potential of aliphatic PCs by expanding their properties as to find suitable alternatives for commercial PC.

In this context, preparation of PCs by ring-opening copolymerization (ROCOP) reaction of CO_2 with epoxides has demonstrated high versatility in the last decades.[83–87] Typically, cyclic epoxides such as cyclohexene oxide (**CHO**) are more prone to produce PCs by reaction with CO_2.[88] Due to their structural resemblance with **CHO**, α-pinene oxide (**APO**) and limonene oxide (**LO**) are attractive, sustainable alternatives to **CHO** when focusing on new types of aliphatic PCs (Fig. 2). In fact, pinenes are monoterpene bicyclic compounds present in turpentine oil, with the main being α-pinene (45–97%), followed by β-pinene (0.5–28%) and traces of other terpenes such as camphene, Δ3-carene and limonene.[89,90]

Turpentine is the volatile fraction of oleoresin obtained from conifers and, depending on the production method, can

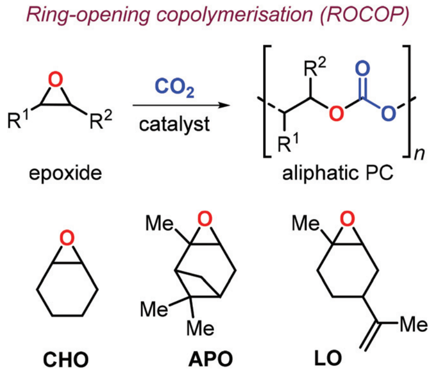

Fig. 2 Ring-opening copolymerisation of epoxides and CO_2 toward aliphatic polycarbonates, and structures of cyclohexene oxide (**CHO**), α-pinene oxide (**APO**) and limonene oxide (**LO**).

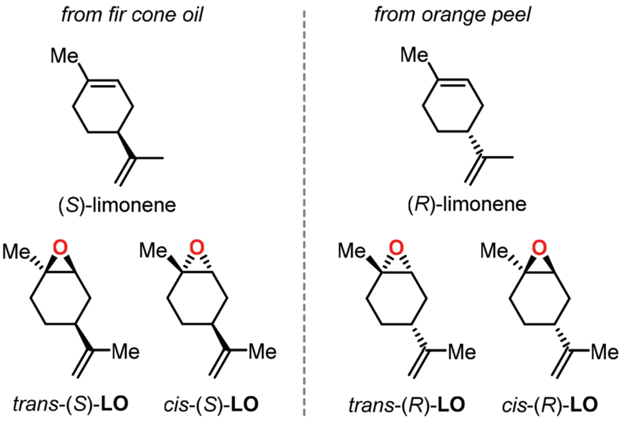

Fig. 4 Structure of limonene enantiomers and limonene oxide stereoisomers.

be divided into sulfate turpentine, gum turpentine, and wood turpentine.[91] Turpentine global production is estimated to be 330 kton per year mainly obtained (70%) as by-product in the pulp industry during the Kraft process.[92,93] The main uses of turpentine oil are in the production of pine oil, flavours, fragrances and resins,[94] and is also attracting interest in the production of biofuels.[95]

Epoxidation of α-pinene, leads to the formation of **APO** (Fig. 3). To date, the only example of a synthesis of poly(α-pinene carbonate) is based on the ROCOP of **APO** and CO_2 promoted by the binary catalyst Cr^{III}(salen) complex **1**/bis-(triphenylphosphine)iminium chloride ([PPN]Cl).[96] In the last few years, much more efforts have been dedicated to the use of **LO** (Fig. 2) as a renewable terpene feedstock in polymer synthesis. The two enantiomers of limonene can be isolated from different natural sources.[97] For example, (*S*)-limonene is present in fir cone oil while (*R*)-limonene is a major constituent in orange peel. Epoxidation of either enantiomer gives **LO** as a *cis*/*trans* mixture (Fig. 4). Since (*R*)-limonene extraction is economically more attractive, (*R*)-**LO** is relatively inexpensive having a *cis* : *trans* ratio of around 46 : 54.

Consequently, the major part of recent polymerisation studies are based on the use of (*R*)-**LO** rather than (*S*)-**LO**. To date, only two catalytic systems are known to promote the formation of poly(limonene carbonate), **PLC**, and both exhibit different features. Copolymerisation of **LO** with CO_2 was described for the first time by Coates *et al.* using the β-diiminate zinc complex **2a** (Fig. 5).[98] Starting from (*R*)-**LO**, **2a** produces **PLC** in a stereoselective fashion (with 98.3% *trans*-configured repeat units) under mild conditions (25 °C, 6.9 bar of CO_2). Deviation from these optimised conditions results into lower degrees of stereocontrol and a strong decrease of catalytic activity. Control experiments revealed that copolymerisation of pure *trans*-(*R*)-**LO** proceeds smoothly, while reaction with pure *cis*-(*R*)-**LO** was unsuccessful. The analysis of the depolymerisation products was performed to examine the origin of the stereoselective conversion of *trans*-(*R*)-**LO**. Starting from **PLC** samples with different content of *trans* units, (1*S*,2*S*,4*R*)-1-methyl-4-(1-methylethenyl)-1,2-cyclohexanediol was isolated as the only product after a hydroxide-induced hydro-

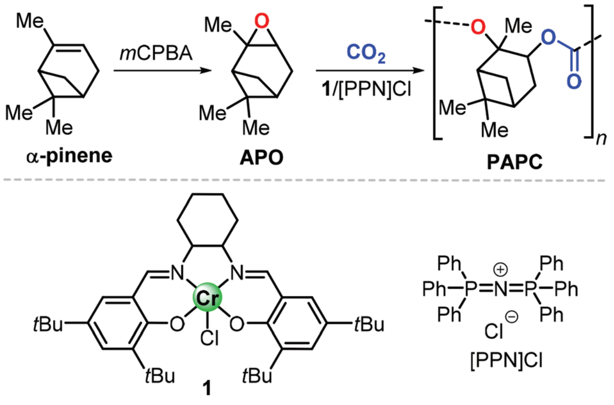

Fig. 3 Synthesis of poly(α-pinene carbonate), **PAPC**, from α-pinene, and structures of Cr^{III}(salen) complex **1** and [PPN]Cl. *m*CPBA stands for *meta*-chloro-perbenzoic acid.

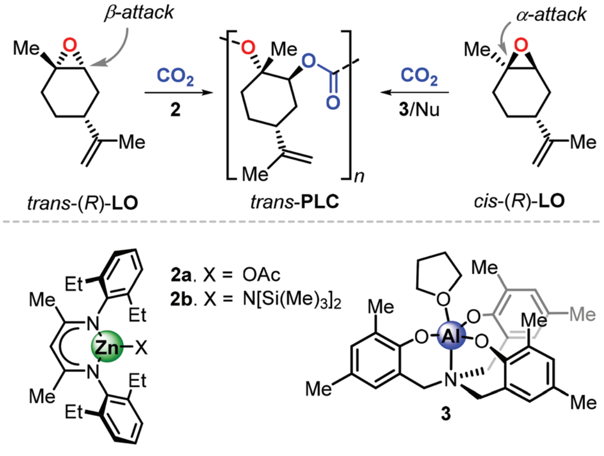

Fig. 5 Preparation of *trans*-**PLC** from *trans*-(*R*)-**LO** and *cis*-(*R*)-**LO** using catalysts **2a–b** or **3**.

lysis. This finding supports the hypothesis that the ring-opening step proceeds by an axial attack which, in the *trans* isomer, occurs on the less hindered β-position (*i.e.*, at a secondary carbon centre), which is kinetically preferred.

More recently, Kleij *et al.* reported on the synthesis of **PLC** promoted by complex **3** in combination with a nucleophilic (Nu) cocatalyst.[99] Copolymerisation of commercial (*R*)-**LO** with CO_2 under relatively mild conditions (42 °C, 5–10 bar of CO_2) resulted in the formation of **PLC** with significant content of *cis*-units (up to 33%), suggesting that the catalyst is able to convert both **LO** stereoisomers. Control experiments revealed that copolymerisation of pure *cis*-(*R*)-**LO** proceeds faster than pure *trans*-(*R*)-**LO**, with a higher degree of stereoselectivity leading to up to 98% *trans* units in the **PLC**. This result, in contrast to the observations done with **2**, was explained by suggesting that the halide-mediated ring-opening of *cis*-**LO** occurs by attack on the more hindered position of the oxirane unit. This hypothesis was supported by detailed computational investigations, which indeed showed that nucleophilic attack on the α-position (at the tertiary carbon centre) is energetically favoured for both **LO** stereoisomers on the basis of an electronic bias.

Complex **3** was later on also used for the preparation of **LO**/**CHO**/CO_2 terpolymers.[100] Depending on the monomer feed composition, gradient terpolymers with an incorporation level of **LO** between 10 and 42% were obtained, and with number average molecular weights (M_n) between 3.6 and 8.2 kDa.

In recent years, several groups studied the material properties of **PLC**. Interestingly, Auriemma, Coates and co-workers described the properties of a **PLC** stereocomplex and reported on its crystal structure.[101,102] Complex **2b** was used to prepare stereoregular poly(*R*-limonene carbonate) and poly(*S*-limonene carbonate) from (*R*)-**LO** and (*S*)-**LO**, respectively. The individual polymer samples were found to be amorphous, but after mixing solutions of the two, a precipitate was observed. The thus formed **PLC** stereocomplex displays the same glass transition temperature (T_g = 120 °C) as the amorphous samples but has a higher decomposition temperature (T_d). A melting transition (typical for semi-crystalline polymers) was not observed probably because the melting temperature (T_m) of the **PLC** stereocomplex is higher than its T_d.

