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Synthesis and depolymerization studies of biohybrid polycarbonates derived from terpenes†

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We here report the catalytic ring-opening copolymerization of 2-menthene oxide (**MO**), a terpene-based monomer derived from *L*-menthol, and CO₂ to provide poly(menthene carbonate), **PMC**, with a maximum molecular weight (*M_n*) of 10.2 kg mol⁻¹. The terpene monomer **MO** can also be combined with both limonene oxide (**LO**) and CO₂ in a formal terpolymerization process providing, depending on the monomer feed ratio, different types of biohybrid polycarbonates (**PLMC**) with different degrees of functionality. These terpolymerizations could be extended to the use of an acyclic terpene oxide and either **MO**/CO₂ or **LO**/CO₂, and a previously reported xylose-derived bicyclic oxetane. A selection of **MO**/**LO** based biohybrid **PLMCs** were conveniently depolymerized under TBD catalysis to regenerate the original mixture (>95%) of terpene oxides thereby providing a suitable starting point for the circular use of these biohybrid macromolecules.

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Biobased polymers are receiving increasing attention from the chemical community as a way to answer to a growing need for materials with an improved sustainability footprint and recyclability while replacing fossil fuel derived analogues.^{1–5} Commercial polycarbonate (PC) produced from bis-phenol A (BPA) is a thermoplastic polymer whose mechanical, thermal and optical properties have enabled a wide range of applications in for instance the automotive and electronics industries.^{6,7} The safe disposal and reuse of commercial PC is, however, complicated by toxicity concerns of BPA metabolites.⁸ Furthermore, the commercial PC production process makes use of diphenylcarbonate (DPC) as a carbonylating agent.⁹ DPC is very toxic for aquatic life while its conversion releases corrosive and toxic phenol as a byproduct. The development of ring-opening copolymerization (ROCOP) of epoxides and CO₂ is intrinsically a much safer alternative to prepare polycarbonates and at present represents the most versatile approach to produce polycarbonates.^{10–12}

Over the years a plethora of epoxide monomers have been shown to effectively participate in catalytic ROCOP providing different kinds of (functionalized) *homo* and *hetero* polycarbonates with control over the microscopic and macroscopic properties.^{13–20} Building on these seminal achievements, a more recent trend has illustrated that bioderived epoxy/oxetane monomers are also suitable precursors to develop new types of polycarbonate macromolecules with a controlled proportion of biocontent.^{21–27} Apart from the trend to devise polycarbonates based on bio-epoxy monomers, there has been interesting progress in the reuse of polycarbonates through catalytic depolymerization, allowing to recycle the polycarbonates into polymerizable monomers and thus getting a step closer to circular materials.^{28–30}

We have been interested in the use of terpene oxides (with a main focus on limonene oxide, a cyclic and rigid precursor) as monomers for both polycarbonate and polyesters produced *via* catalytic ROP.^{31,32} As far as we are aware, the Greiner group reported the only example of the ROCOP of sterically demanding 2-menthene oxide (**MO**) and CO₂ to provide poly(menthene carbonate), **PMC**.³³ Menthene has a rigid and structurally related backbone compared to limonene, and inspired by this work and the proven potential of Al(aminotriphenolate) complexes in coupling reactions involving sterically challenging epoxy compounds/monomers, we set out to prepare a series of high *T_g* biohybrid polycarbonates derived from different combinations of terpene oxide monomers. Such a process should facilitate the control over the ratio between more or less rigid monomers and functionalized ones, thereby creating opportunities to further tailor various macromolecular properties

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through catalytic control with the known poly(limonene) and poly(menthene) carbonates functioning as biopolycarbonate reference materials.

Herein, biohybrid macromolecules are presented that incorporate different combinations of cyclic and acyclic terpene oxides, and a bicyclic sugar-based oxetane.^{27,34} A pre-selected biohybrid polycarbonate containing both menthene and limonene fragments was further decorated with long chain alkyl thiols thereby reducing its glass transition as a way to post-synthetically adjust its processability. In addition, various biohybrid polycarbonates were selectively depolymerized (>95%) to mixtures of epoxy monomers, paving the way for their repolymerization into the pristine biohybrid structures.