Other types of limonene-containing polycarbonates were reported by Greiner, Schmalz and co-workers. They used a living, sequential ROCOP of **LO** and **CHO** with CO_2 using catalyst **2a** which afforded the diblock copolymers poly(limonene carbonate)-block-poly(cyclohexene carbonate)s abbreviated as (PLC-*b*-PCHC)s.[103] Despite the chemical similarity of the two blocks, transmission electron microscopy (TEM) analyses revealed that these copolymers are able to self-assembly into well-defined cylindrical, lamellar, and hexagonally organised morphologies depending on the composition and molecular weight of the PLC-*b*-PCHC copolymer.

Further to this, Greiner, Rieger and co-workers reported a significant improvement of the preparation of **PLC** providing high molecular weights (M_n > 100 kDa) under excellent chemoselectivity control (*i.e.*, carbonate linkages >99%) using catalyst **2a**.[104] Since this catalyst is known to be unreactive towards the incorporation of *cis*-**LO**, they devised a stereoselective synthesis for *trans*-(*R*)-**LO** (Fig. 6).[105]

Notably, the procedure was scaled up to kilogram quantities while obtaining (*R*)-**LO** containing 85% of *trans* isomer. Since protic impurities are well-known to act as chain-transfer agents in the ROCOP process,[106] thereby lowering the molecular weight of the polymers, the monomer was treated with NaH and MeI prior to the copolymerisation with CO_2 to minimise any free alcohol groups present in the by-products. As a result of this protection procedure, the ROCOP proceeded with excellent control over the molecular weight and by tuning the monomer/catalyst ratio, copolymers with M_n values between 25.4 and 108.6 kDa and low dispersity indices ($Đ$ < 1.2) were obtained. The thermal, mechanical and optical properties of these latter **PLCs** were determined and revealed that this type of amorphous polymer shows higher transparency and pencil hardness than technical BPA based polycarbonate, rendering it thus appealing for coating applications. Later on Abetz, Greiner *et al.* also investigated the gas permeability of **PLC**.[107] Interestingly, **PLC** films have a high permeability to gases (68 and 12 barrer for CO_2 and O_2, respectively), with a high selectivity for CO_2 over N_2, and **PLC** was thus proposed as a good candidate for the production of "breathing glass".

Apart from the attracting properties of pristine **PLC**, the presence of free vinyl groups triggered the investigation of post-modification reactions to expand the number of possible applications. Two conceptual approaches have been adopted for the functionalisation of **PLC** with one based on thiol-ene click chemistry, and the other one based on the introduction of epoxide groups providing ample opportunities for well-developed "epoxy" chemistry (Fig. 7). The thiol-ene approach used by Greiner *et al.* allowed for the preparation of **PLC**-based polymers with a wide range of properties.[108] For instance, the introduction of polar ammonium groups gave access to polymers with antibacterial activity, whereas the introduction of alcohol groups increased the hydrophilicity (*i.e.*, a smaller contact angle to water). The installation of alkyl ester groups onto the **PLC** backbone decreased both the T_g and Young modulus (E), resulting in rubbery behaviour.

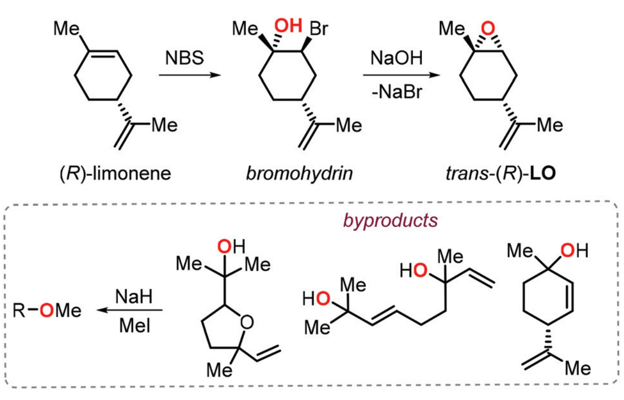

Fig. 6 Stereoselective synthesis of *trans*-(*R*)-**LO** and protection of the alcohol groups in the by-products.

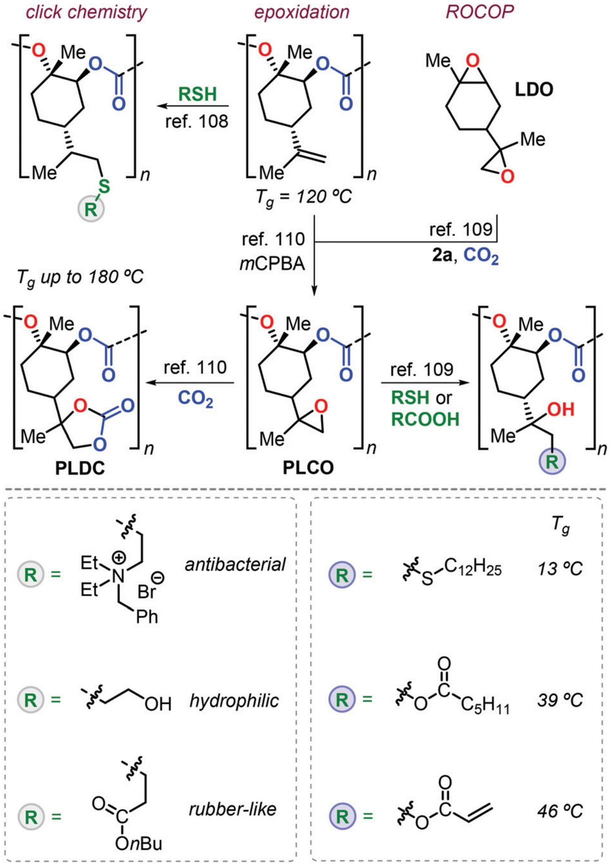

Fig. 7 Functional polymers derived from **PLC** after post-modification using thiol-ene click reactions or epoxy-based chemistry.

The group of Sablong prepared poly(limonene carbonate) oxide, **PLCO**, by regio-selective copolymerisation of limonene dioxide, **LDO**, with CO_2 promoted by **2a**.[109]

Soon after, Kleij *et al.* reported a different synthesis of **PLCO** by simple epoxidation of the double bonds of **PLC** (Fig. 7).[110] Epoxy groups are useful functional groups in ring-opening and cycloaddition reactions giving potential to fine-tune thermal properties. Introduction of long alkyl chains reduces the T_g to 13 °C, while conversion of **PLCO** to poly(limonene dicarbonate), **PLDC**, resulted in record-high T_g values of up to 180 °C.

In the last few years, Sablong, Koning and co-workers investigated the use of low molecular weight **PLC** for coating applications.[111–113] In particular, they reported that **PLC** can be cross-linked through photo-initiated thiol-ene reactions, showing then improved pencil hardness (2*H*) and solvent resistance when compared against non-cross-linked **PLCs.**[114]

End-of-life disposal and polymer reuse are key to sustainable polymer development.[115,116] In this context, **PLC** was proven to be highly stable in a composting environment.[108] While more research is warranted to estimate the potential of **PLC** and its derivatives towards biodegradation, Sablong *et al.* reported that depolymerisation of hydroxyl-terminated **PLC** can be achieved using a relatively simple catalyst (TBD, 1,5,7-triazabicyclo[4.4.0]dec-5-ene) which at elevated temperature allowed the selective re-formation of the initial **LO** monomer (Fig. 8) through a back-biting mechanism.[117] Such controlled depolymerisation can set the basis for efficient recycling of **PLC** and developing sustainable material solutions based on a renewable building block.[118]

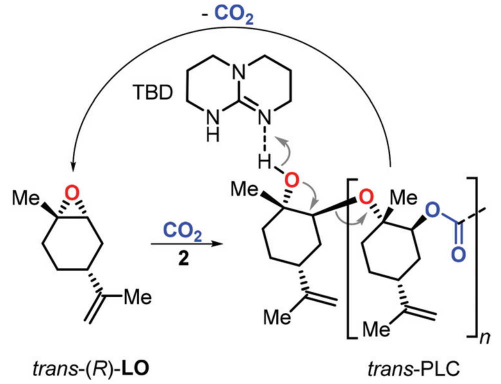

Fig. 8 Depolymerisation mode of **PLC** promoted by TBD.

3. Polyesters

Aliphatic polyesters (APEs) represent one of the most promising classes of sustainable polymers because of their general biocompatibility and facile hydrolytic degradation.[119,120] Synthesis of APEs can be achieved by polycondensation of diols with dicarboxylic acids or esters, ring-opening polymerisation (ROP) of cyclic esters and ring-opening copolymerisation (ROCOP) of epoxides with cyclic anhydrides (Fig. 9).

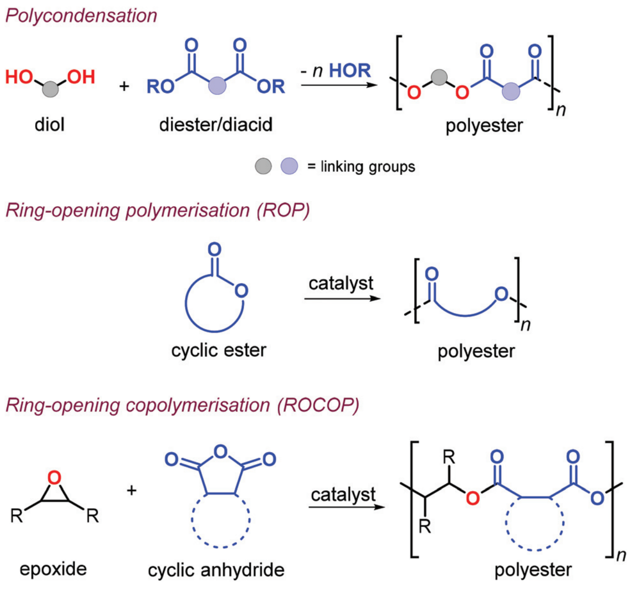

Fig. 9 Aliphatic polyester synthesis by polycondensation and ring-opening (co)polymerisation.

During polycondensation, the by-products (water or alcohol) must be removed and very high conversions are required to obtain high molecular weights usually with $Đ$ values around 2.[121] The ROP of cyclic esters, usually promoted by metal complexes, is one of the most effective ways toward the formation of APEs.[122]

This approach allows for excellent control over the molecular weights and typically with narrow polymer size distributions. Unfortunately, the reaction is often limited to six- and seven-membered cyclic monomers and as such may limit the range of mechanical, thermal and post-synthetic properties.[123] Alternatively, the alternating ROCOP of epoxides and cyclic anhydrides is particularly attractive.[124,125] This method allows for regulating the material properties combining a much larger number of suitable epoxides and anhydride combinations, facilitating thus the incorporation of functional groups useful in post-synthetic modifications.

In 2017, Sieber *et al.* reported the preparation of borneol-based polyesters (Fig. 10).[126] The (−)-borneol, a natural occurring terpenoid, can be prepared from turpentine oil.[127,128] The authors developed a process converting (−)-borneol in 5-*exo*-hydroxyborneol using *Pseudomonas putida KT2440* in a whole-cell biocatalytic approach. The terpene-based diol obtained from this process was successfully copolymerised with succinic acid dimethyl ester obtaining an aliphatic polyester with M_n values in the range 2–4 kDa, and a modest T_g of 70 °C. The use of a Sn-based catalyst was proposed, but its use calls for more sustainable alternatives.

In 2019, Stockman *et al.* reported the synthesis of limonene-based diols and hydroxy-acids (Fig. 11).[129] Limonene was easily converted into diols **a1–2** by a hydroboration-oxidation sequence. Three methods were utilised for the conversion of **a1–2** into hydroxy-acids **b1–2**, and they were classified by a green chemistry metrics evaluation. The most convenient method was the two-step, chemo-selective oxidation of the primary alcohol to carboxylic acid. Diols **a1–2** were subjected to copolymerisation with succinic acid in the presence of various Lewis acidic catalysts to give polymer **d**. Notably, M_n values of up to 30 kDa were obtained using titanium tetra-*n*-butoxide [Ti(O*n*Bu)$_4$], and T_g values between −7 and 23 °C were observed. Depolymerisation of polymer **d** regenerating the initial diols was also demonstrated under basic conditions.

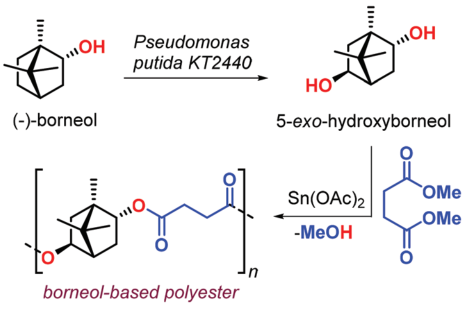

Fig. 10 Biotransformation of (−)-borneol in 5-*exo*-hydroxuborneol and its poly-condensation with succinic acid dimethyl ester.

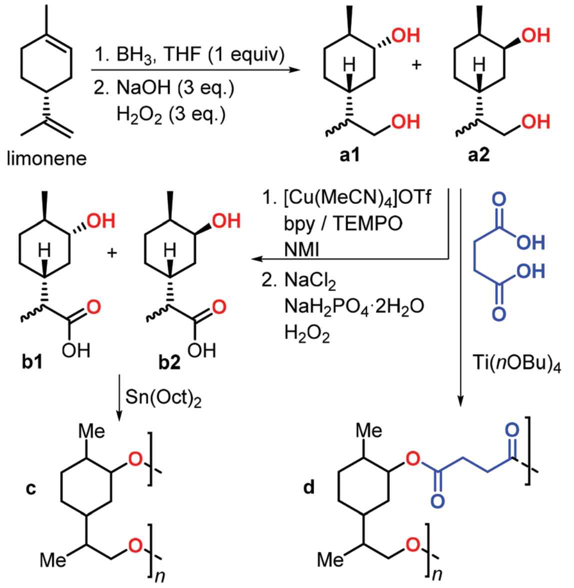

Fig. 11 Synthesis of limonene-based diols **a1–2** and hydroxy-acids **b1–2**, and their polycondensation reactions.

Subsequently, polycondensation reactions involving **b1** and **b2** were investigated. Polymerisation of **b1–2** catalysed by tin-octanoate [Sn(Oct)$_2$] led to the formation of oligomers **c** (M_n < 2.6 kDa) even after very long reaction times (1 month).

In 2019, Nsengiyumva and Miller described the synthesis and thermal behaviour of new camphor-based polyesters (Fig. 12).[130]

Camphor is a bicyclic terpene that can be extracted from the camphor tree[131] or produced in ton-scale from α-pinene,[132] and is used as an aroma in perfumes, as a plasticizer and repellent. Oxidation of camphor produces camphoric acid that has been used as co-monomer in polycondensation reaction with various diols catalysed by *p*-toluenesulfonic acid (*p*-TFA, Fig. 12). High conversions were obtained after 18 h at 180 °C, and M_n values in the range 7–20 kDa were obtained albeit with broad dispersities ($2.7 \leq Đ \leq 6.1$). When using linear α,ω-diols, the resultant T_g value of the polyester depends on the alkyl chain length; these values range from 51 °C when using ethylene glycol down to −16 °C in the case of 1,6-hexane-

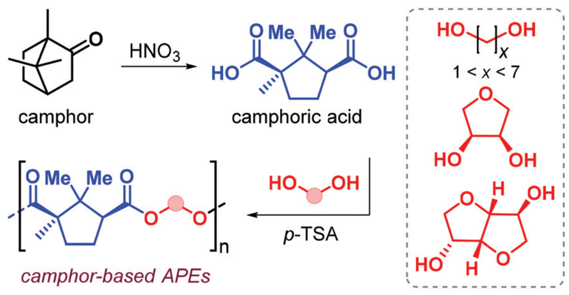

Fig. 12 Camphor oxidation to camphoric acid and its polycondensation with diols.

diol. Upon introduction of conformationally rigid cyclic diols such as erythritol and isosorbide, the T_g values increase to 100 and 125 °C, respectively.

Due to the structural resemblance of poly(ethylene camphorate) (**PEC**) and poly(ethylene terephthalate) (**PET**), copolymerisation of bis(hydroxyethyl) camphorate (**BEHC**) and bis(hydroxyethyl) terephthalate (**BHET**) was studied (Fig. 13). The **PEC-*co*-PET** copolymers were obtained with a wide range of compositions with a **PEC** content from 7.6 to 82.9%.

Interestingly, copolymers with a **PEC** incorporation of up to 20% have T_g's in the range 59–66 °C and T_m values between 180 and 209 °C, which are comparable to those of **PET**. These data clearly emphasize that (partial) exchange of terephthalate for camphorate units does not negative influence the thermal performance parameters.

Some efforts have been devoted to the synthesis of seven-membered lactones from terpenes. Such monomers represent concrete alternatives to petrochemical ε-caprolactone (**CL**). For example, the **PLA** properties can be modulated to some extent by copolymerisation of **LA** with **CL**.[133,134] Biobased lactones are particularly attractive for the synthesis of fully renewable polyesters with improved thermal properties.[135]

In 2005, Hillmyer, Tolman *et al.* described the synthesis of a new polyester by ROP of the lactone (−)-menthide, which was derived from menthol (Fig. 14).[136] Menthol is a cyclic terpene largely used in the fragrance and flavour industry with several thousands of tons produced every year.[137] Baeyer–Villiger oxidation of (−)-menthone, derived from menthol, produces (−)-menthide. The controlled ROP of menthide, promoted by the phenoxy-amine-Zn complex **4** (see Fig. 14), was achieved and poly(menthide)s (**PMs**) with M_n values in the range 3–91 kDa were obtained by simple variation of the monomer-to-**4** ratio. The thermodynamic parameters for this polymerisation process were also determined, and the authors concluded from these studies that the (−)-menthide ring-strain is comparable to that of **CL**.

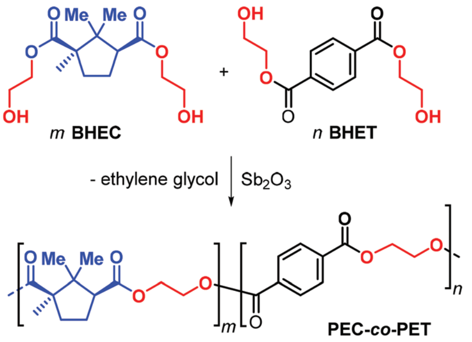

Fig. 13 Copolymerisation of bis(hydroxyethyl) camphorate (**BEHC**) and bis(hydroxyethyl) terephthalate (**BHET**) toward **PEC-*co*-PET**.