Results and discussion

Given the previous success^{31,32,35} we attained with the copolymerization of limonene oxide (**LO**) and CO₂ by binary catalysts comprising Al(III) aminotriphenolate complexes in combination with halide-derived initiators affording poly(limonene carbonate), **PLC**, we started our research by identifying suitable ROCOP conditions for the coupling between limonene oxide (**LO**), 2-menthene oxide (**MO**) and CO₂ (Table 1) promoted by the Al(III) complex **Al^{Me}** and PPnCl (Table 1; PPN = bis(triphenyl)iminium).

The copolymerization of both **LO** and **MO** with CO₂ and promoted by **Al^{Me}**/PPnCl proceeds similarly (entries 1 and 2), though the overall conversion of **MO** (*versus* **LO**) was substantially lower (51 *versus* 75%). This resulted in a slightly lower molecular weight **PMC** ($M_n = 5.21 \text{ kg mol}^{-1}$) compared to **PLC** derived from **LO** and CO₂ ($M_n = 6.84 \text{ kg mol}^{-1}$). From these data it can be inferred that **MO** seems to be less reactive than **LO**.

The next step was to combine both monomers at an equimolar ratio (1:1) and evaluate this formal terpolymerization process (entry 3) in solution phase. A total epoxide (**LO** + **MO**) conversion of 75% was observed, and the isolated terpolymer (abbreviated as **PLMC**) had an M_n of 4.89 kg mol^{-1} with a **LO**:**MO** incorporation ratio of 64:36. The higher incorporation of **LO** can be expected on the basis of the relative reactivity displayed in entries 1 and 2. We then set out to further improve the formation of this hybrid biopolycarbonate **PLMC** (entries 5–10). Increasing the CO₂ pressure in this terpolymerization reaction (*cf.*, entries 3 and 5) improved the molecular weight of **PLMC** ($M_n = 7.12 \text{ kg mol}^{-1}$), which is likely the result of an improved relative propagation-to-chain transfer rate. However, in this latter case also a lower epoxide conversion is noted and the CO₂-enriched reaction medium possibly causes some degree of phase separation that can affect the efficient mixing of the reaction components, and thus the overall epoxide conversion. Time-dependent terpolymerization (entries 3, 6 and 7) showed that after 48 h there is little improvement in total epoxide conversion in line with the eventual viscous nature of the reaction mixture blocking further propagation of the macromolecule.

A lower amount of catalyst and initiator (entry 8) led to lower molecular weight **PLMC** likely due the fact that under

Table 1 Screening conditions for the terpolymerization of a mixture of **MO**, **LO** and CO₂ catalyzed by **Al^{Me}**/PPnCl^a



Entry	LO : MO	Solv.	T/t^b	Conv. ^c (%)	$m:n^d$	M_n/D^e
1	1:0	Tol	45, 72	75	100:0	6.84, 1.26
2	0:1	Tol	45, 72	51	0:100	5.21, 1.19
3	1:1	Tol	45, 72	75	64:36	4.89, 1.25
4	1:1	Tol	60, 72	53	56:44	4.15, 1.12
5 ^f	1:1	Tol	45, 72	38	69:31	7.12, 1.21
6	1:1	Tol	45, 48	71	67:33	4.74, 1.25
7	1:1	Tol	45, 24	57	58:42	4.59, 1.15
8 ^g	1:1	Tol	45, 72	32	78:22	3.76, 1.23
9	3:1	Tol	45, 72	67	79:21	7.09, 1.28
10	1:3	Tol	45, 72	68	37:63	6.25, 1.18
11	1:0	—	45, 72	56	100:0	6.65, 1.37
12	0:1	—	45, 72	60	0:100	7.00, 1.22
13	1:1	—	45, 72	75	65:35	10.2, 1.29
14	3:1	—	45, 72	39	85:15	3.36, 1.19
15	1:3	—	45, 72	43	57:43	7.92, 1.21
16	1:1	—	55, 72	73	64:36	7.92, 1.25
17 ^f	1:1	—	45, 72	71	64:36	8.87, 1.25
18 ^g	1:1	—	45, 72	39	80:20	4.01, 1.24
19	1:1	—	45, 48	67	64:36	4.06, 1.32
20	1:1	—	45, 24	42	68:32	2.27, 1.31