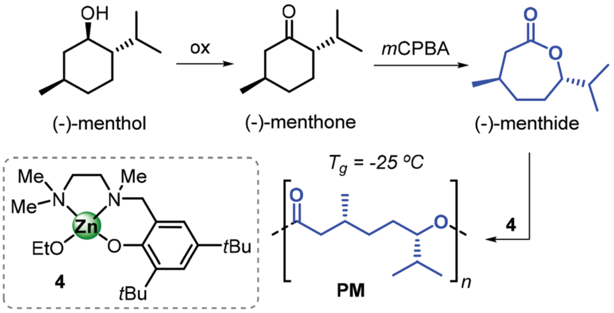

Fig. 14 Synthesis of poly(menthide) from (−)-menthol and structure of the phenoxyamino-Zn complex **4**.

Triblock copolymers (based on **PM**) could also be obtained in combination with other biobased monomers such as lactide and tulipalin A.[138,139] These block copolymers exhibit very good tensile and elastic properties, and consequently are promising candidates for biobased thermoplastic elastomers.

After these initial reports, the same researchers reported on the use of other terpene-based monomers produced from the oxidation of cyclohexanones. Specifically, dihydrocarvide, dihydrocarvide oxide and carvomenthide can be obtained from biosourced carvone, and their ROP promoted by $ZnEt_2$ and benzyl alcohol provides the corresponding polyesters (Fig. 15).[140,141] The presence of functional groups on these monomers has been exploited.[142] For example, reaction of the vinyl groups on poly(dihydrocarvide) (**PD**) with dithiols resulted in the formation of cross-linked gels. Copolymerisation of dihydrocarvide oxide with **CL** yielded cross-linked networks with good shape-memory properties.

More recently, the Jones group reported the synthesis of 4-isopropyl caprolactone from (+)-β-pinene, following a synthetic route similar to that described for carvomenthide (Fig. 16).[143] Ring-opening polymerisation of 4-isopropyl capro-

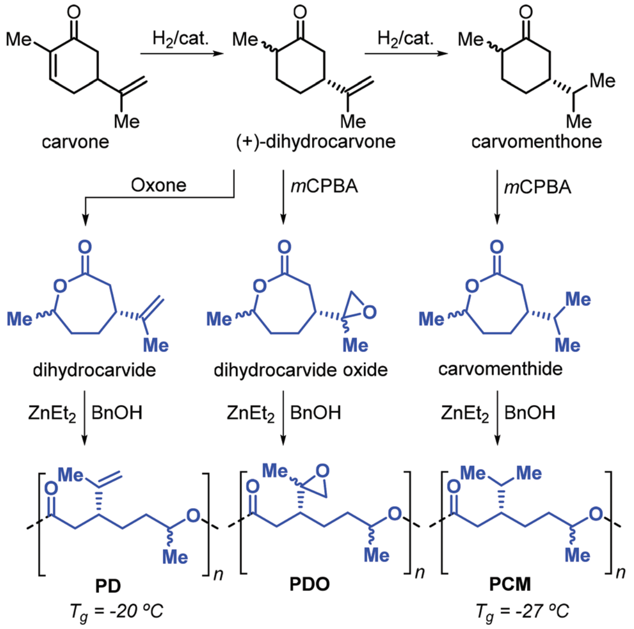

Fig. 15 Synthesis of dihydrocarvide, dihydrocarvide oxide and carvomenthide from carvone, and their ROP toward the corresponding polyesters.

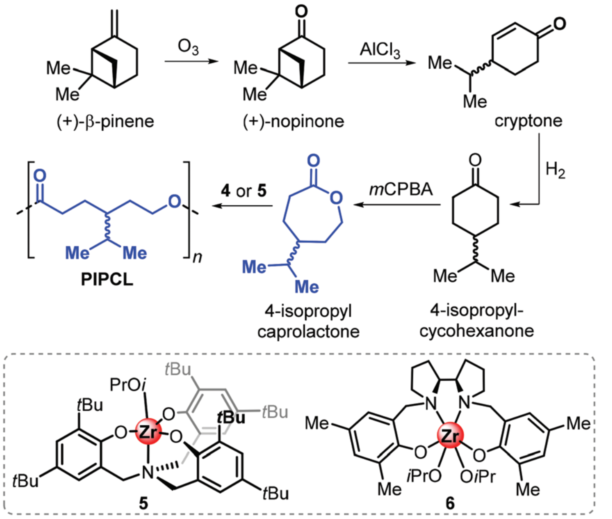

Fig. 16 Synthesis of poly(4-isopropyl-caprolactone) from (+)-β-pinene and structures of ROP catalysts aminophenolate Zr complexes **5** and **6**.

lactone was efficiently conducted in the presence of aminophenolate complexes **5** and **6**.

Importantly, it was found that the conversion of this synthetic, pinene-derived 4-isopropyl caprolactone monomer only produces low molecular weight polymers (M_n up to 4.9 kDa), while the use of the "commercial" 4-isopropyl caprolactone monomer resulted in significantly better polymerisation control allowing to produce polymers with M_n's up to 11.5 kDa. This marked difference was ascribed to the presence of unidentified impurities after the ozonolysis step, which can act as potential chain-transfer agents.

Poly(4-isopropyl caprolactone) (**PIPCL**) has a low T_g of −50 °C, near the value of polycaprolactone (**PCL**). One-pot copolymerisation with **LA** was also feasible and furnished copolymers with a wide range of compositions, but attempts to obtain block-copolymers were unfruitful.

In 2019, Syrén *et al.* disclosed a chemo-enzymatic synthesis of bicyclic (−)-verbanone lactone (Fig. 17).[144] The synthesis starts with the hydrogenation of (−)-verbenone, that can be obtained from (+)-α-pinene through an electrochemical oxidation. Different from the approaches so far described in this section, the traditional Baeyer–Villiger oxidation step was substituted with a biocatalytic oxidation promoted by Baeyer–Villiger monooxygenase (BVMO) and glucose dehydrogenase (GDH). Poly(verbanone lactone) (**PVL**) was obtained by ROP of (−)-verbanone lactone promoted by methane sulfonic acid (MSA) and benzyl alcohol. With this protocol, low molecular weight polymer was obtained (M_n = 3.3 kDa). Unlike other caprolactone-like polyesters, **PVL** showed a relatively high T_g of 26 °C likely being the result of the rigid cyclobutane ring incorporated into the polymer chain.

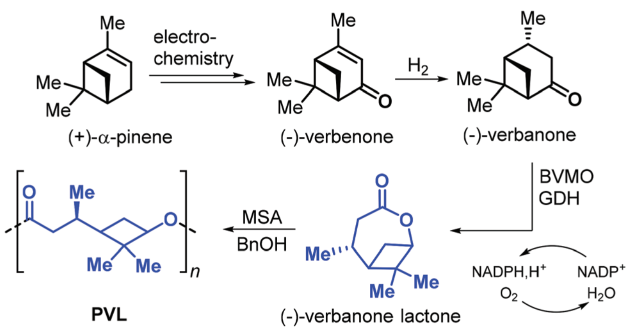

Fig. 17 Chemo-enzymatic synthesis of (−)-verbanone lactone from (+)-α-pinene, and ROP toward poly(verbanone lactone).

Due to the success attained in the preparation of polyesters by ROCOP, in the last years more efforts have been focusing on the identification and use of terpene-based epoxide and cyclic anhydride monomers. Since amorphous aliphatic polyesters generally exhibit moderate T_g values (*e.g.* the T_g of **PLA** is between 50 and 60 °C), they can hardly compete with well-established commodity polymers such as atactic polystyrene (aPS, T_g of around 100 °C). For this reason, most of the recent research in this subdomain of polyester development has put primary attention towards the identification of structurally rigid monomers that, in principle, could give access to polyesters with higher T_g values.[135]

In 2011, Thomas *et al.* described a tandem procedure for the preparation of aliphatic polyesters.[145] This procedure relies on the synthesis of cyclic anhydrides from dicarboxylic acids and dimethyldicarbonate (DMDC) catalysed by a series of salen complexes (**1**, Fig. 3, and **7–9** Fig. 18).

Thus, addition of an epoxide to the *in situ* prepared cyclic anhydrides gave the desired polyesters in a one-pot procedure in which both steps are promoted by the same catalyst. With this method, the authors prepared a number of structurally different polyesters with M_n values in the range 4.3–27 kDa and *Đ* values lower than 1.3. Interestingly, camphoric acid was used for the synthesis of camphoric anhydride (**CA**) and subsequently for the preparation of fully terpene-based polyesters

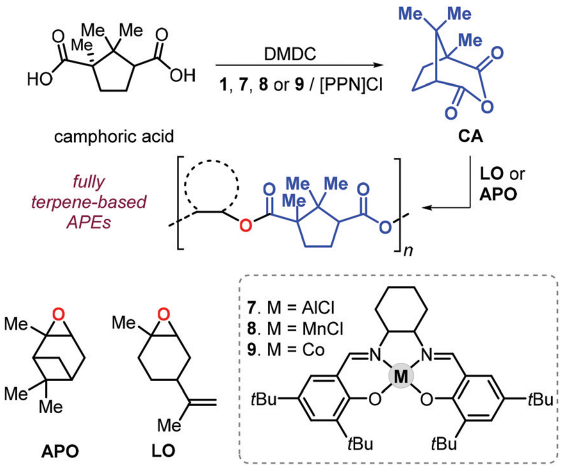

Fig. 18 Sequential, one-pot synthesis of fully terpene-based polyesters based on camphoric anhydride and terpene oxides **LO** or **APO**, and structure of complexes **7–9**.

using **APO** and **LO** (Fig. 18). Later, Thomas, Prunet and co-workers employed this tandem methodology for the preparation of APEs with pendant double bonds by reaction of **CA** and functional epoxides.[146] The post-modification of these APEs by ruthenium-catalysed olefin cross-metathesis was explored. The thermal properties of these allyl glycidyl ether-based polyesters, poly(**AGE**-*alt*-**CA**)s, could be tuned by reaction with various olefins, and the resultant T_g's were in a range from 6 to 96 °C (Fig. 19). Unfortunately, functionalisation of fully terpene-based poly(**LO**-*alt*-**CA**), which exhibit a promising T_g of 112 °C, was not successful probably due to steric hindrance.