^a Reaction conditions: **MO**:**LO** (6.5 mmol) ratio as indicated, **Al^{Me}** (1 mol%) and PPnCl (0.5 mol%), toluene (0.5 M), 15 bar CO₂, 45 °C, 72 h. ^b T denotes the reaction temperature in °C and t is the reaction time in h. ^c Values correspond to the overall epoxide conversion as determined by ¹H NMR (CDCl₃). ^d Determined by ¹H NMR (CDCl₃) using the signal integrals of the methine hydrogens of the **LO** and **MO** based repeat units. ^e M_n values are given in kg mol⁻¹ and $D = M_w/M_n$, all values determined by GPC in THF calibrated with polystyrene standards. ^f Carried out at 30 bar CO₂ pressure. ^g Using 0.5 mol% **Al^{Me}** and 0.25 mol% PPnCl. For the majority of the experiments done, the theoretical mass of the polycarbonates using 1 mol% of **Al^{Me}** is approximately 19.7 kg mol^{-1} with **MO** and **LO** having nearly the same molar mass (154.25 *vs.* 152.24 g mol⁻¹). The carbonate selectivity for all polymers was >95% as evidenced by ¹H NMR.

these conditions the propagation rate would be lower due to a higher dilution of both catalyst components leading to lower epoxide conversion.³⁶ Finally, experiments were conducted with either a three-fold excess of **LO** (entry 9; 3:1) or **MO** (entry 10; 1:3), which resulted in terpolymers with a higher ($M_n = 7.09 \text{ kg mol}^{-1}$, $m:n = 79:21$) or lower amount ($M_n = 6.25 \text{ kg mol}^{-1}$, $m:n = 37:63$) of incorporated **LO**. This is a useful observation as it demonstrates that the monomer feed ratio can be used to dictate the amount of incorporated functionalized monomer (*i.e.*, **LO**; C=C bond) while retaining an essentially fully biosourced origin.



Encouraged by the solution phase results for the terpolymerization of **LO**, **MO** and CO_2 , next we examined a solvent-free approach (Table 1, entries 11–20). Similar trends in terms of M_n and **LO**-to-**MO** incorporation ratios for the produced **PLMC** were seen and with similar order of magnitude conversion levels. Under the best conditions, this biohybrid polycarbonate was isolated with an improved M_n of 10.2 kg mol^{-1} (entry 13; $D = 1.29$; see Fig. 1 for an $^1\text{H NMR}$ comparison), and the more concentrated nature of the monomers is apparently productive towards higher molecular weight polycarbonate. In this latter case, compared to solution-phase results, a comparable epoxide conversion (entries 13 vs. 3; 75%) was noted together with a similar **LO**:**MO** incorporation ratio (entry 13 vs. 3, $m:n = 65:35$ vs. $64:36$). Performing the neat terpolymerization process at 30 bar CO_2 pressure was also successful (entry 17) though the **PLMC** product had a slightly lower M_n of 8.87 kg mol^{-1} . In this latter case, much higher monomer conversion (71%) was comparatively noted (*cf.*, entries 3 and 5) thus compensating for the dilution caused by the CO_2 -expanded liquid phase. The ability to perform the polymerization without solvent adds value to the practical nature of the process and its sustainability in terms of atom-efficiency.

In order to assess the potential recycling of **PLMC**, we carried out depolymerization studies (Table 2) using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as an organocatalyst under various conditions (see the ESI for further details, Fig. S1–S3†).^{28,29} First, toluene was probed as a reaction medium and under reflux, the presence of 4 mol% TBD (entry 1) resulted in

Table 2 Depolymerization of selected biohybrid polycarbonates **P1**–**P3** from Table 1^a



Entry	P	t, TBD	m:n ^b	Conv. ^c (%)	Sel. ^d (%)	m:n ^e
1	P1	24, 4	65:35	27	44	61:39
2	P1	15, 8	65:35	87	79	87:13
3	P1	15, 12	65:35	93	70	83:17
4	P1	15, 16	65:35	>98	98	66:34
5 ^e	P1	15, 12	65:35	>98	93	66:34
6 ^f	P1	15, 11	65:35	>98	>98	59:41
7 ^f	P2	15, 11	85:15	>98	>98	83:17
8 ^f	P3	15, 11	57:43	>98	>98	55:45

P1: $M_n = 10.2 \text{ Kg/mol}$, $D = 1.29$; $m:n = 65:35$
P2: $M_n = 3.36 \text{ Kg/mol}$, $D = 1.19$; $m:n = 85:15$
P3: $M_n = 7.92 \text{ Kg/mol}$, $D = 1.21$; $m:n = 57:43$