The efficient preparation of ABA triblock polyesters from decalactone/cyclohexene oxide/cyclic anhydride monomer mixtures using complex **1** as the catalyst was communicated by Williams and Stößer.[147] In particular, **CA** was used for the preparation of the triblock copolymer poly(decalactone)-*b*-poly(cyclohexene oxide-*alt*-camphoric anhydride)-*b*-poly(decalactone) though, in this case, detailed thermal properties were not described.

In 2015, Coates and van Zee described the copolymerisation of propylene oxide (**PO**) with tricyclic anhydrides **TCA1** and **TCA2** obtained from the Diels–Alder reaction of α-terpinene or α-phellandrene with maleic anhydride in the presence of Cr, Al and Co salphen complexes **10**–**12** (Fig. 20).[148] The resulting polyesters poly(**PO**-*alt*-**TCA1**) and poly(**PO**-*alt*-**TCA2**) exhibit relatively high T_g values of 109 and 86 °C, respectively. This difference in T_g of more than 20 °C indicates that the spatial orientation of substituents has a strong impact. Remarkably, using a hydrogenated version of **TCA1** in the copolymerisation with **PO** produced a polymer with a T_g of 86 °C, supporting the idea that structural rigidity of the repeating unit strongly influences the thermal behaviour of the polymer.

The authors also investigated the effect of the catalyst structure on the polymerisation process. It was established that in the presence complexes **10** and **11**, transesterification and epimerisation reactions occur at high conversions, resulting in broadening of the molecular weights distributions and lower T_g values. The detrimental effect of epimerisation on the T_g was explained by the inversion of *cis*-diester into *trans*-diester units, with the latter believed to be more flexible. On the contrary, the presence of Al-complex **12** led to a well-controlled polymerisation process in which these side-reactions are efficiently suppressed thus maintaining narrow distributions and high T_g values even at high conversions and long reaction time.

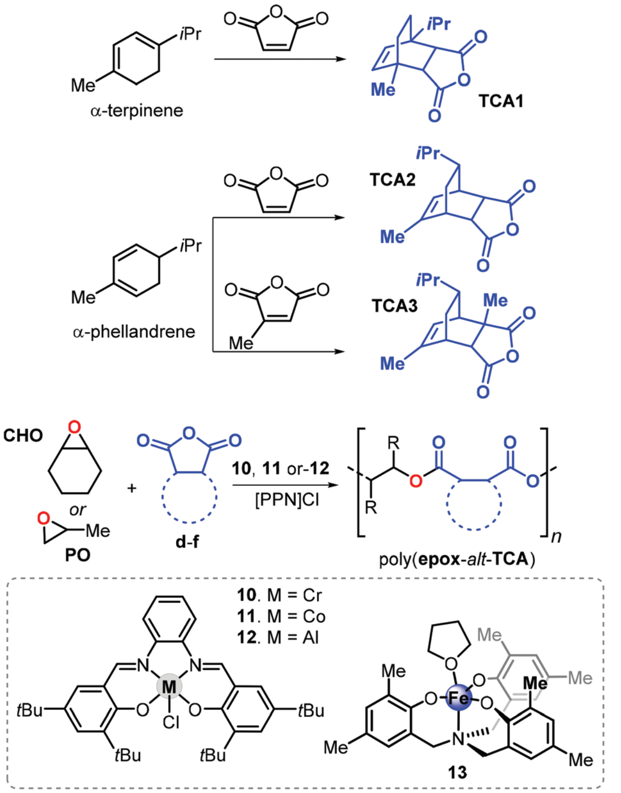

Fig. 20 Synthesis of tricyclic anhydrides **TCA1–3**, their ROCOP affording the corresponding polyesters and structures of complexes **10–13**.

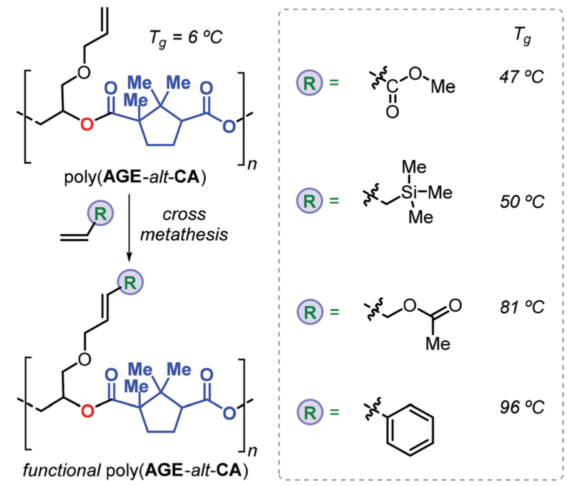

Fig. 19 Functional polymers derived from poly(**AGE**-*alt*-**CA**) after post-modification using cross-metathesis reactions.

A follow-up studies was carried out by Coates and Kleij who envisaged the possibility to obtain polyesters with improved thermal properties by copolymerisation of similar and a wider diversity of biobased tricyclic anhydrides with a more rigid epoxide (**CHO**).[149]

The use of **TCA1**, **TCA2**, and the new terpene cyclic anhydride **TCA3** (Fig. 20), obtained from α-phellandrene and citraconic anhydride, was investigated. Copolymerisation reactions were conducted in the presence of Al-salphen complex **12** and the Fe-aminotriphenolate complex **13**. These new polyesters obtained from **CHO** exhibit higher T_g values when compared with those obtained from **PO**. For example, poly(**CHO**-*alt*-**TCA1**) has a T_g of 184 °C being 75 °C higher than that of poly(**PO**-*alt*-**TCA1**). However, the **CHO**-based polymers had typically lower molecular weights ($4.1 \leq M_n \leq 11.6$ kDa) and relatively broader dispersities ($1.23 \le Đ \le 1.58$), which may be the result of the larger steric demand and lower rate of the insertion of **CHO** into the propagating polymer chain. On the basis of end-group analysis, it was concluded that more extensive chain-transfer phenomena occur when **CHO** was used as epoxide monomer ascribed to the parasitic formation of **CHO**-based alcohols. By choosing the appropriate epoxide/cyclic anhydride monomer ratio, it was possible to tune the T_g such that a wider temperature range of 66 to 184 °C was enabled for these aliphatic polyesters.

Considering terpene-based epoxides such as **APO** and **LO** (Fig. 18) in ROCOP is attractive for the synthesis of renewable polyesters. However, these kinds of monomers are generally sterically congested and therefore relative sluggish to convert, and their application up to now has remained very limited. In 2013, Duchateau *et al.* reported the copolymerisation of **LO** with phthalic anhydride (**PA**) promoted by salphen complex **10**.[150] This polymerisation process required high temperature (130 °C) and neat conditions, yielding poly(**LO**-*alt*-**PA**) with M_n's up to 7.4 kDa, $Đ$ values of around 1.4 and a maximum T_g of 82 °C.

More recently, Kleij *et al.* investigated the synthesis of semi-aromatic polyesters by ROCOP of various terpene-based epoxides with both **PA** and 1,8-naphthalic anhydride (**NA**) with complex **13** as catalyst (Fig. 21).[151] Copolymerisation of **LO** proceeded under mild condition (65 °C) both under neat and solution conditions and the performance of the catalyst **13** may be explained in terms of the higher geometrical flexibility of the aminotriphenolate complex compared to salen metal complexes. The poly(**LO**-*alt*-**PA**) obtained from *cis*/*trans*-**LO** displayed a T_g of 131 °C (M_n = 10.5 kDa), while that obtained from *cis*-**LO** had a higher T_g of 141 °C (M_n = 16.4 kDa). Copolymers obtained from **LDO** are characterised by low glass transition temperatures. It is likely that this copolymerisation process is not well-controlled due to the presence of two "branching" points in the monomer, and thus a higher potential for cross-linking of growing polymer chains. As a result, the copolymer had a broad molecular weight distribution ($Đ \approx 2$) and a relatively low T_g of 59 °C.

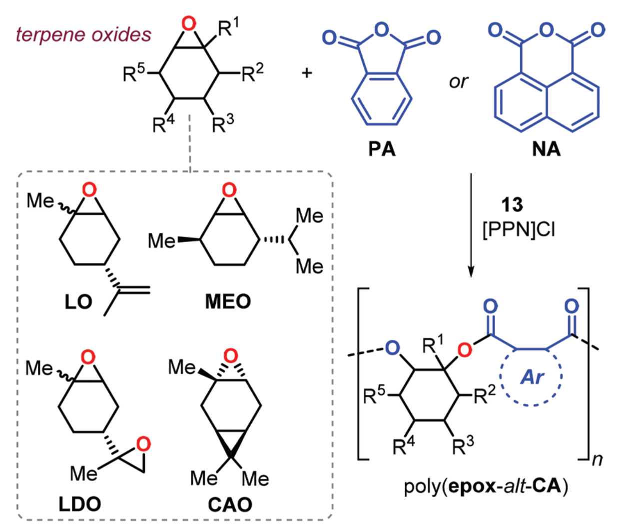

Fig. 21 Synthesis of rigid semi-aromatic polyesters from phthalic anhydride and terpene-based epoxides. For **13** see Fig. 20.

Copolymerisation of **PA** with other structurally different terpene-based epoxides such as menthene oxide (**MEO**) and carene oxide (**CAO**) was also performed (Fig. 21). The reaction rate observed for **CAO** conversion was expectedly lower than noted for **LO** yielding only oligomers (M_n < 3.7 kDa) with a T_g of 130 °C. Interestingly, poly(**MEO**-*alt*-**PA**) was isolated with an appreciable M_n (12.7 kDa) and a T_g of 165 °C. Remarkably, the structurally more rigid poly(**LO**-*alt*-**NA**) copolymer showed a T_g of 243 °C. However, only low molecular weight oligomers were obtained in this case (M_n < 2.2 kDa) with a decomposition temperature T_d^{10} of 268 °C.

4. Polyurethanes

Polyurethanes (PUs) are employed in a wide range of applications such as foams, insulating materials, paints, liquid coatings, sealants, fibres and elastomers, among others.[152] Commercial PU synthesis is based on polyaddition reactions between isocyanates and polyols (Fig. 22a).[153] (Aryl)isocyanates are prepared by reaction of amines with highly toxic and hazardous phosgene in an energy-intensive process. Exposure to isocyanates negatively affects human health and as such rep-

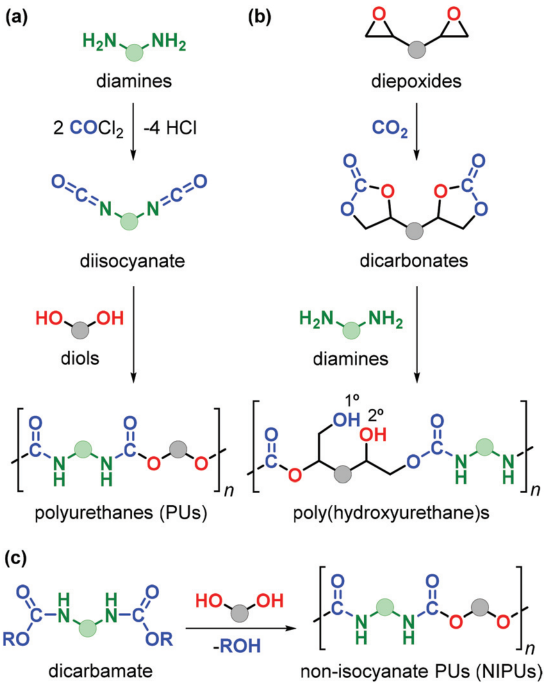

Fig. 22 Synthesis of (a) polyurethanes from diisocyanates and diols, (b) poly-hydroxyurethanes from di(cyclic carbonates) and diamines, and (c) non-isocyanate polyurethanes from dicarbamates and diols. The coloured spheres represent connecting units.

resent an aspect to be improved in PU production.[154] Additionally, the production of commonly employed polyols (such as polyethylene oxide and polypropylene oxide) fully relies on the use of fossil fuels.

The design of non-isocyanate based polyurethanes (NIPUs) has recently emerged as a highly active area in polymer chemistry.[155,156] One effective route to NIPUs is the polyaddition reaction between di(cyclic carbonates) and diamines (Fig. 22b). This alternative process has become more appealing and relevant due to the development of more efficient and sustainable methods for the production of cyclic carbonates from CO_2 and epoxides.[157–161] Furthermore, with many research efforts now being devoted to the production of diamines from renewable sources,[162] new opportunities have become available to sustainabilise PU production. NIPUs obtained through this latter route are sometimes also referred to as poly(hydroxyurethane)s because of the presence of primary (1°) and secondary (2°) alcohol groups within the polymer chain with the latter typically prevailing.

The presence of –OH groups results into an additional hydrogen-bonding network increasing the polarity, thermal stability, adhesion properties and water uptake thereby advancing the discovery and development of new materials.[153] The synthesis of NIPUs can be achieved by polycondensation reaction of diols with other functional monomers such as dicarbamates (Fig. 22c), however this approach is hampered by the use of phosgene for the production of such monomers.[163] In spite of the high attractiveness of this new route towards NIPUs, the number of renewable biosourced terpene-based monomers for NIPU production remains so far highly limited.[164]

The research group of Mülhaupt investigated the use of limonene dicarbonate (**LDC**) for the preparation of poly-hydroxyurethanes.[165] The **LDC** was prepared by reaction of **LDO** with carbon dioxide catalysed by tetrabutyl ammonium chloride (TBAC, Fig. 23). Notably, the reaction was conducted on a kilogram scale, and high temperature and pressure (*i.e.*, 140 °C and 30 bar) were necessary to reach full conversion.

Linear polyurethanes were afterwards obtained by reaction of **LDC** with alkyl primary diamine (**DA**) under neat conditions, with the product features depending on the **LDC**/**DA** ratio (Fig. 23). When an equimolar mixture of **LDC** and **DA** was used, small oligomers with M_n values in the range 960–1840 Da were obtained. These oligomers exhibit T_g's and T_m's in the range of 33–62 and 80–100 °C, respectively, depending on the nature of the diamine reagent. When **DA** or **LDC** was present in excess during the stepwise polyaddition polymerisation, amine- or carbonate-terminated oligomers were formed.

The authors prepared a number of NIPU thermosets by curing **LDC** with polyfunctional amines including commercial hyperbranched polyethyleneimines (*i.e.*, Lupasol®) with variable content of primary amine groups. Brittle NIPUs were obtained, with high E moduli ($2400 \leq E \leq 4100$ MPa), and low elongation at break ($\varepsilon_{break} \leq 2\%$). This behaviour was ascribed to the rather rigid nature of the limonene units in these polymer structures.

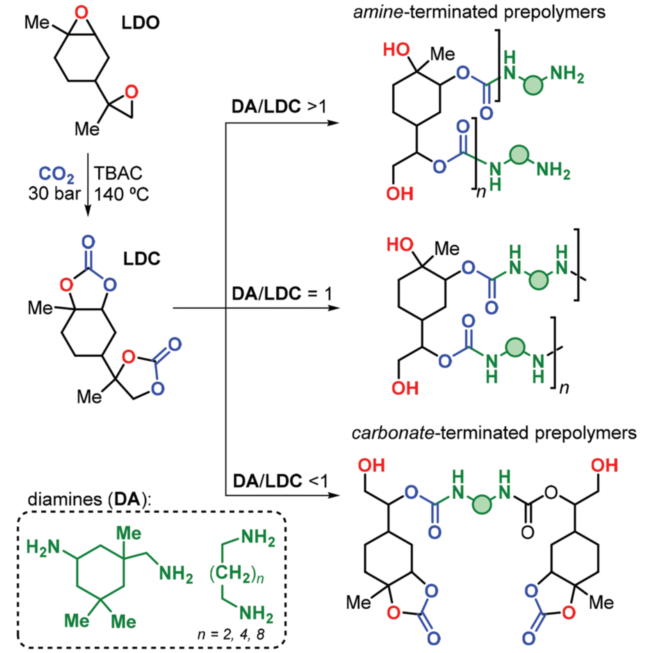

Fig. 23 Preparation of limonene dicarbonate (**LDC**) and its polyaddition reaction with diamines (**DA**) towards limonene-based NIPU prepolymers.

More recently, the same research group described an improved procedure for the preparation of *trans*-**LDC** using consecutive crystallisations,[166] and the stereochemical assignment was corroborated by X-ray crystallography. Linear NIPUs were obtained by reaction of **LDC**-based oligomers (obtained in the presence of excess of diamine, Fig. 23) with carbonated 1,4-diglycidyl ether. Notably, the authors demonstrated the positive impact of the monomer purity on the final properties of the NIPU thermosets prepared from **LDC** and Lupasol®. Extensively purified **LDC** led to the formation of colourless and transparent materials, in contrast to the dark samples obtained with crude **LDC**. Moreover, higher T_g (94 *vs.* 50 °C), E modulus (4370 *vs.* 2400 MPa) and tensile strength at break (σ_B, 53 *vs.* 7 MPa) were achieved thus pointing at the importance of the impurity profile on the final NIPU performance.

Apart from the application of cyclic carbonate reagents, in 2013 Firdaus and Meier reported the synthesis of limonene-based dicarbamate monomers, and their use in the synthesis of NIPUs by a polycondensation reaction with diols.[167] The synthesis starts with a thiol-ene click addition of cysteamine hydrochloride to (*R*)- and (*S*)-limonene yielding diamines **d1–2** (Fig. 24). Subsequently, carbamate groups were introduced by reaction with dimethyl carbonate (DMC) catalysed by TBD (Fig. 24).