^a Reaction conditions: polycarbonate (100 mg), toluene (0.5 mL), 15 h, 111 °C. ^b Values for the starting polymer as determined by $^1\text{H NMR}$ (CDCl_3). ^c Determined by $^1\text{H NMR}$ (CDCl_3) of the depolymerized polymer sample. ^d Total epoxide selectivity, the remaining products were the cyclic carbonates. ^e The solvent was CH_3CN . ^f The solvent was CH_3CN (0.5 mL), at reflux (82 °C). **P** stands for the polymer sample used, *t* is the reaction time in hours and TBD is the organocatalyst with the amount indicated in mol%. LC = cyclic limonene carbonate, MC = cyclic 2-menthene carbonate.

a modest conversion (27%) of preselected **P1** (see for details entry 13, Table 1) after 24 h. Under these conditions, the “epoxide” selectivity, *i.e.* the relative amount of formed **LO** and **MO**, was 44% while the remainder of the converted polycarbonate were the respective cyclic carbonates LC (limonene carbonate) and MC (2-menthene carbonate). By reducing the reaction time to 15 h but increasing the amount of TBD (8–16 mol%; entries 2–5), a much higher epoxide selectivity and quantitative conversion of **P1** could be achieved. We finally identified optimized conditions, reported in entry 6, by using acetonitrile instead of toluene as solvent in the presence of 11 mol% TBD, providing a total epoxide selectivity of >98% at full conversion of **P1** (>98%). Furthermore, the **LO**:**MO** ratio in the crude reaction mixture (59:41) was only slightly lower than originally determined in **P1** (66:34), thus reasonably in line with its terpene constitution. To further evaluate the depolymerization, two other samples (**P2**: entry 14, and **P3**: entry 15, see Table 1) were also treated under similar reaction conditions (results in entries 7 and 8, Table 2). From the obtained data it can be concluded that quantitative polymer conversion takes place producing epoxide mixtures close to those originally determined for **P2** and **P3** by $^1\text{H NMR}$ spectroscopy (see ESI for details, Fig. S1–S3†). The high epoxide selectivity for the depolymerization of **P1**–**P3** holds great promise to recycle these monomers into **PLMC** using $\text{Al}^{\text{Me}}/\text{PPNCl}$, providing a catalysis-enabled circular process.

The biohybrid **PLMCs** have typically high glass transitions (T_g 's) comparable to parent **PLC** (Table 3) due to the presence of the more bulky menthene fragments, and some signs of



Fig. 1 $^1\text{H NMR}$ spectral comparison between **PLC**, **PMC** and the **PLMC** from entry 13 in Table 1. A selected zoom of the region where the methine and olefinic H are resonating is shown. For more detailed peak assignments, see the ESI, Fig. S53.†



Table 4 Co- and terpolymerization reactions using **MO**, **LO**, **CO** or **OX** with CO_2 catalyzed by $\text{Al}^{\text{Me}}/\text{PPNCl}^{\text{a}}$

Entry	Monomers	Conv. ^b (%)	P	<i>m</i> : <i>n</i> ^c	<i>M_n</i> / <i>D</i> ^d
1	CO	25	P4	—	1.34, 1.00
2 ^e	LO + CO	41	P5	9 : 1	4.62, 1.24
3 ^e	MO + CO	36	P6	9 : 1	2.26, 1.10
4 ^f	OX	10	P7	—	1.51, 1.41
5 ^g	OX	85	P7	—	4.28, 1.09
6 ^e	LO + OX	14	P8	>99 : 1	1.81, 1.10
7	MO + OX	20	P9	>99 : 1	2.12, 1.13
8 ^g	MO + OX	96 ^h	P9	<1 : 99	1.62, 1.07

^a Reaction conditions: monomer ratio 1 : 1 (where applicable), neat, 65 °C, 15 bar CO_2 , 72 h. ^b Values correspond to the overall epoxide conversion as determined by ^1H NMR spectroscopy (CDCl_3). ^c Determined by ^1H NMR (CDCl_3) using the signal integrals of the methine hydrogens of the **LO** and **MO** based repeat units. ^d M_n values are given in kg mol^{-1} and $D = M_w/M_n$, all values determined by GPC in THF calibrated with polystyrene standards. Note that *crude* samples from entries 1, 3, 4 and 6–8 were measured, whereas the data related to entries 2 and 5 are from the isolated oligo/polymers. ^e Reaction was performed at 50 °C. ^f Reaction was performed at 70 °C for 48 h using 2.9 mmol of **OX** in toluene as a medium. ^g Reaction was performed at 100° and 20 bar CO_2 pressure for 72 h using 2.9 mmol of **OX** in toluene (0.25 M) as a medium. ^h Conversion refers to **OX**, the conversion of **MO** was <5%.