Polyurethanes of type poly(**f**-*alt*-**g**) were prepared by TDB-catalysed polycondensation reaction of **f1–2** with biobased diols **g1–3** previously described by the same group.[168] Molecular weights as high as 12.6 kDa were obtained with *Đ* values between 1.8 and 2.2. Interestingly, copolymerisation with **g2** (containing flexible alkyl chains) led to semi-crystalline samples with T_m up to 69 °C. On the contrary, NIPUs that are

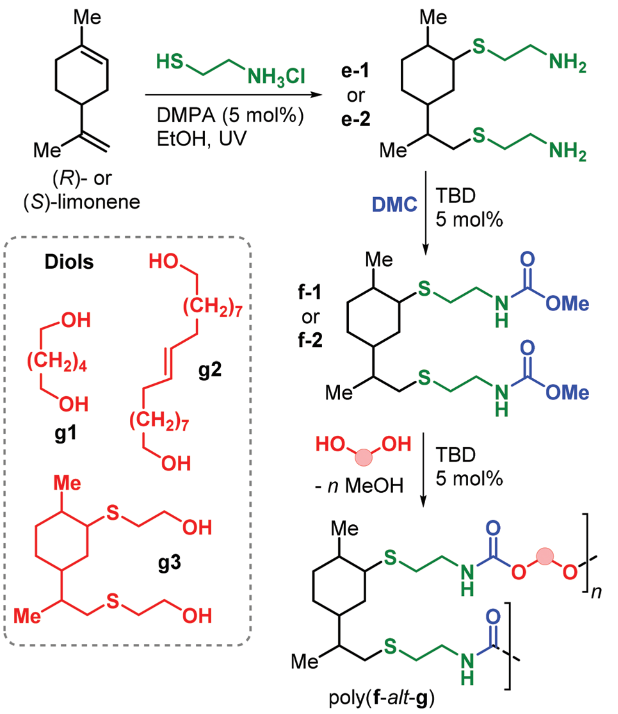

Fig. 24 Synthesis of diamine and dicarbamate monomers **e1–2** and **f1–2**, and limonene-based NIPUs poly(**f**-*alt*-**g**).

more rigid (obtained from **g1** and **g2**) are amorphous with T_g values in the range 14.6–18.5 °C.

5. Polyamides

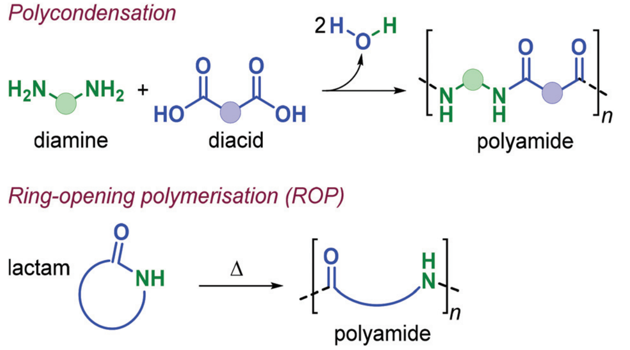

Fig. 25 Polyamide (PA) synthesis by polycondensation and ring-opening polymerisation.

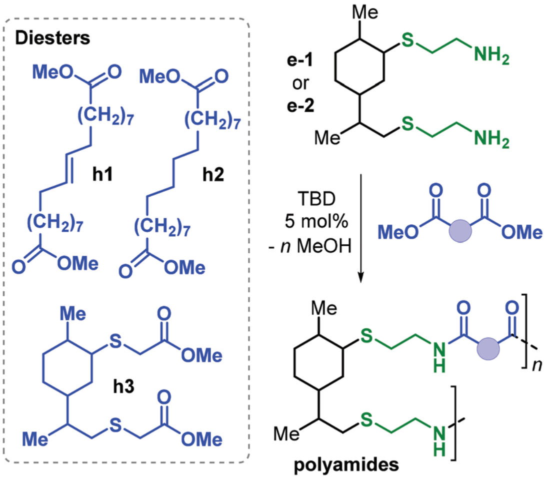

Fig. 26 Synthesis of limonene-based polyamides poly(**e**-*alt*-**h**).

Polyamides (PAs) represent a commercially relevant class of polymers. Thanks to excellent mechanical and thermal properties, PAs are mainly used for the production of fibres and engineering plastics employed in transportation, electronics, packaging and customer products.[121] Polyamides are generally prepared by polycondensation of diamines with dicarboxylic acids, or by ROP of lactams such as in the production of Nylon-6,6™ and Nylon-6™, respectively (Fig. 25). As for the other polymer types discussed in this review, commercial PA production is currently based on non-renewable raw materials, and efforts are ongoing towards the identification of renewable monomers, especially focusing on novel diamine and diacid reagents.[27,162,169] The use of terpene-based monomers in PA polymer formation, however, remains underexplored.

Together with renewable PUs, Firdaus and Meier also reported the synthesis of limonene-based PAs using limonene-based diamine monomers **e1–2** described in Fig. 24. Specifically, polyamides of type poly(**e**-*alt*-**h**) were prepared by TBD-catalysed polycondensation reaction of **e1–2** with bio-based diesters such as castor-oil and limonene-derived diesters **h1–3** that were previously described by the same group (see Fig. 24).[168] In the case of flexible diester **h1** (Fig. 26), the resultant PAs had M_n's of up to 10.6 kDa. Copolymerisation of **e1–2** with **h2** and **h3**, however, led to significantly lower molecular weights in the range 5.5–7.8 kDa. This difference was ascribed to the formation of crystalline domains when **h2** was used as diester as it contains a long saturated alkyl chain, and in the case of **h3** it was proposed that the bulkiness of the diester affected propagation.

Interestingly, the more rigid PA obtained from **h3** is amorphous with a T_g of 41.5 °C. Contrary, PAs based on flexible diesters **h1** and **h2** are semi-crystalline having a T_m as high as 102 °C.

The same authors also explored the effect of limonene-based monomer incorporation in Nylon-6,6™ by copolymerisation of diamines **e1–2**, adipic acid and hexamethylenediamine. The presence of cycloalkane moieties in the PA polymer affects its crystallisation behaviour. Differential scanning calorimetry (DSC) analyses showed multiple, broad endothermic peaks between 120 and 215 °C depending on the content of **e1–2**.

The use of terpene-based lactams for the synthesis of polyamides has been investigated by Rieger, Winnacker and co-workers. In 2013, they reported the preparation of stereo-regular polyamide oligomers **oligo-i1** and **oligo-i2** (M_n <

2.8 kDa), obtained by anionic and acid-catalysed ROP of lactams **i1** and **i2** (Fig. 27).[170] These lactams were prepared from (−)-menthone *via* Beckmann rearrangement of appropriate oxime precursors.[171] The two regio-isomers showed different behaviour with **i2** being more reactive. Conceptually, this approach is comparable to the preparation of lactones from cyclic ketones described in section 3 (Fig. 14). Following an early polymerisation attempt reported by Kono and co-workers,[172] a regio-selective procedure for the preparation of **i1** was developed,[173] using hydroxylamine-*O*-sulfonic acid as catalyst. The thermal properties of **oligo-i1**, obtained through anionic ROP, were determined.[174] Remarkably, semi-crystalline **oligo-i1** exhibits a melting temperature of around 300 °C, which is significantly higher than that of Nylon-6™ (220 °C).

Building further on these results, Winnacker *et al.* described the synthesis of the stereo-regular polyamide **poly-j1** starting from nopinone-based monomer **j** obtained by a procedure similar to that used for lactams **i1** and **i2** (Fig. 28).[175,176]

The rigid and stereo-regular structure of **poly-j** provides excellent thermal properties with a T_m > 308 °C and a T_g of around 150 °C. Further to that, the interaction of human keratinocytes (HaCat cells) with films of **poly-j** blended with polyethylene glycol has been examined, demonstrating the potential of biobased polyamides in biomedical applications such as regenerative skin replacement.[177,178]

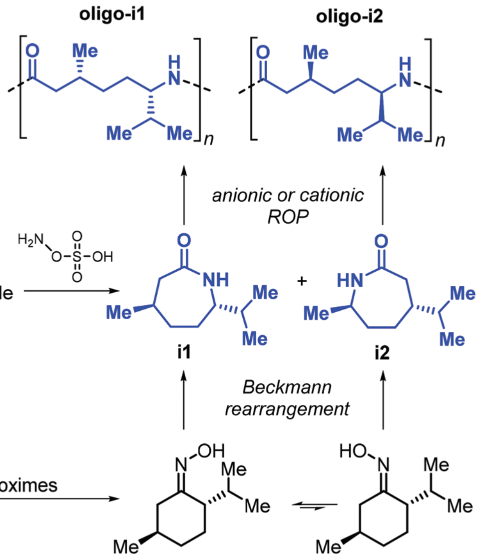

Fig. 27 Synthesis of lactams **i1** and **i2** from (−)-menthone, and structures of polyamide oligomers **oligo-i1** and **oligo-i2**.

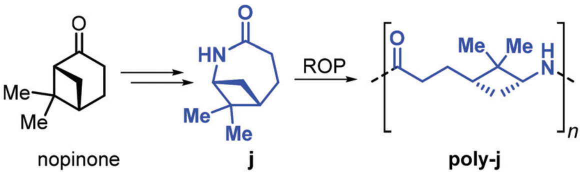

Fig. 28 Nopinone derived lactam **j** and its ROP to form polyamide **poly-j**.

In 2019, Sieber and co-workers achieved the ROP of β-lactams **k2** and **k3**, and ε-lactams **k1–4** obtained from α-pinene and (+)-carene, respectively (Fig. 29).[179] The β-lactams **k2** and **k3** were synthesised by [2 + 2] cycloaddition of chlorosulfonyl isocyanate to either α-pinene or (+)-carene. The synthesis of ε-lactams **k1** and **k4** was carried out by a four-step procedure involving the oxidation of the starting materials to their ketones, oxime formation and finally Beckmann rearrangement. The anionic ROP of lactams **k1–4** led to the formation of the corresponding PAs **poly-k1–5**. In the case of **poly-k4** a relatively high M_n of 33 kDa was attained.

Apart from **poly-k4** (which showed a T_g of 120 °C), no other thermal transitions could be detected by DSC analysis of all the other pinene- and carene-based polyamides. The authors argued that either the exceptionally bulky structures of these polymers prevent crystallisation, or that these materials have melting temperatures higher than their decomposition temperatures with their T_m's then amounting to or being beyond 400 °C.

In a related contribution from the same group, a modified synthetic procedure for monomer **k5** was presented involving the stereoselective chemo-enzymatic oxidation of (+)-carene, producing the monomer with opposite stereochemistry to **k4**.

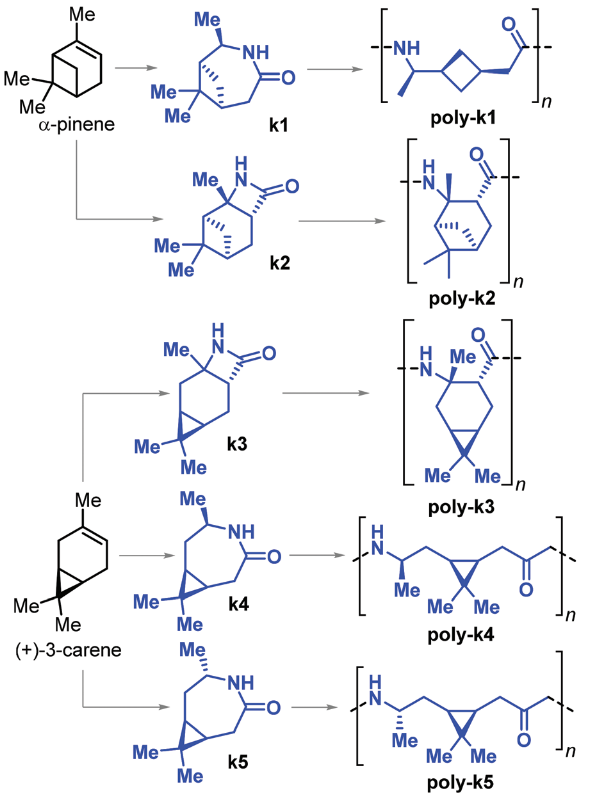

Fig. 29 β-Pinene derived lactams **k1** and **k2**, (+)-3-carene derived lactams **k3–5** and polyamide polymers **poly-k1–5**.

The syntheses of both monomers were scaled up to molar amounts.[180] In the same work, the crystal structure of **poly-k5** was reported, and this polyamide was shown to have a T_g and T_m of 105 and 280 °C, respectively.

6. Outlook and conclusion

Despite the enormous and increasing attention for the selection of new, cheap and renewable feedstock for the production of sustainable polymers, the use of terpenes has still been relatively unexplored. With the exception of terpene-based polyolefins which have matured substantially, recent developments have also shown interesting progress in the fabrication of other types of polymers (polycarbonates, polyesters, polyurethanes and polyamides).

As a direct consequence of the infancy of this research topic, most research efforts so far have been focussed on the synthesis of terpene-based monomers and their polymers. Much less attention has been devoted to the characterisation of key thermal, mechanical properties and/or surface properties, and demonstration of the full potential of these alternative raw materials and processes is thus an ongoing endeavour. There is obviously still a need for a broad-screen benchmarking of the performance of these terpene-based polymers against petroleum-based materials in future research work surrounding this topic.

At this stage, it is hard to realise a fair comparison between well-known established polymers and the emerging terpene-based alternatives described in this review. However, easy to obtain thermal data (such as T_g and T_m) are commonly used as a first approximation to identify possible applications because of their correlation with the polymer structure. In this respect, the incorporation of terpene monomers (or derivatives thereof) has shown in some cases advantages associated with the rigidity and/or functionality of these compounds. In order to credit these (preliminary) advantages, a collection of thermal data for selected petroleum-based commercial polymers is given in Fig. 30.[181–185]

The use of **LO** revealed the possibility to obtain functional polycarbonates with properties similar to that of **PCHC** in its pristine form, and furthermore can be properly modified post-synthetically to obtain different materials covering a wide range of thermal properties similar to those of **PPC** and even **BPA-PC** (Fig. 7). In the case of polyesters, the main driver has so far been the identification of alternatives for **PCL**. Successful results in this respect have been described starting from different terpenes such as (−)-menthol (Fig. 14), (+)-β-pinene (Fig. 16) and carvone (Fig. 15). Especially in the latter case, the presence of additional functional groups offer the possibility to obtain shape-memory materials that cannot be prepared from **PCL**. Moreover, owing to the structural rigidity offered by (bi)cyclic terpene scaffolds, it has been possible to obtain polyesters with properties similar to **PET** (such as in the case of camphor-based polyesters, Fig. 13) or with very high T_g values when combining terpene-based anhydrides and epoxides (Fig. 20 and 21).

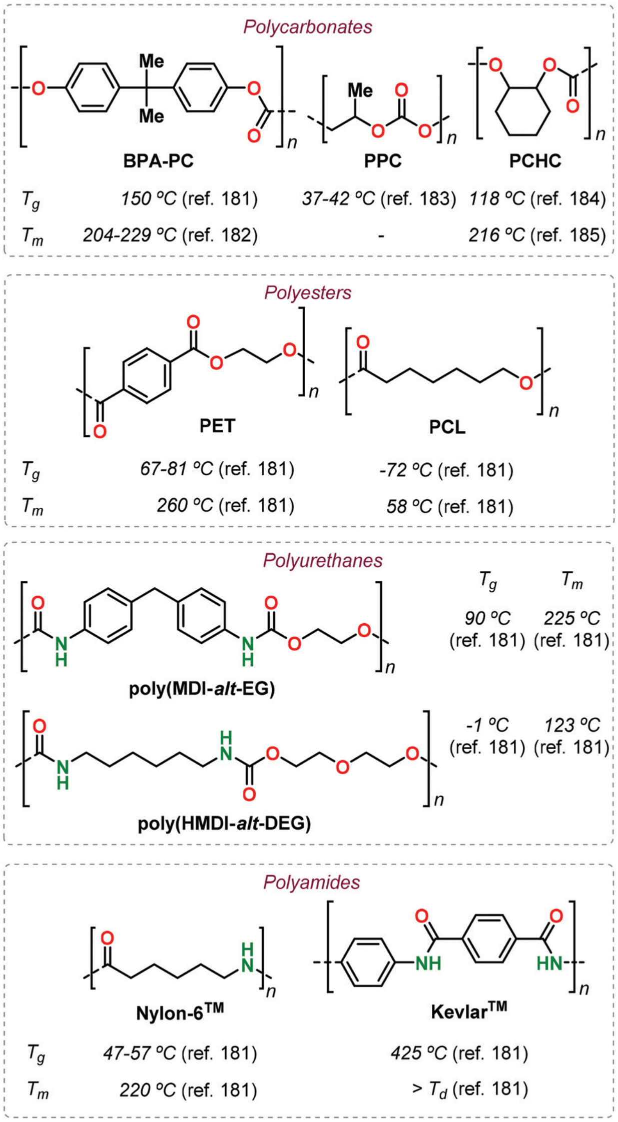

Fig. 30 Thermal properties of representative petroleum-based commercial polymers.

The preparation of polyurethanes from terpenes remains largely underexplored, with the only examples known being based on limonene. Nonetheless, the preparation of both polyhydroxyurethanes (Fig. 23) and polyurethanes (Fig. 24) have been reported featuring properties resembling those of aliphatic PUs such as **poly(HMDI-*alt*-DEG)** (Fig. 30) but are still far from those obtained using semi-aromatic PUs (**poly(MDI-*alt*-EG)**, Fig. 30).

Similar to polyurethanes, few examples of terpene-based polyamides have been reported to date, but polycondensation and ROP approaches have been both considered. Semi-crystalline aliphatic PAs, with thermal properties superior to well-established PAs such as Nylon-6™, have been attained from structurally rigid precursors like nopinone, α-pinene and (+)-3-carene (Fig. 28 and 30). Clearly, the synthesis of bio-based PAs with properties close to those of Kevlar-6™ remains an important goal to achieve.

Concluding, terpenes are typically available on a reasonable scale from inexpensive bio-renewable sources (*e.g.*, pinene and limonene), and do not compete with the food supply chain. The presence of olefin groups gives ample opportunities for chemical modifications such as those realized by addition and epoxidation reactions, providing additional possibilities to forge tailor-made materials with the desired mechanical, thermal, optical, conductive or medicinal features. In addition, exploring further post-functionalisation is facilitated in those cases where more than one type of double bond with different reactivity is embedded in the terpenoid structure. Terpenes additionally offer structural modularity (*i.e.* they can be linear, cyclic or polycyclic in nature) giving thus potential to use them to fabricate new materials with a wider window of properties than can be realised with most of the conventional monomers currently used in the polymer industry.

This mini-review thus describes the highly attractive nature of terpenes and their versatility in the creation of novel biosourced polymers, and their use in the requisite sustainable materials of the future. The information gathered herein prospectively provides impetus for future research and advances of new terpene-based formulations in the vibrant area of polymer science, and will undoubtedly reveal more, yet unidentified potential of this class of renewable raw materials.

Conflicts of interest

There are no conflicts to declare.

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