activation of **OX** takes place (96% conversion as measured by ^1H NMR with low M_n for the oligomer **P9** formed; $M_n = 1.62 \text{ kg mol}^{-1}$) though with virtually no incorporation of **MO**. The combined data collected for samples **P4–P9** in Table 4 demonstrate that matching the relative reactivities of somewhat related monomers is not an easy task as multiple parameters such as sterics, electronics and stability need to be simultaneously controlled.

Conclusions

In summary, we here describe a catalytic process that allows to combine different monomers derived from terpenes (**LO** and **MO**) thereby creating access to nearly fully biobased polycarbonates

with different degrees of double bond densities. The thermal properties can be significantly altered by introducing different amounts of long-chain alkyl groups *via* classic radical-mediated thiol–ene chemistry providing brush-type highly viscous, oily materials that show an increased macromolecular ordering expressed by their respective melting temperatures. Selected biohybrid **PLMC** samples were subjected to catalytic and controlled degradation allowing to selectively generate the initial monomers (**LO** and **MO**), which in principle should allow for their repolymerization to either **PLC**, **PMC** or **PLMC**. Furthermore, the depolymerization-based NMR data help to confirm the initially assessed terpene monomer incorporation ratios. Preliminary studies with other types of monomers (acyclic **CO** and xylose-derived **OX**) illustrate the need for combining biobased monomers with similar reactivities to be able to create a wider range of polycarbonates with modular thermal, mechanical and structural (*cf.*, functionality) properties. Future work focuses on a wider use of terpene-based monomers to forge new types of biobased polymers with control over their macromolecular architectures and functionality.

Experimental section

Typical procedure for the terpolymerization of **MO**, **LO** and CO_2

Inside a glove box, a 50 mL autoclave was charged with complex Al^{Me} (33.0 mg, 65.7 μmol , 0.01 equiv.) and PPNCl (18.3 mg, 32.8 μmol , 0.005 equiv.) dissolved in limonene oxide (**LO**, 3.88 mmol, 1 equiv.) and 2-menthene oxide (**MO**, 3.28 mmol, 1 equiv.). The reactor was then closed and pressurized to 15 bar of CO_2 . The mixture was allowed to stir at 45 °C for 72 h. Hereafter the reactor was first cooled to r.t. and carefully depressurized. An aliquot was collected to determine the epoxide conversion by ^1H NMR (CDCl_3) analysis. The mixture was dissolved into a minimum amount of dichloromethane and then poured into acidified methanol (1 M) under stirring causing precipitation of the polymer product. The precipitate was washed twice with cold methanol and dried for 24 h under vacuum at 50 °C. All terpolymerization reactions were carried out in similar fashion, and the collected analytical data for selected **PLMC** products **P1–P3** (31–57% isolated yield, white solids) can be found in the ESI.†

Typical procedure for the depolymerization of the terpolymers

In a typical procedure, in a glovebox a Schlenk tube equipped with a stirring bar was charged with a preselected **PLMC** (**P1–P3**; 0.10 g, 0.654 mmol carbonate repeat units) and TBD (16.5 mg, 0.118 mmol, 0.18 equiv.). The reaction mixture was dissolved in acetonitrile (0.5 M) and kept at gentle reflux (82 °C) for 15 h. The reaction was monitored by ^1H NMR spectroscopy (CDCl_3), taking small aliquots from the reactive mixture. At the end of the reaction, the crude product was analyzed by ^1H NMR to determine the percentage of each component (primarily **LO** and **MO**) and their relative ratio. An example of how this was done can be found in the ESI.†



Author contributions

TS, EL and JT carried out all syntheses regarding the monomer and carbonate polymers. AWK and AB assisted with continuous feedback during the project and scientific input. TS, EL and AWK designed the project, while AWK and AB wrote the manuscript with feedback from all authors.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts of interest to declare.

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